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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

Development and Transfer of Technology Series

No. 13

FERTILIZER MANUAL

UNITED NATIONS

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna

Development and Transfer of Technology Series No. 13

FERTILIZER MANUAL

UNITED NATIONS
New York, 1980

INTIB

The Industrial and Technological Information Bank (INTIB), a pilot operation in 1977-1978 and an ongoing part of UNIDO activities since 1980, is an information service to developing countries, the specific purpose of which is to assist them in the process of selection from alternative technologies. INTIB is mandated to cover 20 sectors of industry of particular importance to developing countries. It has a dual function: to provide information in the form of printed technological profiles of the alternatives available and to process and analyse information to answer individual inquiries.

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Preface

This addition to the Development and Transfer of Technology Series, provided as a service of the Industrial and Technological Information Bank (INTIB) of the United Nations Industrial Development Organization (UNIDO), is intended to replace a publication of the same name that appeared in 1967.[1] Other numbers in the series dealing with fertilizers are *Process Technologies for Phosphate Fertilizers* (No. 8) and *Process Technologies for Nitrogen Fertilizers* (No. 9).

The new *Fertilizer Manual* was prepared by the International Fertilizer Development Center (IFDC), with substantial contributions by the secretariat of UNIDO. Except for the preface, the text reproduced here is identical to that being separately published by IFDC and has not been edited within UNIDO.

The aim of the *Manual* is to describe in clear, simple language all major fertilizer processes, their requirements, advantages and disadvantages and to show illustrative examples of economic evaluations. It comprises five parts:

Part one—history of fertilizers, world outlook, role of fertilizers in agriculture, raw materials, glossary of fertilizer-related terms;

Part two—production and transportation of ammonia and all important nitrogen fertilizers;

Part three—characteristics of phosphate rock, production of sulfuric and phosphoric acid, all important phosphate fertilizers, including nitrophosphates and ammonium phosphates;

Part four—potash fertilizers, compound fertilizers; secondary nutrients and micronutrients; controlled-release fertilizers; physical and chemical properties of fertilizers and their determination;

Part five—planning a fertilizer industry, pollution control, economics of fertilizer production, problems facing the world fertilizer industry.

Special emphasis is given to the economics of fertilizer production. Basic cost data are for manufacturing operations in the industrial areas of Europe and the United States of America since conditions in developing countries vary widely. However, there are examples and discussions of how the economics of various processes is likely to be affected by conditions in some developing countries. Estimated costs are given in sufficient detail to assist those who may wish to adapt the estimates to their own situation.

In comparison with the previous manual,[1] the treatment of phosphate fertilizers and compound fertilizers has been greatly expanded. New chapters have been added on controlled-release fertilizers and on the physical and chemical properties of fertilizers. The scope of treatment of nitrogen fertilizers is about the same as in the previous manual. Two new chapters were added on transport and storage of ammonia and on factors affecting the choice of a nitrogen fertilizer. Overall, only 20% of the new manual can properly be termed a revision of the old one; 80% is entirely new.

The preparation of the *Manual* was under the direction of Travis P. Hignett, IFDC Special Consultant, who, besides acting as the chief reviewer and editor, wrote all chapters with the following exceptions: chapter III was prepared by H. R. Tejeda of IFDC; chapter X by F. P. Achorn of the Tennessee Valley Authority (TVA); chapter XVIII by R. C. Smith of AMAX,

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[1] *Fertilizer Manual* (ST/CID/15) (United Nations publication, Sales No. 67.II.B.1).

Inc.; chapter XXII by George Hoffmeister, Jr., of TVA; chapter XXIII and chapter XXVI (except for the section on modules, platforms, and barges, which was supplied by C. J. Pratt of the World Bank), by the secretariat of UNIDO. A major part of chapter V was taken from a world-wide study of the fertilizer industry prepared by UNIDO in 1976.

Much of the statistical information on supply and demand of fertilizers was provided by FAO.

All chapters were reviewed and commented on in draft by staff members of the secretariat of UNIDO. In addition, all chapters were reviewed by the reviewers selected from the staffs of various manufacturers, associations and institutes throughout the world, TVA, FAO, the World Bank and IFDC itself. However, the views expressed are those of the authors and do not necessarily reflect those of either IFDC or the secretariat of UNIDO.

It is unavoidable in preparing a work of this size that some of the information will become obsolete by the time it is printed. Readers should keep in mind that when authors use the terms "current" or "present", they are referring to 1978 unless otherwise specified.

ACRONYMS OF ORGANIZATIONS

ADIFAL	*Latin American Association for Development of the Fertilizer Industry
AID	Agency for International Development
ANDA	Associação Nacional para Difusão de Adubos
AOAC	Association of Official Agricultural Chemists
APEA	Association des Producteurs Européens d'Azote
ASEAN	Alliance of Southeast Asian Nations
ASTM	American Society for Testing Materials
BASF	Badische Anilin-und Soda-Fabrik
CAST	Council for Agricultural Science and Technology
DSM	Dutch State Mines
EEC	European Economic Community
ESCAP	Economic and Social Commission for Asia and the Pacific
FAI	Fertiliser Association of India
FAO	Food and Agriculture Organization of the United Nations
FCI	Fertilizer Corporation of India
FCIA	Foreign Credit Insurance Association
FIAC	Fertilizer Industry Advisory Committee
GUANOMEX	Guanos y Fertilizantes de Mexico
ICI	Imperial Chemical Industries
ICIS	International Centre for Industrial Studies
IDA	International Development Association
IDCAS	Industrial Development Centre for Arab States
IFDC	International Fertilizer Development Center
ILO	International Labor Organization
IMI	Israel Mining Industries
IRRI	International Rice Research Institute
ISMA	Originally "International Superphosphate Manufacturers Association"
NFDC	National Fertilizer Development Center (TVA)
OECD	Organization for Economic Cooperation and Development
OMVS	*Senegal River Development Organization
OPEC	Organization of Petroleum Exporting Countries
PEC	Société Potasse et Engrais Chimiques
SAI	Scottish Agricultural Industries
SBA	Société Belge d'Azote
SELA	*Latin American Economic System
TVA	Tennessee Valley Authority
UKF	Unie van Kunstmestfabrieken br
UN	United Nations
UNCTAD	United Nations Conference on Trade and Development
UNIDO	United Nations Industrial Development Organization

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*Translation.

ABBREVIATIONS FOR COUNTRIES

FRG	Federal Republic of Germany
GDR	German Democratic Republic
PRC	People's Republic of China
U.K.	United Kingdom of Great Britain and Northern Ireland
U.S.	United States of America
U.S.S.R.	Union of Soviet Socialist Republics

CLASSIFICATION OF COUNTRIES

For statistical purposes the UN standard classification is used for developed and developing countries:

Developed Countries

Includes North America (Canada and United States), Western Europe, Eastern Europe (including U.S.S.R.), Japan, Israel, South Africa, Australia, and New Zealand.

Developing Countries

Includes Latin America (all American countries not included in "North America"), Asia (except Japan and Israel), Africa (except South Africa), and Oceania (except Australia and New Zealand). Turkey is included in Asia although it is partly in Europe.

Note: Use of country names in connection with specific locations does not imply a judgment by IFDC as to the boundaries of any country when those boundaries are disputed.

Regional Grouping of Countries:

Where a regional grouping of countries is given (e.g., "Middle East"), such groupings are taken from a referenced source of information. Use of such groupings does not imply any judgment by IFDC as to its validity nor does it necessarily imply approval of the group name.

MATHEMATICAL SYMBOLS, ABBREVIATIONS, AND CONVERSION FACTORS USED IN THIS MANUAL[a]

Monetary Value

$	U.S. dollar (unless otherwise indicated)
¢	cent = $0.01
mill	$0.001
Rs	rupee

Linear Measurement

m	meter = 3.28 feet (ft) = 39.37 inches (in)
cm	centimeter = 0.01 meter = 0.3937 inch (in)
mm	millimeter = 0.001 meter
μm	micrometer or "micron"
km	kilometer = 0.62 mile (mi)

Area Measure

m^2	square meter = 10.76 square feet (ft^2)
cm^2	square centimeter = 0.155 square inch (in^2)
km^2	square kilometer = 0.386 square mile (mi^2)
ha	hectare = 10,000 square meters (m^2) = 2.471 acres (A)

Weight

g	gram = 0.032 troy ounce (oz) = 0.035 avoirdupois ounce (oz)
mg	milligram = 0.001 gram (g)
μg	microgram = 0.000001 gram (g)
kg	kilogram = 1,000 grams (g) = 2.205 pounds (lb)
t	ton (metric) = 1,000 kg = 2,205 lb = 1.102 short tons (st) (All "tons" in this manual are metric tons unless otherwise stated.)
g-mole	gram mole = the molecular weight of a compound multiplied by 1 gram

Volume

m^3	cubic meter = 35.34 cubic feet (ft^3) = 1,000 liters (l)
cm^3	cubic centimeter = 0.061 cubic inch (in^3)
l	liter = 0.264 U.S. gallons (gal) = 1.057 quart (qt)
bbl	barrel (of petroleum) = 42 gallons (gal) = 159 liters (l)
ml	milliliter = 1 cubic centimeter (cm^3) approximately
Nm^3	cubic meter (of gas) measured at "normal" temperature and pressure (0^{o}C and 1 atm)
Tcm	trillion cubic meters

Yields or Application Rates

kg/ha	kilograms per hectare = 0.892 pounds per acre (lb/A)
t/ha	tons per hectare = 14.87 bushels per acre (bu/A)(wheat) 15.93 bu/A of maize (The bushel is a unit of volume (35.24 liters) but is usually determined by weighing grain and dividing by a standard weight per bushel which is characteristic of the specific grain.)

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[a] Factors for converting metric units to English or SI units (Système International d'Unités) or vice versa.

Weight per Unit of Volume (Density)

sp gr	specific gravity = the ratio of the weight of a substance to the weight of an equal volume of water at 4°C; no dimensions; numerically equal to density in g/cm^3
g/cm^3	grams per cubic centimeter = 62.43 pounds per cubic foot (lb/ft^3)
kg/m^3	kilograms per cubic meter = 0.0624 lb/ft^3
t/m^3	tons per cubic meter = g/cm^3

Note: For definitions of true, apparent, and bulk densities or specific gravities, see chapter XXII.

Concentrations

g/l	grams per liter
mg/m^3	milligrams per cubic meter
$\mu g/m^3$	micrograms per cubic meter

Work-Energy-Heat

cal	calorie = 4.184 joules (J)
kcal	kilocalorie = 1,000 cal = 3.968 British thermal units (Btu)
kJ	kilojoule = 0.239 cal
GJ	gigajoule = 10^9 joules = 0.948 million Btu = 0.239 million kcal

Power

W	watt = 1 joule per second (J/s)
kW	kilowatt = 1,000 watts (W) = 1.34 horsepower (hp)
kWh	kilowatt-hour = 3,413 Btu

Heating Value per Unit of Volume or Weight (Also Heat of Formation)

cal/g	calories per gram = kilocalories per kilogram (kcal/kg) = 1.8 Btu/lb = 4.187 J/g
$kcal/m^3$	kilocalories per cubic meter = 0.1123 Btu/ft^3

(Used to denote heating value of fuel gas; the temperature and pressure should be stated; usually O°C and 1 atm in scientific work. The natural gas industry uses "standard conditions" of 60°F and 14.7 lb/in^2.)

Pressure

kg/cm^2	kilograms per square centimeter = 14.7 pounds per square inch (lb/in^2)
atm.	atmosphere = 14.7 lb/in^2 = 1 kg/cm^2 (approximately)
atm.	101.325 kilonewtons per square meter (kN/m^2) = 101.325 kilopascals (kPa)
mm Hg	millimeters of mercury = 133.3 Pa = 0.0013 atm
psia.	pounds per square inch absolute
psig.	pounds per square inch gauge

Temperature

°C	degrees Celsius or centigrade; °C x 1.8 + 32 = °F
°F	degrees Fahrenheit (°F - 32) 5/9 = °C

Plant Capacity or Production Rate

tpd	tons per day
tph	tons per hour
tpy	tons per year

Note: All tons are metric unless otherwise specified.

Other Abbreviations

f.o.b.	free on board = cost at plant or port including loading on a ship or other conveyance
pH	logarithm of the reciprocal of the hydrogen ion concentration in grams per liter ($pH = \log 1/H^{+}$ g/l). A solution of pH 7 is neutral; lower pH's are acidic and higher pH's are alkaline.
dia	diameter
CRH	critical relative humidity
LPG	liquefied petroleum gas
LNG	liquefied natural gas
SNG	substitute (or synthetic) natural gas
HTS	high temperature shift (catalyst)
LTS	low temperature shift (catalyst)
LHV	low heating value (gas)
CEC	cation exchange capacity

Abbreviations of Common Fertilizer Materials

For abbreviations of the names of common fertilizer materials and definitions of fertilizer-related terms, see chapter IV.

Particle Size - Screen Size

For comparison of screen sizes in different systems, see chapter XXII, table 2.

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PART ONE

INTRODUCTION AND BACKGROUND

I History of Chemical Fertilizers

Introduction

Through centuries of ancient and medieval times, men have been deeply interested in improving crop yields by the addition of various mineral or organic substances. Until the last 200-300 years, however, the approach to the subject was highly empirical; it was found by accident or by trial and error that applications of various organic wastes or mineral substances to the soil dramatically improved plant growth. Illustrations are manure, ground bones, wood ashes, saltpeter, and gypsum. But the results were not predictable; a treatment that benefited one field might have no effect or even an adverse effect on another.

The difficulties of early scientists may be illustrated by van Helmont's account of his experiment in Belgium in the 17th century:

> "I took an earthen vessel into which I put 200 pounds of soil dried in an oven, then I moistened it with rainwater and pressed into it a shoot of willow tree weighing 5 pounds. After exactly 5 years the tree had grown up and weighed 169 pounds and 3 ounces. But the vessel had never received anything but rainwater or distilled water to moisten it when necessary. At the end I dried the soil once more and got the same 200 pounds I started with, less about 2 ounces. Therefore, the 164 pounds of increased weight of wood, bark, and root came from the water alone."

Van Helmont considered the 2-ounce loss in weight of the soil to be within experimental error. Since nothing but water had been added and since air surrounding the plant had no apparent weight, his conclusion that all the increased weight came from water seemed logical. At that time the prevalent theory was that of Aristotle who believed that all matter was composed of four elements--earth, air, fire, and water.

Other scientists observed the stimulating effect of various materials. Note the claim of Digby in 1660:

> "By the help of plain saltpeter, I have made barrenest ground outgo the richest in giving a prodigious bountiful harvest."

As the science of chemistry progressed and more chemical elements were discovered, scientists became interested in determining the chemical composition of plants. Early in the 19th century vegetable substances were found to consist principally of carbon, hydrogen, and oxygen. The hydrogen and oxygen could come from water, but where did the carbon come from? This led to the humus theory--the theory that decomposing animal and vegetable material in the soil supplied carbon and constituted, with water, the true food of plants. Although it was soon proved that plants obtain most of their carbon from the carbon dioxide in the air, the humus theory persisted in various modifications for many years.

As more and more chemical elements were identified, scientists became interested in determining the amount and relative importance of various mineral elements in plants. The importance of an element was at first thought to be proportional to the amount found in the plant, a theory soon disproved.

The foundation for the modern fertilizer industry was laid by Liebig, starting in 1840. He stressed the value of mineral elements derived from the soil in plant nutrition and the necessity of replacing those elements to maintain soil fertility. He recognized the value of nitrogen but believed that plants could get their nitrogen from the air. He envisioned a fertilizer industry with nutrients such as phosphate, lime, magnesia, and potash prepared in chemical factories. He recommended treatment of bones with sulfuric acid to render the phosphate more readily available.

Perhaps as important an influence as his scientific contribution was Liebig's philosophy:

> "Perfect agriculture is the true foundation of all trade and industry--it is the foundation of the riches of nations. But a rational system of agriculture cannot be formed without the application of scientific principles for such a system must be based on an exact acquaintance with the means of vegetable nutrition. This knowledge we must seek through chemistry."

Liebig propounded the "Law of the Minimum," which is still a useful concept despite its lack of quantitative exactness. This law states that, if one of the nutritive elements of the soil or air be deficient or lacking in availability, growth will be poor even when all other elements are abundant. If the deficient element is supplied, growth will be increased in proportion to the amount supplied up to the point where the supply of that element is no longer the limiting factor. Increasing the supply beyond this point is not helpful since some other element is now in minimum supply and becomes the limiting factor.

The concept of the law of the minimum has been modified as additional elements have proved to be essential in plant nutrition and has been extended to include other factors such as moisture, temperature, insect control, weed control, light, plant population, and genetic capacities of plant varieties. In fact, modern advances of agriculture have consisted mainly of identifying successive limiting factors and correcting them. Although it is not possible to define a precise point at which one element ceases to become a limiting factor and another takes its place, many situations are found in which an element to which there previously was no yield response becomes important after fertilization with adequate amounts of other needed elements. Thus, attainment of optimum yields is likely to involve a complex mix of nutrients in combination with several other inputs.

Although Liebig's precepts were widely accepted, various other schools of thought flourished for many years. For example, a chief of the Bureau of Soils in the U.S. Department of Agriculture in the early 1900's maintained that the soil was an inexhaustible resource that would supply forever all needed mineral elements if managed properly. He thought proper cultivation, rotation of crops, and prevention of erosion would solve all fertility problems. He held that the good effects noted from the use of fertilizer resulted from neutralizing or destroying toxic substances in the soil and that these same effects could be better obtained by crop rotation and cultivation.

Indeed, most soils do contain an abundance of mineral elements in comparison with the annual requirements of crops. But many of the soil minerals are not readily available. Without addition of fertilizer, crop yields sooner or later approach a minimum level that is insufficient to repay the farmer's efforts or to supply world food needs.

Chemical Fertilizers

Phosphate Fertilizers

The first phosphate fertilizer as such--ground bones--was used widely in Europe during the early part of the 19th century. When the supply of animal bones ran short, human bones were gathered from battlefields or burial places. Treatment of bones with sulfuric acid began about 1830 and soon became a common practice. Dilute acid was used, and the product was a slurry which was distributed in wooden casks. Potash salts and sulfate of ammonia or nitrate of soda sometimes were added, thus producing the first liquid mixed chemical fertilizers.

In about 1840 treatment of phosphate rock with sulfuric acid was found to yield an effective phosphate fertilizer, which was called superphosphate.

The first successful commercial superphosphate production was started by Lawes in England in 1842. Others followed, and by 1853 there were 14 manufacturers in the United Kingdom and several in other countries. By 1870, 80 factories were reported to be operating in the United Kingdom.

Many of the early factories were primitive; ground rock and sulfuric acid were mixed in kettles or vats by manual labor with paddles or hoes. However, by 1862, Lawes was using a continuous mixer with a capacity of 100 tpd. Some modern plants produce 1,000 or more tons per day, but smaller plants serving local areas generally are favored since it is seldom economical to ship the low-analysis material very far.

The history of production of concentrated or triple superphosphate is associated with the production of phosphoric acid. The first known commercial production was in the 1870s in Germany where the objective was to utilize a low-grade phosphate rock with a high content of iron and aluminum. A very dilute phosphoric acid was produced by batch extraction and filtration of the rock, and this was concentrated by evaporation. The acid was used to acidulate more phosphate rock. Other plants soon were built in Europe and America. However, most of them were small, and much of the product was used in sugar clarification rather than for fertilizer.

Triple superphosphate did not become an important fertilizer material until the 1950s. In contrast with ordinary superphosphate, triple superphosphate has a higher content of phosphate than the phosphate rock from which it is made, thus its production is best carried out near the source of the rock in large plants, with shipment of the product to local mixing plants or to farmers.

Although ammonium phosphate had long been known to be an effective fertilizer and small quantities had been produced in several countries from time to time, it did not become a popular fertilizer until the 1960s. Ammonium phosphates are now the leading form of phosphate fertilizer in the world.

Development of the nitrophosphate fertilizers was started in Europe in the 1930s. Several processes were developed, and subsequent improvements have added to their efficiency and improved the quality of the products. Their popularity in Europe has increased, and several plants have been built in other continents. Many of the plants are quite large, producing 1,500 or more tons of product per day.

Direct application of raw, finely ground phosphate rock has been practiced to a substantial extent in the United States, Russia, and China and to some extent in other countries. The practice is declining in the United States. However, recent information indicates that the value of raw phosphate varies widely with variations in the character of the ore and the crop and soil on which it is used. There are indications that reactive rocks may be useful sources for at least part of the phosphorus requirement of many crops grown on acid soils.

Early sources of phosphate rock were small deposits in England, Ireland, Spain, France, Germany, and the United States (South Carolina). Most of these deposits are no longer mined because of their low grade or because they have been virtually exhausted. Present supplies are mainly from other areas of the United States, Russia, and Morocco with smaller outputs from the Near East, Egypt, Tunisia, Algeria, South Africa, Brazil, Togo, Senegal, and Pacific Islands. New discoveries have abounded during the last few years, and several new deposits appear to be very large and capable of producing a good grade of rock. To name a few, deposits in Australia, Peru, Arabia, Venezuela, Colombia, Iran, and India have interesting possibilities. So many discoveries have been made in the last few years that one wonders whether many more will follow.

Nitrogen Fertilizers

For many years the need for supplying nitrogen in fertilizers was considered to be of secondary importance, although the essential role of nitrogen in crop production was recognized. Natural supplies, with a system of crop rotation, were deemed adequate. Fixed nitrogen is supplied in rainwater (about 5 kg/ha), and atmospheric nitrogen is fixed by certain leguminous crops that were included in the rotation. Return of crop residues and waste materials helped to conserve the nitrogen supply. These natural supplies were supplemented by small amounts of fertilizer nitrogen from guano, Chilean nitrate of soda, and various organic wastes.

Coal contains about 1% nitrogen, about half of which is evolved as ammonia in byproduct coke ovens or some types of gas producers. Starting in the latter part of the 19th century, this nitrogen became a growing source of fertilizer nitrogen. Most of it was in the form of ammonium sulfate; smaller amounts were supplied as gas liquor, a dilute solution of ammonia.

As a growing population made it evident that world food needs could be met only by an increased supply of fixed nitrogen, research in several countries was concentrated on fixation of atmospheric nitrogen. Three commercially successful processes emerged. In 1903 the arc process was introduced commercially in Norway. Nitrogen and oxygen were combined to form nitric oxide (NO) at a very high temperature (about 3250°C) in an electric arc; at lower temperatures the nitric oxide reacted with more oxygen to form nitrogen dioxide (NO_2), which was hydrated in the presence of excess air to form nitric acid. The nitric acid was converted to the end product, calcium nitrate, by reaction with limestone.

At about the same time the calcium cyanamide process was perfected. Calcium carbide, produced by reaction of lime with coke in an electric furnace, was converted to calcium cyanamide ($CaCN_2$) by reaction with pure nitrogen extracted from the air. The product could be used directly as a fertilizer, or it could be hydrolyzed to form ammonia.

The economics of the arc and cyanamide processes depended on low-cost electricity; at best, both were costly.

Direct synthesis of ammonia from nitrogen and hydrogen was first carried out successfully on a commercial scale in Germany in 1913. Plants were built in several other countries after the first world war. Most of these plants derived their hydrogen-nitrogen synthesis mixtures from the reactions of coke with steam and air.

The first ammonia plants were quite small, 25-50 tpd, and costs remained high. Much of the ammonia was used to produce explosives or industrial chemicals. Fertilizer use remained small because chemical nitrogen was too expensive for liberal use on farm crops other than those of high cash value. Even as late as 1950 many agriculturists advocated that principal reliance for nitrogen supplies be placed on legumes grown in rotation with other crops.

Successive improvements in ammonia production have lowered the cost to the point that its liberal use in crop production is economically attractive. Notable among these improvements was perfection of processes for reforming natural gas or naphtha to supply the hydrogen-nitrogen synthesis gas and for increasing the scale of operation.

The use of centrifugal compressors, starting in the 1960s, made possible large, single-stream ammonia plants of 1,000- or even 1,500-tpd capacity. These large ammonia plants are capable of producing ammonia much more economically than the older, smaller plants that used reciprocating compressors.

At first the final products--ammonium sulfate, calcium nitrate, sodium nitrate, and calcium cyanamide--were all low-analysis materials (15%-21% N). Ammonium nitrate (34% N) began to be an important fertilizer material in the 1940s and became the leading form in the 1960's. More recently, urea production (46% N) has grown rapidly and is now the leading form, worldwide. Direct application of ammonia (82% N) to the soil, either in anhydrous form or in aqueous solution, is growing rapidly in some countries.

Potash Fertilizers

Early sources of potash were wood ashes, sugar beet wastes, and saltpeter. The salt deposits in Germany were opened in 1860 and dominated the world market for 75 years. Low-grade, unrefined ores such as manure salts (20%-25% K_2O) and kainite (19% K_2O) were the first products. The development of refining methods gradually increased the grade of commercial products. High-grade potassium chloride (60%-62% K_2O) is now the main product. Potassium sulfate and potassium nitrate are the principal nonchloride potash fertilizers. They are more expensive and hence are used only on crops or soils for which the chloride is unsuited. Important potash deposits were found in other countries, and production started in France (1910), Spain (1925), Russia (1930), United States (1931), and Canada (1960). Large deposits occur elsewhere and may be utilized in the future.

Other Nutrients

One of the important early fertilizers was gypsum, which supplied sulfur and calcium. Its use was said to have originated when a German plasterer observed that small amounts of plaster spilled from his wheelbarrow made the grass along the pathway grow lush and green. In any event, gypsum for agricultural use became known as "land plaster."

Later, superphosphate and ammonium sulfate supplied adequate amounts of sulfur, even though their primary purpose was to supply phosphorus and nitrogen. Likewise, basic slag which is widely used in Europe for its phosphorus content also supplies calcium and various micronutrients. In most industrial countries, millions of tons of sulfur from combustion of fuels pass into the atmosphere and are subsequently brought down by rainfall. In most such areas the deliberate addition of sulfur to fertilizer has not proved necessary, but there are important exceptions. As the removal of sulfur from stack gas becomes widespread for the prevention of atmospheric pollution, we may need to supply more sulfur in fertilizers. In many less industrial areas the need for sulfur is already well known.

Limestone and dolomite are widely used to supply calcium and magnesium when needed. Other magnesium materials include magnesium silicate, calcined brucite (MgO), magnesium sulfate, and langbeinite (K_2SO_4-$2MgSO_4$).

The importance of most micronutrients in crop production was not recognized until the 20th century. Iron is an exception: Gris (France) discovered in 1844 that chlorosis of some plants can be corrected by spraying them with iron salts. Liebig noted the presence of manganese in plant ash but doubted that it was a nutritive element. It was not until 1905 that manganese was recognized as essential to plant growth. Then followed copper and boron in the 1920s, zinc (about 1930), molybdenum (1939), and chlorine (1954). Still other elements that are not strictly essential may, in some cases, be economically important in increasing crop yields or improving quality. Silicon, sodium, and cobalt are examples.

Compound Fertilizers

Most of the early experimenters in chemical fertilizers, such as Murray and Liebig, worked with mixtures that contained several nutrient materials. However, as the fertilizer industry developed in Europe, the major practice was the separate production of straight fertilizers, each containing only one primary nutrient.

In contrast, the early development of the U.S. fertilizer industry was mainly along the line of providing compound fertilizer. Starting from these extremes, the practices of the two areas are converging. The trend is toward supplying 80%-90% of the phosphate and potash and smaller proportions of the nitrogen in compound fertilizer, which also may contain secondary or micronutrients. Much of the nitrogen is supplied as a straight material. In Japan, as in Europe, the trend is toward increasing proportions of compound fertilizer.

The reason for the growing popularity of compound fertilizer is that farmers no longer have the time or inclination to apply several fertilizers separately, nor do they have facilities to mix them. Also formulations are becoming more and more complex as farmers strive for higher yields and greater productivity. However, nitrogen is often applied separately because timing is important, and supplemental dressings of nitrogen during the growing season often are needed for best results. Also, some straight nitrogen materials, such as anhydrous ammonia, are much cheaper than the same amount of nitrogen in compound fertilizers.

At first compound fertilizers were made by simple mixing of low-grade materials--guano, superphosphate, ammonium sulfate, potassium chloride, and waste organic materials. Limestone often was added as a filler and to neutralize acidity of superphosphate. Ammoniation of superphosphate became popular in the 1930s; ammoniation supplied nitrogen economically and improved the physical properties of the superphosphate. Light ammoniation in batch mixers characterized early practice. Gradually, the various waste organic materials were eliminated, often because a better use was found for them. For example, cottonseed meal became more valuable for stock feed. Analyses of products rose as fillers were eliminated.

With the higher analyses came increased caking problems. Increased use of mechanical application equipment by farmers called for dependably free-flowing material; thus, granulation became popular starting in the 1950s.

Analyses of compound fertilizer rose further as triple superphosphate replaced ordinary superphosphate, and ammonium nitrate or urea replaced ammonium sulfate or sodium nitrate. Later, still higher analyses were attained by liberal use of phosphoric acid and ammonia in the formulations. Compound fertilizer preparation was no longer a simple mechanical job but a complex chemical engineering operation. As such, its economics depended on large-scale operation. Small local mixers expanded to large regional manufacturers; they became bulk blenders or dealers; or they went out of business.

Bulk blends became popular in some countries as a method by which a local mixer could supply whatever mix the farmer needed in simple equipment at low cost. Granular materials such as diammonium phosphate, muriate of potash, and ammonium nitrate or urea were produced by large companies having the facilities and capabilities for chemical manufacture and granulation and having favorable raw material costs. These products were shipped in bulk to blenders offering prescription mixing, custom application, and many other services to the farmers. The success of this system depends to a large extent on dependable, low-cost transportation. Covered, hopper-bottom rail cars protect the material from the weather, minimizing spillage, and make unloading easy. Barge transport or ocean shipment is also suitable between points on waterways.

More Intensive Agriculture

Changes in agriculture have been no less dramatic than developments in fertilizer technology, and these have played a large part in increasing the demand for fertilizers.

When the world population was relatively small and when land and labor were plentiful, there was little need for increasing yields per hectare. For example, at the beginning of the 20th century, about half of the farms in the original 13 colonies of the United States had been abandoned. Farmers and immigrants moved on to new, richer lands in the Ohio and Mississippi valleys. Chemical fertilizers were so expensive that they were used only on high-value cash crops such as cotton and tobacco. Abandoned farmland in some cases regains a part of its native fertility through natural processes; trees reach deep in the subsoil for their supply of mineral elements and fallen leaves deposit it in the topsoil. Rocks weather and release their mineral elements in a more available form. Natural fixation processes--meteorological and microbiological--build up the nitrogen content of the fallow soil. In other cases, severe erosion may cause more damage than nature can repair.

The richer soils of the Mississippi valley were farmed for 75-100 years without fertilizer. Farms of those days and even 50 years ago were, to a large extent, subsistence farms. Draft animals supplied the motive power for farm machinery and transportation. Farm animals supplied meat, eggs, milk, and butter. Grain, vegetables, and fruit raised on the farm supplied the family's food. A large part of the nutrients in farm crops was returned to the soil as crop residues and manure. Legumes such as clover or alfalfa were grown in rotation and plowed under to supply nitrogen to cereal crops.

Cyril Hopkins, in his popular book The Farm That Won't Wear Out (1913), recommended a farming system that conserved soil nutrients by return of crop residues, animal wastes, and green manure. Since phosphorus and sometimes lime were often deficient, he recommended application of ground rock phosphate at 5- to 10-year intervals and limestone when necessary. Nitrogen was furnished by legumes in rotations. The soil supply of potash was considered adequate for the foreseeable future. He warned against use of chemical fertilizers because of their high cost and transitory effect. For example, at that time the delivered cost of superphosphate was four times that of ground rock phosphate.

Hopkins gave examples of how his system increased profits from farm operation. The system was indeed profitable under the conditions existing 65 years ago, and yields were much better than the national average but still low by present-day standards.

Many countries have passed through this stage when low yields, utilization and conservation of native soil fertility, and bringing new land under cultivation were adequate and economical methods for supplying food needs. Today the rapidly growing population leaves few countries that choice. Yields per hectare must be greatly increased in many developing countries as they have been in developed (and some developing) countries. Increased fertilizer use is a necessary requirement for intensive agriculture. More of the farm produce now leaves the farm to feed workers in the cities. Decreased use of draft animals releases more food for people, but less manure is available. These factors mean that less of the nutrient content of crops is returned to the soil. On the other hand, higher yields mean more crop residues and increased importance of returning crop residues to the soil.

A major landmark in the intensification of agriculture is the development of high-yielding varieties of cereal crops. Starting in the 1930s, the development of hybrid corn played a major role in increasing yields and fertilizer use. Also, the varieties adapted to climatic conditions (drought-resistant or early-maturing, for example) extend the area in which this crop can be grown. Improved varieties of wheat and rice followed, and improvement is continuing with these and other crops. These improved varieties are much more responsive to fertilizer and have been a large factor in increased fertilizer use.

Statistical Review of Growth in Fertilizer Production and Consumption: 1950-76

Statistics showing annual fertilizer production and consumption for the years 1950 through 1976 are shown in tables 1 and 2, respectively. The tables show production and consumption by nutrient (N, P_2O_5, and K_2O) and by economic class of countries (developed and developing). Table 3 shows world totals, including preliminary estimates for 1978.

World consumption generally followed the same trends as world production. However, in 1975 consumption decreased for the first time. This decrease is generally attributed to the extremely high prices of fertilizers on the world market. Now that prices have declined to a more reasonable level, consumption is again increasing as shown in table 3.

TABLE 1. WORLD FERTILIZER PRODUCTION - HISTORICAL DATA, 1950-76 (MILLIONS OF TONS)

	Developing Countries[a]				Developed Countries[a]			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
1950	0.35	0.27	0.01	0.63	3.73	5.59	4.21	13.5
1951	0.43	0.34	0.02	0.79	4.25	5.93	4.94	15.1
1952	0.45	0.36	0.02	0.83	4.49	6.13	5.40	16.0
1953	0.51	0.37	-	0.88	5.02	6.16	5.87	17.1
1954	0.59	0.41	0.01	1.01	5.59	6.60	6.32	18.5
1955	0.58	0.45	0.02	1.05	6.29	7.34	6.84	20.5
1956	0.59	0.54	0.04	1.17	6.94	7.71	7.14	21.8
1957	0.72	0.56	0.06	1.34	7.49	7.94	7.65	23.1
1958	0.77	0.60	0.09	1.46	8.24	8.20	7.66	24.1
1959	0.86	0.64	0.10	1.60	9.00	8.68	8.17	25.9
1960	0.93	0.72	0.12	1.77	9.43	9.24	8.61	27.3
1961	1.04	0.79	0.14	1.97	10.37	9.56	8.68	28.6
1962	1.14	0.76	0.14	2.04	11.12	9.86	9.25	30.2
1963	1.43	0.85	0.16	2.44	12.2	10.5	9.69	32.4
1964	1.72	1.01	0.19	2.92	13.8	11.7	10.6	36.1
1965	2.02	1.15	0.30	3.47	15.4	12.7	11.8	39.9
1966	2.24	1.30	0.39	3.93	17.7	14.2	13.4	45.3
1967	2.49	1.48	0.38	4.35	19.8	15.3	14.1	49.2
1968	2.79	1.75	0.41	4.95	22.4	16.0	14.8	53.2
1969	3.44	2.01	0.43	5.88	24.9	16.3	15.4	56.6
1970	4.07	2.32	0.59	6.98	26.1	17.0	16.1	59.2
1971	4.59	2.59	1.00	8.18	28.3	18.2	16.9	63.4
1972	5.61	3.11	1.13	9.85	29.3	19.3	18.3	66.9
1973	6.61	3.54	1.22	11.4	31.2	20.1	19.0	70.3
1974	7.24	3.97	1.10	12.3	33.3	21.2	21.1	75.6
1975	7.99	4.22	1.25	13.5	34.3	21.5	22.5	78.3
1976	9.17	4.25	1.31	14.7	34.8	20.5	22.2	77.5

a. Classification of countries is the United Nations standard except that South Africa and Israel are included in developing countries.

Source: UNIDO, "Draft World-Wide Study of the Fertilizer Industry: 1975-2000," December 1976. Data for 1976 from FAO, Annual Fertilizer Review, 1977.

World production has increased from about 14 to 105 million tons in the 28-year period as shown in figure 1. The average of the annual percentage increases for 1950 through 1975 is 7.8%.[1] The average of the last 10 annual increases (1966-75) is also 7.8%. Thus, there is no clear trend in the rate of increase. However, 7.8% of 14 million tons is 1.1 million tons, whereas 7.8% of 92 million tons is 7.2 million tons. Thus, the trend is toward ever-increasing annual increments of tonnage of production.

The rate of increase in nitrogen fertilizer production has been more rapid than for phosphate or potash as shown in figure 2 and table 4. For the 26-year period (1950-75) nitrogen fertilizer production increased over 10 fold, whereas phosphate and potash increased by a factor of 4.4 and 5.6, respectively.

The percentage rate of increase in developing countries is higher than in developed countries. In a recent 5-year period (1971-75), production in developing countries increased by 64% as compared with 24% for developed countries. However, the tonnage increase in developed countries was greater than that in developing countries by a factor of 3--roughly 15 versus 5 million tons.

Each year production has exceeded consumption by amounts ranging from 1% to 10%. The difference averaged 5.3% for the 10-year period 1965-74 as compared with 3.8% for the previous 15 years indicating that the percentage difference is increasing. This is a matter of some importance that is sometimes overlooked. It is sometimes assumed that production and consumption are "in balance" when they are equal, whereas production has substantially exceeded consumption even in periods of acute shortage. Therefore, when planning production or supply to meet consumption goals, allowance should be made for at least 5% apparent loss. The apparent loss may vary from one country to another, depending on its reporting system and its distribution system.

The reasons for the apparent loss are numerous and worth considering since some 5 million tons of nutrient, over 10 million tons of actual material, are involved. It is often stated that the apparent loss can be explained by increase in stocks in storage and in the distribution system. Increased stocks can be a factor; however, the accumulated difference between consumption and production for the last 26 years is 58 million tons (nutrient basis) or in the order of 150 million tons actual weight. Thus, it seems unlikely that increased stocks can explain a major portion of the difference.

The most likely explanation of the apparent loss is some combination of discrepancies introduced by

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[1] Throughout this manual years given in statistical data refer to the split year ended June 30 of the year stated, for example "1975" refers to the split year 1974-75.

TABLE 2. WORLD FERTILIZER CONSUMPTION - HISTORICAL DATA, 1950-76 (MILLIONS OF TONS)

	Developing Countries[a]				Developed Countries[a]			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
1950	0.56	0.36	0.09	1.01	3.19	5.41	4.04	12.6
1951	0.59	0.41	0.11	1.12	3.73	5.81	4.43	14.0
1952	0.68	0.48	0.14	1.30	4.01	5.77	4.86	14.6
1953	0.87	0.51	0.15	1.53	4.60	6.06	5.20	15.9
1954	0.96	0.60	0.19	1.75	5.16	6.51	5.48	17.2
1955	0.94	0.60	0.23	1.78	5.69	7.14	6.11	18.9
1956	1.24	0.66	0.27	2.17	5.82	7.45	6.51	19.8
1957	1.45	0.76	0.31	2.52	6.19	7.68	6.87	20.7
1958	1.58	0.83	0.35	2.76	6.69	7.87	7.08	21.6
1959	1.81	0.86	0.38	3.04	7.47	8.38	7.56	23.4
1960	1.95	0.94	0.42	3.31	7.80	8.90	7.83	24.5
1961	2.45	1.05	0.54	4.04	8.51	9.03	7.96	25.5
1962	2.49	1.10	0.54	4.12	9.15	9.51	8.15	26.8
1963	2.77	1.27	0.58	4.61	10.4	10.1	8.76	29.3
1964	3.33	1.47	0.68	5.48	11.7	11.0	9.36	32.1
1965	3.65	1.58	0.73	5.95	12.8	12.2	10.3	35.3
1966	4.23	1.77	0.84	6.84	14.7	13.0	11.4	39.1
1967	5.33	2.11	1.00	8.44	16.5	13.9	12.0	42.5
1968	5.51	2.34	1.12	8.97	18.5	14.5	12.9	45.9
1969	6.80	2.81	1.34	11.0	19.7	15.2	13.4	48.3
1970	7.70	3.25	1.47	12.4	21.0	15.6	14.0	50.5
1971	8.77	3.51	1.80	14.1	23.0	16.3	14.9	54.2
1972	9.45	4.09	1.93	15.5	23.8	17.0	15.7	56.5
1973	10.6	4.59	2.24	17.4	25.2	18.0	16.6	59.8
1974	11.4	5.34	2.61	19.3	27.3	18.9	18.1	64.3
1975	11.7	5.49	2.85	20.0	27.2	17.4	17.1	61.7
1976	12.8	5.53	2.73	21.1	30.4	18.6	18.6	67.6

a. Classification of countries is the United Nations standard except that South Africa and Israel are included in developing countries.

Source: UNIDO, "Draft World-Wide Study of the Fertilizer Industry: 1975-2000," December 1976. Data for 1976 from FAO, Annual Fertilizer Review, 1977.

TABLE 3. TOTAL WORLD FERTILIZER PRODUCTION AND CONSUMPTION

	Tons of N + P_2O_5 + K_2O x 10^6				
Year	Production	Annual Increase, %	Consumption	Difference	Difference, % of Production
1950	14.13		13.61	0.52	3.7
1951	15.89	12.5	15.12	0.77	4.8
1952	16.83	5.9	15.90	0.93	5.5
1953	17.98	6.8	17.43	0.55	3.1
1954	19.51	8.5	18.95	0.56	2.9
1955	21.55	10.5	20.68	0.87	4.0
1956	22.97	6.6	21.97	1.00	4.4
1957	24.44	6.4	23.22	1.22	5.0
1958	25.56	4.6	24.36	1.20	4.7
1959	27.50	7.6	26.44	1.06	3.8
1960	29.07	5.7	27.81	1.26	4.3
1961	30.57	5.2	29.54	1.03	3.4
1962	32.24	5.5	30.92	1.32	4.1
1963	34.84	8.1	33.91	0.93	2.7
1964	39.02	12.0	38.58	0.44	1.1
1965	43.37	11.2	41.25	2.12	4.9
1966	49.23	13.5	45.94	3.29	6.7
1967	53.55	8.8	50.94	2.61	4.9
1968	58.15	8.6	54.87	3.28	5.6
1969	62.48	7.4	59.30	3.18	5.1
1970	66.18	5.9	62.90	3.28	5.0
1971	71.58	8.2	68.30	3.28	4.6
1972	76.75	7.2	72.00	4.75	6.2
1973	81.70	6.4	77.20	4.50	5.5
1974	87.90	7.6	83.60	4.30	4.9
1975	91.70	4.4	81.60	9.90	10.8
1976	93.88	2.4	89.70	4.18	4.5
1977	99.25	5.7	95.95	3.30	3.3
1978[a]	105.39	6.1	99.39	6.00	5.7
Average		7.3			4.8

a. Preliminary.

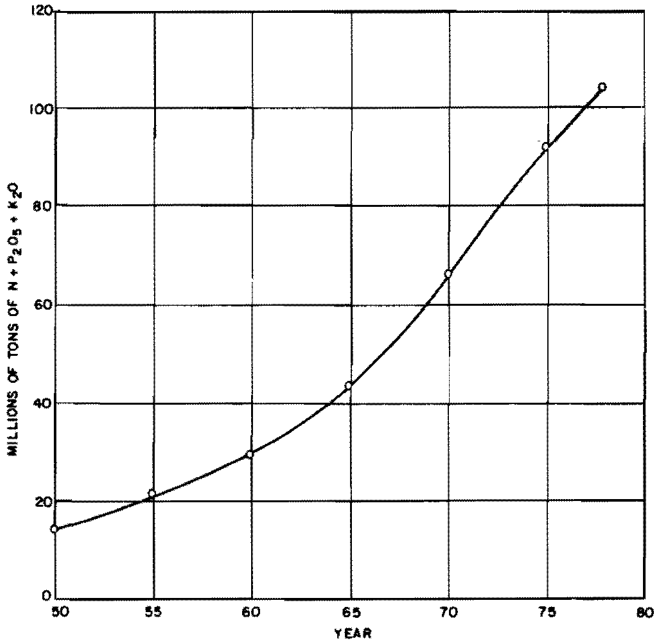

Figure 1. World Production of Fertilizers, 1950-78.

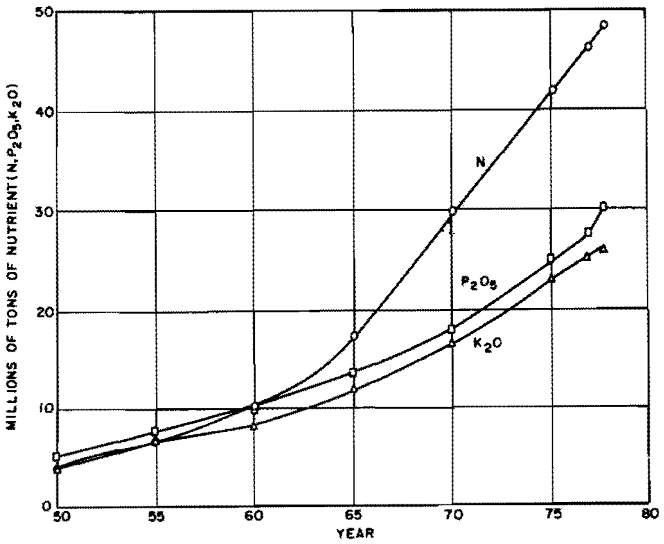

Figure 2. World Fertilizer Production by Nutrients, 1950-78.

reporting systems, actual losses, and diversion of fertilizers to other uses. Reporting systems vary from one country to another; thus, various sources of discrepancies may occur. Two likely sources are overage in analysis and overage in weight. Production reports are often based on exact analysis and weight, whereas consumption is often based on guaranteed minimums. Until 1966 the U.S. Department of Agriculture reported consumption in the United States on the basis of actual analysis of representative samples of the various fertilizers consumed. After that date the reports were based on the guaranteed analysis. For the year 1965 a comparison was made which showed that consumption reported on the basis of guaranteed analysis was about 1% less than consumption based on actual analysis. Likewise, when fertilizers are sold in bags, the producer often seeks to avoid penalties for under-weight bags by slightly overfilling in order to allow for inaccuracies in weighing. In some studies of the accuracy of bag-packing machines, an average of about 1% overweight seemed typical.

Losses in storage and distribution may include leakage and pilferage and losses due to wrecks, fires, and floods. Fertilizers may be rendered unusable because of exposure to weather or humid atmosphere or because of contamination in storage or shipment.

Finally, many fertilizers have alternative uses such as for animal feed supplement, fire-fighting,

TABLE 4. WORLD PRODUCTION OF FERTILIZERS BY NUTRIENTS

Year	Countries[a]	Tons x 10^6 of Nutrients			
		N	P_2O_5	K_2O	NPK
1950	Developing	0.35	0.27	0.01	0.63
	Developed	3.73	5.59	4.21	13.5
	Total	4.08	5.86	4.22	14.13
1955	Developing	0.58	0.45	0.02	1.05
	Developed	6.29	7.34	6.84	20.47
	Total	6.87	7.79	6.86	21.52
1960	Developing	0.93	0.72	0.12	1.77
	Developed	9.43	9.24	8.61	27.3
	Total	10.36	9.96	8.73	29.07
1965	Developing	2.02	1.15	0.30	3.47
	Developed	15.4	12.7	11.8	39.9
	Total	17.42	13.85	12.10	43.37
1970	Developing	4.07	2.32	0.59	6.98
	Developed	26.1	17.0	16.1	59.2
	Total	30.17	19.32	16.69	66.18
1975	Developing	7.99	4.22	1.25	13.5
	Developed	34.3	21.5	22.5	78.3
	Total	42.29	25.72	23.75	91.8

a. Classification of countries is the United Nations standard except that South Africa and Israel are included in developing countries.

Source: UNIDO, "Draft World-Wide Study of the Fertilizer Industry: 1975-2000," December 1976.

de-icing and various chemical uses. While most countries report such uses separately, it is quite likely that some materials originally produced for fertilizer use are actually diverted to other uses.

Production in developing countries as a group has lagged behind consumption. In 1976 production in developing countries was 14.7 million tons of NPK while consumption was 21.1 million tons. Allowing for 5% apparent loss production of 22.2 million tons would be needed for a balance; thus, the net deficiency was 7.5 million tons. The deficiency was met by net imports from developed countries.

II Outlook for the Fertilizer Industry (1978-2000)

Introduction

This chapter is based to a large extent on the UNIDO draft report, "World-Wide Study of the Fertilizer Industry 1975-2000," (December 1976). This study was revised and issued in September 1978 as UNIDO/ICIS document 81. Unless otherwise indicated the discussion in this chapter is based on the earlier draft. However, the main conclusions were not greatly different.

World fertilizer production and consumption are expected to continue to increase but at declining annual percentages. Table 1 and figure 1 show projections of world fertilizer consumption from the UNIDO study which will be discussed in more detail in chapter XXVI. Table 2 shows the projections from the revised report, which are only slightly different.

Up to 1972, the cost of fertilizers declined steadily as advances in technology, increase in size of manufacturing plants, and improvements in distribution more than offset steadily rising labor and construction costs. Starting in 1973, a dramatic increase in construction and raw material costs has reversed this trend.

No further advances are expected in technology which will be of sufficient magnitude to offset the sharply increased cost of plant construction and of some raw materials. Increasing the size of fertilizer plants beyond that of the present large plants will yield only minor lowering of production costs, which may be offset by increased distribution costs. Therefore, it seems inevitable that the cost of fertilizers will increase in the future unless there are unforeseen technological breakthroughs (which are always possible).

Future rise in costs can be slowed by technological improvements and more efficient operation of production facilities. Perhaps a more hopeful field for improvement lies in more efficient physical distribution, better utilization of applied nutrients, and higher operating rates of existing plants.

Fertilizer Use

The estimated world demand in 2000 is 264 million tons of nitrogen (N), phosphate (P_2O_5), and potash (K_2O) as compared with 83.6 million tons in 1974, a

TABLE 1. PROJECTIONS OF FERTILIZER DEMAND BASED ON 1964-65 TO 1974-75 AND ON THE JOINT WORKING GROUP ESTIMATES FOR 1979-80 (CLASSIFICATION OF COUNTRIES IS UNITED NATION STANDARD CLASSIFICATION)[a]

	1980	1985	1990	1995	2000
			-million tons-		
			Nitrogen Demand		
Developed countries	37.5	47.6	58.9	71.4	85.1
Developing countries	18.1	25.4	33.9	43.6	54.5
World	55.6	73.0	92.8	115.0	139.6
			P_2O_5 Demand		
Developed countries	22.8	26.7	31.0	35.6	40.6
Developing countries	7.6	10.8	14.4	18.6	23.3
World	30.4	37.5	45.4	54.2	63.9
			K_2O Demand		
Developed countries	22.8	27.8	33.3	39.3	45.8
Developing countries	4.3	6.3	8.6	11.3	14.4
World	27.1	34.1	41.9	50.6	60.2
			NPK Demand		
Developed countries	83.1	102.1	123.2	146.3	171.5
Developing countries	30.0	42.5	56.9	73.5	92.2
World	113.1	144.6	180.1	219.8	263.7

a. Developed countries include North America, Western Europe, Eastern Europe, U.S.S.R., Japan, Israel, South Africa, Australia, and New Zealand. Developing countries include Latin America, Asia (except Japan and Israel), Africa (except South Africa), and Oceania (except Australia and New Zealand).

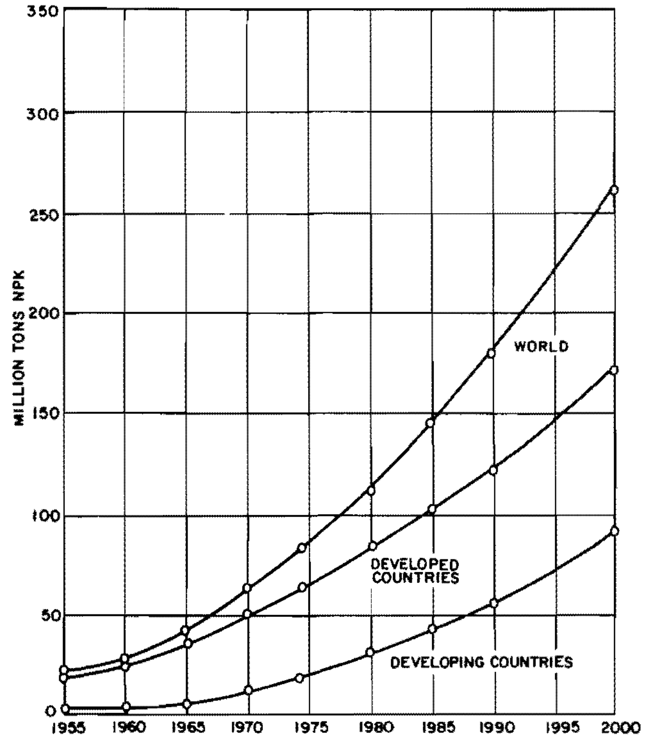

Figure 1. World Fertilizer Use: Projections 1980-2000 by R. Ewell.

3.2-fold increase (figure 1). Assuming an average nutrient content of 42% ($N+P_2O_5+K_2O$), the gross weight of annual fertilizer use would be 629 million tons by the year 2000.

Fertilizer use in developing countries is expected to increase from 19.3 million tons in 1974 to 92 million tons in 2000 ($N+P_2O_5+K_2O$ basis). This is a 4.8-fold increase. The estimates are based on probable demand and not on food requirements. It is likely that an estimate based on food requirements for adequate nutrition of the increasing population would be higher for most developing countries and lower for many developed countries. Naturally, any long-range forecast is subject to many uncertainties, and no great accuracy can be claimed for the present forecasts. However, they serve the purpose of indicating the order of magnitude of needed expansion of the fertilizer industry, especially in developing countries.

The developing countries as a whole are expected to maintain a nutrient ratio of $N:P_2O_5:K_2O$ which is equal to approximately 4:2:1 through the 1974-2000 period, whereas developed countries are expected to increase the nitrogen component from a 1.4:1.0:1.0 ratio in 1974 to 2.2:1.0:1.1 in 2000. Thus, the greater part of the growth will be in nitrogen fertilizer in both groups. The worldwide nutrient ratios should not be assumed to imply an optimum ratio for any individual country; country ratios should and do vary widely according to the needs of their soil, crops, and levels of management.

The following tabulation shows the present and forecasted fertilizer use in terms of per capita and per hectare in developed and developing countries:

Fertilizer Use on a per-Capita and per-Hectare Basis

	kg/Capita[a]		kg/Hectare	
Year	Developed Countries	Developing Countries	Developed Countries	Developing Countries
1974	58	6.7	109	22
1980	73	9.4	149	32
1990	100	14.1	225	55
2000	130	18.7	322	83

[a] Based on population growth forecasts (see chapter XXVI).

It will be noted that the rate of increase of fertilizer use per capita is substantially less in developing countries than the tonnage rate, and the per-capita rate in developing countries will remain far

TABLE 2. REVISED PROJECTIONS OF FERTILIZER DEMAND

	1979	1983	1988	2001
	-million tons-			
		Nitrogen Demand		
Developed countries	34.4	41.7	51.3	82.0
Developing countries	17.0	22.8	32.7	63.5
World	51.4	64.5	84.0	145.5
		P_2O_5 Demand		
Developed countries	22.1	27.2	30.7	48.3
Developing countries	7.4	10.3	14.5	27.9
World	29.5	37.5	45.2	76.2
		K_2O Demand		
Developed countries	21.9	26.3	33.3	54.6
Developing countries	3.4	4.6	6.6	12.3
World	25.3	30.9	39.9	66.9
		NPK Demand		
Developed countries	78.4	95.2	115.3	184.9
Developing countries	27.8	37.7	53.8	103.7
World	106.2	132.9	169.1	288.6

Source: "Second World-Wide Study of the Fertilizer Industry: 1975-2000" (1978) UNIDO, Vienna, Austria.

below that of the developed countries. This is partly because of the relatively rapid population growth rate in developing countries.

The rate per hectare in developing countries will be well below the rate at which maximum yields of most crops are obtained, whereas in developed countries the rate per hectare will approach an upper limit of economic effectiveness in the year 2000 unless further advances in high-yielding crop varieties and cultivation and application methods increase the yield potential.

Fertilizer Production

Production of fertilizers in developing countries as a group has lagged behind fertilizer use. In 1976 production was only 70% of use. As a result, developing countries are importers of fertilizers; in 1976 the deficit amounted to 7.5 million tons (nutrient basis) assuming a supply:consumption ratio of 1.05. This situation, combined with rapidly increasing needs and presence of necessary raw materials, provides an opportunity for developing countries to establish fertilizer manufacturing industries and thereby help improve their economies. The UNIDO study suggests that developing countries should construct a sufficient number of fertilizer plants to become at least self-sufficient as a group in nitrogen and phosphate fertilizers. This would mean that, by the year 2000, about 40% of the world's production facilities for nitrogen and phosphate fertilizers would be located in developing countries. It should be noted that "self-sufficiency" is intended to mean a balance between exports and imports; it does not imply an absence of trade between developed and developing countries. Also it does not imply that each country should be self-sufficient, merely that the developing countries as a group should seek to attain self-sufficiency.

Potash production was not considered in the UNIDO study for two reasons. First, strictly speaking, potash production is not a manufacturing industry; it is a mining and beneficiation industry. Second, very few developing countries have known potash reserves of sufficient size and quality for commercial production. On the other hand, the raw materials for manufacturing nitrogen and phosphate fertilizer are abundant in developing countries as a whole and fairly widely (although unevenly) distributed.

The estimated capital cost for constructing the required number of nitrogen and phosphate fertilizer plants during the period of 1980 to 2000 is summarized below.

U.S. $ Billions[1]		
Developing Countries	Developed Countries	Total
48	51	99

The capital cost requirement is based on 1975 U.S. dollars and does not allow for inflation. It does not include capital requirements for mining and refining raw materials, transportation and distribution of products, and necessary improvements of infrastructure; these costs cannot be precisely estimated but might well increase the world total to over $300 billion.

All nitrogen fertilizer was assumed to be derived from ammonia with a small percentage as byproducts (mainly ammonium sulfate) from other industries. All new ammonia plants were assumed to have a rated capacity of 1,000 tpd. Larger or smaller plants may be economically preferable in specific situations, but the effect on overall cost would be comparatively small.

It is predicted that natural gas will be the feedstock for the majority of new ammonia plants, its use ranging from 72% in 1980-85 to 64% in 1990-2000. Naphtha feedstock will be used in only about 5% of the new plants, heavy fuel oil in about 15%, and coal in 9% (1980-85) to 17% (1990-2000). The choice of feedstock affects the capital cost of ammonia plants; coal-based plants cost nearly twice as much as those based on natural gas.

The amount of anhydrous ammonia used directly as fertilizer is expected to be approximately 10% of all nitrogen fertilizer. Ammonium sulfate and the nitrogen content of ammonium phosphate will supply another 10% of total nitrogen fertilizer. The remaining 80% is assumed to be urea or ammonium nitrate, either straight or in compound fertilizers. The cost calculations are based on urea, but ammonium nitrate costs will not be significantly different for the purpose of the study.

The production of nitrogen fertilizer is highly capital intensive; 60%-90% of the product cost consists of capital-related costs (depreciation, interest, profit, maintenance, etc.), depending on type and cost of feedstock, plant capacity, and percentage of utilization of capacity. Operation at a low percentage of rated capacity sharply increases product costs. In this connection the study assumes that all plants completed after 1980 will reach an average of 90% of rated capacity within 3-4 years after startup. Installed capacity in 1974 was operating at about 60% of design in developing countries, but some improvement has been achieved more recently.

All new phosphate plants were assumed to have a capacity of 600 tons or more of P_2O_5 per day. Smaller or larger plants may be economically preferable in many cases. It was assumed that the production of new (after 1980) plants would be in the form of DAP (50%), MAP (30%), and TSP (20%). Other products such as nitrophosphates may be better choices in specific cases, but the effect on overall worldwide production costs was not considered significant for the purposes of this study. It is recognized that there will continue to be a place for SSP and other low-analysis products that have local agronomic advantages or are better adapted to utilization of local resources. Some of these processes have comparatively low capital requirement for production facilities, but the expense of transporting the low-analysis products is higher per unit of plant nutrient unless sulfur is needed as a fertilizer nutrient. The use of ground phosphate rock for direct application was not considered in this study since ground rock is not a manufactured product. However, if its use becomes more widespread, it would decrease the need for chemically manufactured phosphates.[2]

The use of compound fertilizer is expected to increase in most countries; it is assumed that by the year 2000 65% and 86% of the P_2O_5 will be supplied as compound fertilizers in developing and developed countries, respectively. The cost of production of compound fertilizers was not taken into account except insofar as it represents a minor addition to the cost of granulating DAP or as in the case of nitrophosphates when it replaces the cost of separate

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[1] Throughout this manual the term "billion" shall mean 1,000 million or 10^9.

[2] In 1974-75, use of ground rock phosphate reported by FAO was 1,204,289 tons of P_2O_5, equivalent to 5.3% of world P_2O_5 consumption. However, several countries (including China) did not report rock phosphate use separately. Total use is believed to be approximately 7%-8%.

granulation (or prilling) of nitrogen and phosphate fertilizers. The preparation of compound fertilizers in local plants by mixing, bulk blending, or granulation was considered to be part of the distribution and marketing system.

Value of Production

At present international price levels (July 1976), the value of the world's annual fertilizer production in the year 2000 is expected to be very roughly $60 billion. Since present prices are somewhat depressed because of surplus production, it is likely that the actual value would be substantially higher. The average value of the increased agricultural products resulting from fertilizer use has been estimated at about four times the retail cost, based on results from FAO's fertilizer program. Since the retail cost is likely to be at least 50% above the wholesale, f.o.b. factory, or port price, it seems likely that the value of increased annual agricultural products would be 6 times 60 or $360 billion. This is, of course, no more than an order of magnitude estimate and even so it makes no allowance for inflation.

Raw Materials

From the information which will be presented in chapter V, it seems unlikely that the development of the fertilizer industry from 1980 to 2000 will be seriously hindered by shortages of raw materials. There are abundant supplies of phosphate rock, potash, coal, and sulfur. Supplies of natural gas, and especially of petroleum products, are less plentiful. If past experience is any guide, further reserves will eventually be discovered. However, they are likely to be substantially higher in price because of greater costs of development and extraction. In 1980 the demand for ammonia feedstock will constitute only 3.5% of current gas production and less than 1% of the oil and coal production. The industry can expect a gradual increase in the cost of these premium raw materials, and this may result in a significant shift to coal as a raw material for ammonia toward the end of the century.

Phosphate rock is widely, if unevenly, distributed in both developed and developing countries, and there is no fear of any continuing shortage. In recent years, the rate of discovery has far exceeded the rate of use. The present trend to lower grades of rock may continue and may require rock producers and consumers to exercise greater sophistication in their evaluation, specification, grading, and selection of rock for phosphate fertilizer manufacture. Supplies available for export are controlled by relatively few countries, and therefore availability and price may not always be dictated by the law of supply and demand.

It is difficult to assess the changes which may occur in the supply of sulfur because of the variety of forms in which it is produced and the fact that the major reserves, in coal and in gypsum, are not at present economically competitive sources. An increase in the use of natural gas and petroleum products coupled with improving environmental standards will lead to a steady increase in the recovery of elemental sulfur and in the recovery of sulfur dioxide produced in the combustion of fuels or in smelting operations. For most of the period under review, elemental sulfur will continue to be the major source, but it is possible that toward the end of the period there will be a shift toward other and more expensive forms.

There are ample reserves of potash. But a very significant fact about these is that they lie mainly in a few developed countries. Therefore, unless other deposits are found and exploited in the developing countries--a process that would probably take some 10 years or so--most of the developing countries will have to rely on imports for the foreseeable future.

Water is consumed in large quantities in the manufacture of fertilizers. The usage of water can be reduced by appropriate design of cooling systems, but fertilizer plants will always be large water consumers. Water is an important factor in the operation of fertilizer plants and may be a decisive one in determining location. The problem of water supply is a key factor in ammonia production, for example in the Persian Gulf area. It is also a problem in the production of phosphate rock in Peru, north Africa, and west Asia.

Organic Fertilizer Materials

Organic and chemical fertilizers play a complementary role in increasing food production; chemical fertilizers stimulate the production of organic materials, and return of waste organic materials supplements chemical fertilizers and reduces the quantity required. The total amount of nutrient elements in organic wastes is impressive; in 1971 the estimated NPK content of available organic materials exceeded that of chemical fertilizers in developing countries by a factor of about 7:1. However, most of these "waste" materials are already being used either for fertilizers or for fuel or other purposes. Those that are not being used present difficult technical, economical, or social problems because of their low concentration of nutrient elements and sometimes because of potentially harmful effects resulting from their use.

Improved efficiency in the use of organic waste materials is desirable, and many promising studies are in progress for the purpose of recovering fertilizer and/or energy values and for removing pollutants. These developments are very worthwhile, but the amount of fertilizer recovered in addition to that already being recovered is not likely to be a very large percentage of future fertilizer needs. Disposal of urban wastes will become an increasing problem as cities grow and may or may not afford opportunities for fertilizer products.

Organic materials are beneficial in improving the physical properties of the soil and its moisture-retention capacity. Therefore, recycling crop residues to the soil is good agricultural practice and should be encouraged. As use of chemical fertilizers increases, crop yields increase and more crop residues are available to recycle and thus build up the content of organic matter in the soil.

Location of Fertilizer Plants

Plant location should be selected to minimize capital requirements and operating and distribution costs. The desired end result in most cases is to minimize the cost of fertilizer delivered to the farmer. However, other considerations often enter into plant location decisions, such as national security or self-sufficiency, saving of foreign exchange, and assistance to less-developed regions. All of these are valid considerations, but the effect on fertilizer cost and hence on food production must be considered.

Planning fertilizer production and marketing on a regional basis has many advantages. Plant location analyses have shown that a substantial saving in capital and operating cost can result when the planning is done on a regional rather than a national basis. Such planning will go a long way toward utilizing the resources of each country in the region, such as natural gas for ammonia production in one country, sulfur or sulfuric acid in another, phosphate rock in a third, and perhaps potash in a fourth. A compromise may be considered in which countries that do not have raw materials may establish enough indigenous production to supply a percentage of their needs and depend on imports for the remainder. When regional cooperation is not feasible, bilateral or trilateral agreements may be useful.

Marketing

The term "marketing" is used to include distribution, transportation, and sale of fertilizers to farmers. Its object is to ensure that the right kind of fertilizer is on hand at the right place and time and to convince the farmer that he should buy and use it. All of these functions are critical.

In addition to storage at the factory, there must be, in most cases, regional and village centers for storing and distributing fertilizers to ensure timely availability. Accurate estimates must be made of fertilizer demand in each local area so that each center can receive its supply in advance of seasonal needs. Careful planning is needed to utilize available transportation facilities--waterways, railroads, and highways--to minimize costs. Transportation facilities will need to be improved and extended to cope with the increased tonnage of fertilizer that must be moved to the farmers and the increased tonnage of agricultural product that must be moved to its market.

To provide the right kind of fertilizer for various crops and regions, it may be useful to provide mixing facilities at regional or local distribution centers. These facilities may use simple mixing, bulk-blending, or granulation processes. When there is a local need for secondary or micronutrients, these materials may be added. Such marketing centers, to be effective, need coordination with recommendations from research or extension groups and from farmer education programs.

The total capital requirement for marketing may approach or equal the cost of manufacturing facilities. This includes the cost of transportation facilities and regional marketing centers equipped with facilities for bulk blending or granulation, bagging, and storage. It also includes district distribution centers and working capital to cover cost of material in storage and credit costs.

If farmers are to use increased amounts of fertilizer, they must be convinced that it will be profitable. Fertilizer use can be made more profitable in only the following three ways:

1. By lowering fertilizer cost,
2. By increasing fertilizer effectiveness, and
3. By increasing the price of agricultural products.

The first line of attack on fertilizer cost should be to maximize the efficiency of the manufacturing and marketing systems.

Fertilizer effectiveness can be increased by the use of better products, better balance of nutrients, better timing and placement, improved plant varieties, better cultivation practices, water control, weed control, and protection of crops from pests and diseases.

The price that the farmer receives for his products may be increased by improving the systems for marketing and processing agricultural products.

Even when farmers are convinced that increased fertilizer use will be profitable, many of them will be unable to buy it unless some source of credit is available. Therefore, some system of agricultural credit for fertilizer purchase usually is essential. Even more ideal would be the availability of financing all inputs that are essential to make the best use of fertilizer.

In addition to the actions mentioned above, fertilizer use may be made more attractive to the farmer by various artificial means, such as fertilizer subsidies, tax concessions, credit subsidies, or crop subsidies. These methods tend to be expensive and sometimes less effective than expected. Often it may be more effective to spend the same amount of money on improving the effectiveness of fertilizer use and the efficiency of manufacturing and distribution.

Relatively few countries have sufficient resources to become entirely self-sufficient in fertilizer production; thus, marketing as well as production on a regional basis may be mutually beneficial to countries in a region.

Financing

A study of financing of fertilizer projects in developing countries was made to indicate trends in sources of finance.

In order of percentage of occurrence (not necessarily the amount of monetary contributions), the sources of financing of 10 projects were:

1. Foreign enterprise, including equity participation
2. Host country government participation
3. World Bank group
4. Foreign financial institutions
5. Owner financing
6. Local financial institutions
7. Regional development bank or fund
8. Bilateral government aid or concessional loan
9. Suppliers' credits through export-import banks or other arrangements.

Large-scale projects in developing countries include the participation of the following elements:

1. Foreign enterprise through equity participation, technology, know-how, equipment, training, and marketing.

2. The determined commitment of the host country's government through financing, guarantees, provision of local labor, and infrastructure.

3. International financing whether provided by world, regional, or commercial banks or a consortium thereof.

Certain trends have been noted that may be projected into the future to provide the greatly increased financing that will be required by forecast growth of the fertilizer industry in the remainder of the century.

One trend is the increasing number of joint ventures with an increasing number of partners combining their strengths to surmount the problems of costs, risks, technology, marketing, and raw material supply.

Another trend is the move toward public rather than private sector ownership, particularly of production units. This may be due to an increasing incidence of donor financing tied to governmental rather than private firms.

More thorough planning and examination of all technical and marketing problems help to establish the soundness of a project and thereby attract both loan and equity capital.

Countries with a wealth of raw materials that provide a steady income will develop their fertilizer industry by direct financing, often in cooperation with an industrialized partner who will contribute technical and administrative expertise. These countries may also contribute to financing projects in other developing countries through loan or equity capital.

It is unlikely that unilateral governmental aid from industrialized countries will play a major role in financing because the amount of capital is too large. However, the indications are that international financing will increase and will be adequate to finance sound projects provided that there are mutual benefits, mutual trust, and a spirit of give and take.

Manpower

The projected development of the fertilizer industry will require increased personnel with professional expertise, including engineers, scientists, managers, marketing experts, skilled maintenance and instrumentation craftsmen, as well as larger numbers of operators, and semiskilled workers. The estimated total number of additional workers that will be required between the years 1980 and 2000 is shown below:

World Total	340,000
Developing Countries	209,000

The estimate includes only those who are directly and exclusively concerned with production and distribution. It does not include workers in mining, beneficiation, and transport of raw materials; retail merchants that sell fertilizers along with other farm supplies; or many ancillary industries, such as bag production, fertilizer application machinery, equipment manufacturing, construction, etc. Probably a million or more workers and particularly those of agricultural extension, cooperatives, and fertilizer dealers will require some sort of training in fertilizer production or handling and related work; in addition, hundreds of millions of farmers who use the fertilizers will need to be trained to use them properly. Furthermore, as workers retire, younger people must be trained to replace them.

The magnitude of training these larger numbers of people in developing countries is such that careful planning of training programs will be required. When necessary, a staff of foreign experts should be employed to supervise the initial operation of the plant and train native replacements. The use of foreign experts or advisors might well continue to a diminishing extent for 3 years or as long as is necessary to achieve efficient production and distribution.

Pollution Control

The extent of control of gaseous and aqueous effluents from fertilizer plants may depend on national priorities and plant location. However, it should not be overlooked. Even when a plant is located in a sparsely inhabited area, the plant workers must necessarily live nearby. If the environment deteriorates because of plant emissions, employee dissatisfaction and poor labor relations may result. Pollution may adversely affect other industries and even cause widespread illness or death in extreme cases. In the case of rivers flowing through other countries, international complications may result.

Chapter XXIII outlines the types of liquid and gaseous effluents and solid wastes that are likely to originate from fertilizer plants and the measures that are commonly used to minimize their effect on the environment.

In general, pollution control should aim to:

1. Protect the health and welfare of employees in the plant by controlling in-plant atmospheric quality and minimizing contact with toxic substances.
2. Prevent damage to crops, animals, people, and aquatic life in nearby areas from atmospheric or aqueous pollution.
3. Preserve the quality of rivers and lakes so that other industries and people that use the water will not be adversely affected.
4. Control discharge of effluents into oceans, seas, estuaries, or harbors to prevent damage to the fishing industry, other industry, or tourism.

Policies of Governments and International Agencies

Obviously, the successful expansion of the fertilizer industry in developing countries at the forecast rate will depend strongly on policies of individual governments and international organizations. An IFDC report, Suggested Fertilizer-Related Policies, (Technical Bulletin, IFDC T-10, August 1977) discusses some policies that will help achieve these goals. In view of the wide variety of socioeconomic systems involved in the numerous countries, acceptable policies will vary from one country to another. Therefore, suggested policies are often stated in terms of objectives which the policies are intended to accomplish.

National objectives that should be emphasized are:

1. Stimulation of exploration to discover and to define the extent and quality of resources of raw materials needed for fertilizer manufacture. Such stimulation may be promoted by policies that attract investment capital through joint ventures, leases, concessions, or other agreements based on equitable sharing of products or profits or alternatively by national exploration programs.
2. Performance of research and development work including economic studies to determine the best use of resources to meet the present and long-term future needs of the countries. Conservation and environmental aspects should not be neglected.
3. Development of plans for fertilizer production and distribution systems that would provide for maximum efficiency and economy by using a level of technology that is commensurate with the needs and abilities of the countries. Policies aimed at increasing utilization of fertilizer production capacity and reducing production and distribution costs should be emphasized.
4. Stimulation of fertilizer use with emphasis on decreasing cost through more efficient production and distribution and increasing the efficiency of fertilizer use through agro-economic research and farmer education. Direct or indirect subsidies should be used only after considering alternatives.
5. Utilization and development of human resources, giving due consideration to the selection of level of technology, training programs, and personnel policies that reward efficiency and achievement.
6. Close coordination of all concerned organizations at the working level. Particular emphasis should be placed on coordinating infrastructure development and agricultural programs with fertilizer production and/or distribution.
7. Exploration of possibilities for integrating fertilizer manufacture with other industries. These possibilities should be sought for and consummated when advantageous. For example, a copper-smelting industry may be planned in

such a way that it will produce sulfuric acid for a phosphate fertilizer production unit.

International organizations should adopt or continue policies to carry out research and development in areas that will be of general benefit to developing countries. Priority should be given to increasing the quantity and efficiency of fertilizer use through:

1. Promotional activities to demonstrate the value of fertilizers for increasing crop production and to assist in market development.
2. Development and use of improved forms or compositions of fertilizer materials, especially those that may be more effective in tropical or subtropical agriculture.
3. Improvement of placement and timing of application and proper balance of nutrients.
4. Other improved practices (water control, plant protection, etc.).
5. Development of new varieties of plants that utilize fertilizer more efficiently or supply part of their requirement through symbiotic nitrogen fixation.

International organizations should also assist through research and development on utilization of difficult ores of types that occur in several developing countries. This activity may include improvements in mining and beneficiation techniques, selection or adaptation of processes, or development of new processes.

Identification or development and adoption of appropriate technology processes would be very helpful to many countries in early stages of development. Such processes should employ small, simple, inexpensive plants, often with liberal use of labor.

International organizations should gather, evaluate, and disseminate information on technology and economics of manufacture, distribution, and use of fertilizers; this information should include the results of research and development outlined above.

International financial agencies should support new facilities when investment capital cannot otherwise be obtained. They should support projects aimed at the transfer of new technology, including low-level technology when appropriate.

Appropriate international organizations should improve the collection, evaluation, and dissemination of data relating to fertilizer consumption, demand, and supplies, including correlation with food production and raw material supplies. They should use this information to make more accurate and timely forecasts of needs to promote orderly development of the industry. The UNIDO/FAO/World Bank Working Group on Fertilizers has been giving this matter extensive attention.

III Role of Fertilizer in Agriculture

Introduction

Agriculture has been constantly evolving since the initial agricultural revolution some 10,000 years ago. This initial revolution was the result of domestication of plants and animals to serve man's needs and led to the generation of food production in excess of the requirements of the agricultural population. This agricultural surplus was available for consumption by city dwellers, and the growth of local trading centers and cities began. This development of urban centers allowed man's energies to be channeled into nonagricultural activities and led to the advances in scientific knowledge and subsequent technological advances upon which modern agriculture is so heavily based (1).

Along with this increased food production capacity came increases in the human population (2). The increased population growth then exerted further pressure on food supplies which led to increased areas brought under cultivation, more intensive cultivation of existing arable land, or improved technology. Often the output-enhancing factors were operating concurrently; the strength of each factor depended upon the relative scarcity of the inputs into the agricultural production process (3). In general, however, agricultural output expanded primarily through increases in the area brought under cultivation and grazing. Historically, the pressures created by a rising man:land ratio were relieved partially by famines which reduced the population and by migration to less densely settled areas which increased the land supply. The great migrations from the Chinese river valleys to other parts of China and to Southeast Asia as well as European migration to Oceania and the New World were due, in part, to pressures on agricultural land and an almost static agricultural production technology.

The overriding factor leading to pressures on the land resources prior to the 20th century was the decline in soil fertility which accompanied permanent agriculture. The slash and burn system was used extensively in most areas not located in well watered river valley-river delta systems where annual silting tended to restore some soil nutrients. As population increased, the fallow period declined, soil fertility declined, and finally, under continuous cropping, a stable but low level of yield was usually reached (4, 5). Even temperate areas such as Europe existed for very long periods of time on forest fallow, shifting cultivation on bush and grassland, and various forms of short fallow-systems (6). The low-level equilibrium yield levels achieved under permanent rainfed or irrigated agriculture were occasionally shifted upwards due to technological improvements such as the English agricultural revolution which resulted in the Norfolk crop-rotation system relying heavily upon forage and green manure crops and higher levels of manure application to improve soil fertility. Nevertheless, the system remained dependent almost exclusively on inputs supplied from the farming sector (7).

The industrial revolution began the chain of events which has led to present-day agriculture in the developed countries which is characterized by heavy purchases of inputs from the nonagricultural sector and the widespread application of science and technology to the agricultural production process. Foremost among these modern purchased inputs is chemical fertilizer.

The transition from preindustrial agriculture, which was characterized by long-run annual rates of increase in agricultural output of about 1%, to modern-day agriculture characterized by growth rates in output of from 2% to 4% has been heavily dependent upon overcoming the soil fertility problems mentioned earlier. Although some progress in this area has been achieved by more intensive use of crop rotations and green manuring, the overwhelming influence in increasing the supply of crop nutrients has been through increased application of chemical fertilizers.

The Contribution of Fertilizer to Agricultural Output

Several studies are available which attempt (1) to estimate the contribution of fertilizers to increased agricultural output over time or (2) to estimate the proportion of current agricultural output which is accounted for by the fertilizer input. In general, the developing countries have only a small proportion of *total* food output attributable to fertilizer use, but the contribution of fertilizer to subsequent *increases* in output is much higher (8). A more balanced relationship exists within most developed countries. The contribution of fertilizer depends heavily upon the sources of increased output--increased area brought under cultivation or increased yield per hectare cultivated. Although fertilizer applications may be necessary to bring new lands under cultivation, its major influence acts through the yield-increasing component. Pinstrup-Andersen discusses the methods of estimating the relative contribution of fertilizer to output (8). Table 1 summarizes his estimates for the Developing Market Economies for cereal crops only. Herdt and Barker, using a 10:1 response ratio assumption, estimated that the *maximum* contribution of fertilizer to total cereal production in South and Southeast Asia in 1971-72 was 9.4%, while the contribution of fertilizer to cereal production increase as of 1971-72 was 51.2% (9). Ewell speculates that as much as 50% of the increased grain production during the last 20 years was attributable to increased fertilizer use (10). In the United States, Christensen, *et al.*, estimated that about 55% of U.S. grain yield increase over the 1940-55 period was due to fertilizer while the Council for Agricultural Science and Technology (CAST) estimated that about one-third of U.S. grain production was due to fertilizer (11, 12). Shaw and Durost attributed 25% of the 2,511 kg/ha yield increase for U.S. maize between 1929 and 1962 to

TABLE 1. ESTIMATED CONTRIBUTION OF FERTILIZER TO CEREAL GRAIN PRODUCTION IN DEVELOPING MARKET ECONOMIES 1948-52 AND 1972-73

	Africa	Latin America	Near East	Far East	Developing Market Economies
Total increase in annual cereal production (10^6 tons)[a]	12.339	40.527	21.000	81.518	155.413
Estimated annual increase due to fertilizer (10^6 tons)[b]	2.523	10.779	9.240	26.226	48.243
% of total production increase due to fertilizer[b]	20.4	26.6	-	32.2	31.0
% of total yield increase due to fertilizer[b]	36.4	64.9	-	49.2	57.0
Estimated compounded annual rate of increase in cereal production due to fertilizer, %[c]	-	1.03	0.97	0.62	0.75
% of share of compound annual rate of production increase due to fertilizer	-	27.1	32.5	28.0	29.8
% of total yield increase due to fertilizer	-	66.1	85.1	42.8	54.8
Estimated % of total 1972-73 production due to fertilizer[d]	6.6	16.2	-	15.0	15.2

a. Based on FAO's *Production Yearbook* estimates.
b. Estimated on the basis of increases in fertilizer use for cereals and an average response rate of 10 kg of cereal grains per 1 kg of fertilizer (nutrients).
c. Based on the production function estimates of Evenson (18).
d. Total production due to fertilizer estimated on the basis of the average response ratio of 10:1.

Source: Adapted from Pinstrup-Andersen (8).

fertilizer use while Auer and Heady, using 1939-61 U.S. Midwest yields for corn, estimated 508 out of a total increase of 1,620 kg/ha as the contribution of fertilizer (13, 14). This approach was extended by Auer, Heady, and Conklin in analyzing the increase in yield of maize in the U.S. Midwest during the 1939-61 period (15). Their partitioning of yield increases during the period is shown in the following tabulation:

	kg/ha	% of Total Yield Increase
Yield in 1939	1,883	-
Yield in 1961	3,503	-
Yield increase	1,620	100.0
Increase attributed to:		
Increased fertilizer use	508	31.4
Variety improvement	578	35.7
Production location	289	17.8
Other factors	245	15.1

The period was one in which improved varieties were rapidly adopted which may account for the relatively large effect of this factor. More recently, Perrin and Heady provided estimated effects of nitrogenous fertilizers on a number of U.S. Midwest crops (16). Their results indicated that, during the later 1960s and early 1970s, nitrogen fertilizer was by far the major factor contributing to maize yields, about equal in importance to hybrid seed for grain sorghum, but much less important as a contributor to dryland wheat yields. Finally, TVA estimates put the current contribution of fertilizer to total U.S. crop output as 37% (17).

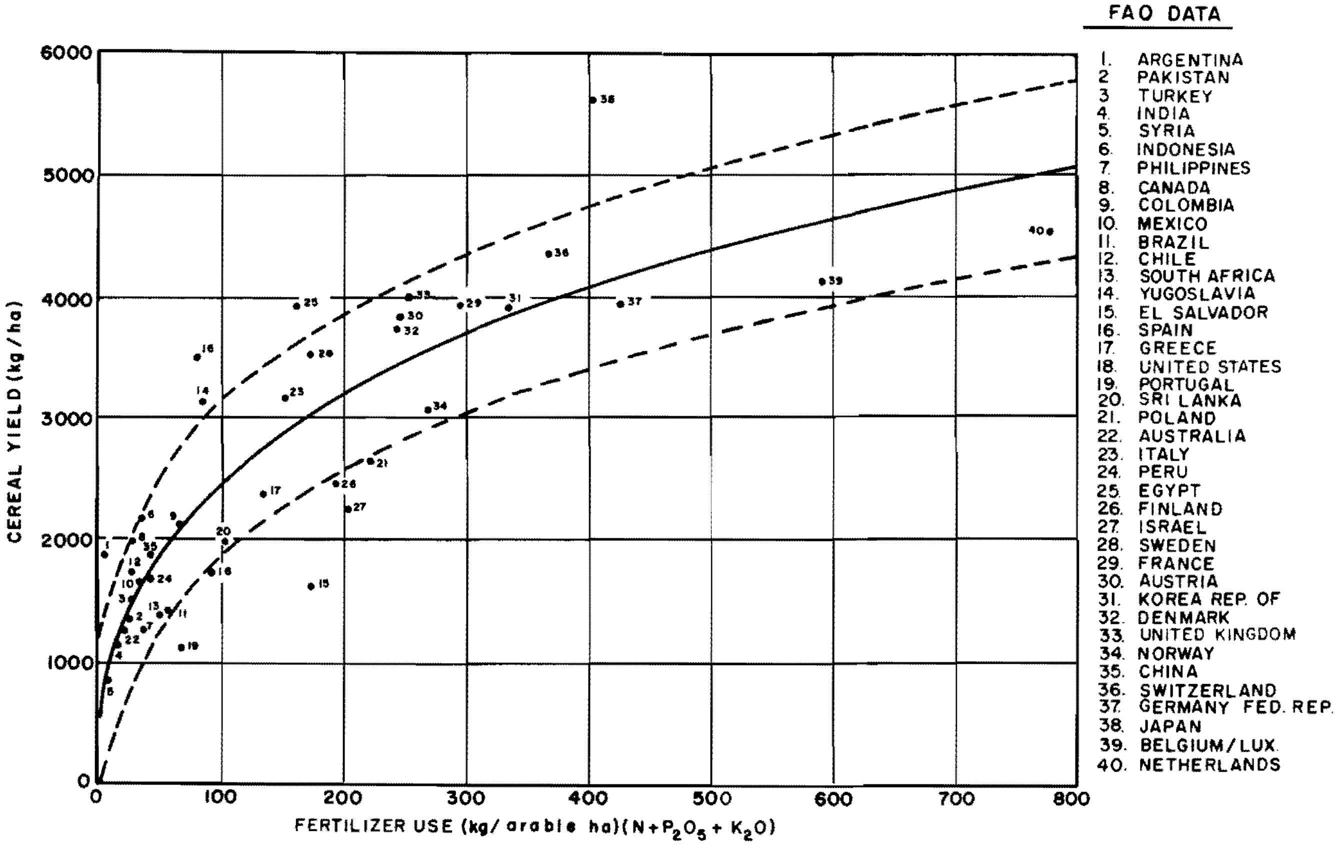
Regardless of how important fertilizer has been in increasing output, it seldom is the only factor limiting agricultural production or is the complete answer to overcoming food supply problems. Overemphasis on a single production input detracts from the complex and interrelated nature of the agricultural production process (18). The key role of providing the adequate inputs which complement fertilizer use has become labeled as the "package approach." Schultz has characterized traditional agriculture as an agricultural system which is, in general, poor but efficient (19). It is also a system in which no single factor can be identified as the constraining element to increased output and productivity. High rates of return to any single factor such as fertilizer are difficult to obtain because one or more additional factors constrain the economic response obtained by fertilizer (or other input) use. Therefore, increased rates of return to traditional agriculture as a whole are obtainable only through the provision of a new or improved package of production technologies. The typical components of a package are new or improved irrigation and drainage facilities, crop varieties with the genetic capability to exhibit large responses to higher levels of inputs, fertilizer materials and fertilization practices, and improved capabilities to control crop pests and diseases.

In a more general vein, a close historical relationship exists between cereal yields and fertilizer use per hectare of arable land (figure 1). This illustrates that, as yields increase, the ability of the soil to supply adequate amounts of nutrients decreases and fertilizer use rises. Observations which lie well above the confidence limits for the curve represent areas of very high native soil fertility (United States, Argentina), very favorable input:output price ratios (Yugoslavia, Japan), or very favorable environmental factors such as solar radiation and irrigation (Egypt). Observations lying below the curve represent cases where the necessary complement of technical-managerial inputs is not adequately supplied (El Salvador) or a single major input (such as irrigation water) is in short supply (Portugal, Israel). However, it should be noted that the fertilizer application rates shown for each country in figure 1 are obtained by dividing the total use of N + P_2O_5 + K_2O in that country by the total estimated arable hectares in that country. The resulting application rate obtained may differ considerably from the application rate on grain cropland. In some countries, cash or nonfood crops receive heavier fertilizer applications than grain crops. In some countries much or even most of the fertilizer used is not applied to arable cropland but to grassland (pasture or rangeland). In such cases, a deceptively high figure is obtained by dividing the fertilizer use by arable hectares (e.g., Netherlands and Australia).

This chapter proceeds by examining some of the key fertilizer-related inputs which contribute to profitable fertilizer use (particularly soil-plant-fertilizer relationships). The economics of fertilizer use is then discussed with reference to the various levels at which economic analysis is used within the fertilizer sector.

The Effect of Fertilizers in Crop Production

An analysis of the crop production system provides an adequate perspective to identify the role



Source: Private Communication from J.W. Couston.

Figure 1. National Use of Fertilizer and Grain Yields, 40 Countries, 1972-76.

of fertilizers in crop production. The leading features of the production system are summarily reviewed in the subsequent sections, with special emphasis in those aspects bearing a direct relationship to fertilizers. The development of the soil profile and the effects of physical, chemical, and biological soil properties are discussed in relation to the natural levels of soil nutrients available for plant growth. Then, the effect of fertilizer nutrients upon crop yield is analyzed and, finally, the modification of the fertilizer effect by genetic crop characteristics, cultural practices, and moisture availability is presented.

The Soil

The environmental components of the crop production system are soil, water, air, and solar energy. The following is a definition for "soil" given by Buckman and Brady (20):

"The soil may be defined as a natural body, synthesized in profile form from a variable mixture of broken and weathered minerals and decaying organic matter, which covers the earth in a thin layer and which supplies, when containing the proper amounts of air and water, mechanical support and, in part, sustenance for plants."

The first concept in the definition is that the soil is a natural body, developed primarily through the effect of soil-forming factors on the parent material, which is the ground bedrock. The factors which influence this formation are (1) climate, in particular, temperature and precipitation; (2) living organisms, especially the native vegetation; (3) nature of parent material, with respect to texture, structure, chemical composition, and mineralogical composition; (4) topography of the area; and (5) time.

The development of the soil is marked by the appearance of soil horizons, which are horizontal layers differing in physical, chemical, and biological properties. The sequence of horizons constitutes the soil profile. The soil-forming factors differ in their intensity from one place to another; thus, different soils are characterized by different soil profiles.

The differentiation of the soil profile into a sequence of horizons occurs primarily through the process of weathering. Rainfall water percolating downward through the original parent material produces mechanical changes and chemical reactions within the profile. The mechanical effects consist primarily of downward movement of the finer particles such as clay, silt, and finely divided organic matter, leaving an eluviated horizon of light color dominated by coarser particles. This lighter colored layer is generally designated the A horizon. Organic acids, produced by decaying organic matter, increase the leaching capacity of the percolating rain water and are responsible for chemical reactions during the eluviation process. Clay and soluble nutrients are some of the principal products of these reactions.

As the downward velocity of the percolating water slows, the materials being elúviated settle and deposit, developing layers of deposited fine material which are darker colored due to the accumulation of organic matter. This layer is designated the B horizon of the soil profile.

Lying below the B horizon is the bedrock material least affected by the soil-forming process. This bedrock may consist of true parent material but, in some cases, the upper horizons (A and B horizons) have been derived from parent rocks in another location and transported to the present location by the action of wind, water, or ice. Thus, the upper horizons may be quite unrelated to the underlying C horizon material. The A and B horizons constitute the agricultural soils or the solum.

The soil contributes to crop growth by providing the mechanical support for plants and by acting as the medium through which roots obtain mineral nutrients, oxygen, and water.

Physical Properties of Soils--Differences in the soil-forming factors and parent material have produced the great variety of soils that can be observed around the world. These differences are reflected in the properties and composition of the soil horizons. Some of the most apparent physical properties of the horizon are the depth, color, particle-size distribution, and structure.

The depth is the distance between the upper and lower boundaries of a given horizon. For the purpose of crop production, the depth of the agricultural soil or "solum" is defined as the depth of the A plus B horizons.

Color is an important element in differentiating soil horizons. Two of the principal soil components defining soil color are the organic matter content and the stage of oxidation of the iron compounds. Dark-colored horizons are associated with high organic matter content while light colors indicate low organic matter levels. Red color is typical of highly weathered tropical soils, with oxidized iron compounds.

The particle-size distribution or soil texture reflects the relative proportion of clay, silt, and sand particles in the soil horizon. The A horizon tends to have a coarser texture while the B horizon has a finer texture as a consequence of the accumulation of fine particles eluviated from the A horizon. Medium-textured soils are generally the best for agricultural production.

The structure of the soil reflects the degree of aggregation of the soil particles into soil aggregates. The aggregates provide the soil horizons with a network of pores of different sizes that permit the flow of air as well as the percolation and retention of soil water necessary for plant growth. The water stability of the aggregates is a desirable quality of the soils since it permits the free drainage of excessive water without disrupting the network of pores, thus avoiding the condition of water saturation which is undesirable for the growth of most plants. Organic compounds, produced by the decomposition of soil organic matter, play a major role as binding agents for soil particles, thus enhancing the water stability of these aggregates.

The effect of physical soil properties upon plant growth and yield is reflected in the quality of the soil as support for plant growth and on the capacity of the soil to supply air, water, and plant nutrients to the roots.

Chemical Properties of Soils--The most important chemical soil property in relation to plant growth is the ability of soils to supply the plants with the essential nutrients needed to complete their life cycle. Seventeen chemical elements are required by plants to complete their growth and reproduction stages. Some essential elements are required in rather large quantities and are called macronutrients; a second group is required in somewhat smaller quantities and are called secondary nutrients; and the remaining elements are required in relatively small quantities and called micronutrients. The estimated uptake per hectare of a 9.4-ton/ha maize crop is shown in table 2.

The carbon and part of the oxygen are taken by leaves from the air. The rest of the oxygen and the hydrogen are taken from the water absorbed by the roots. All of the remaining nutrients normally are taken up by the roots from the so-called soil solution. The soil solution consists of the available soil water adsorbed to the soil particles within tensions of between 1/3 and 15 atm and the anions and cations dissolved from the soil solids. What is really important to plants is the fraction of the chemical element in the soil that is soluble in the soil solution rather than the total amount of the element itself. The proportion of nutrients available to plants is not a fixed fraction of the total soil nutrients but depends, to a certain extent, on some properties of the soil and may vary with time and cropping practices.

The availability of nutrients in soils is affected primarily by chemical soil properties like parent material composition, soil acidity or pH, cation exchange capacity (CEC), and organic matter content. Each of these factors is discussed in turn.

Parent materials differ in their chemical composition. This fact is illustrated in table 3, where the elemental composition of four different types of rocks is presented. After the process of soil formation has taken place, the concentration of elements in a typical resulting soil is no longer the same as in the parent material. Table 4 shows the concentration of elements in eight soils. In general, the process of weathering tends to decrease the concentration of soluble cations like Ca, Mg, K, and Na, which are partly dissolved and leached by the rainfall water. On the other hand, highly insoluble elements like Si, Fe, Mn, and Al tend to increase their relative concentration since they stay in place after resisting the solvent effect of the percolating water. Another effect of the soil-forming process is

TABLE 2. NUTRIENTS TAKEN UP BY A MAIZE CROP, INCLUDING THE ROOTS, TO PRODUCE A YIELD OF 9.4 TONS OF MAIZE PER HECTARE

Substance	Chemical Symbol	Uptake, kg/ha	Substance	Chemical Symbol	Uptake, kg/ha
Hydrogen	H	-[a]	Iron	Fe	3.36
Oxygen	O	11,424[b]	Manganese	Mn	0.50
Carbon	C	8,736[c]	Boron	B	0.11
Nitrogen	N	317	Molybdenum	Mo	Trace
Phosphorus	P	58	Chlorine	Cl	Trace
Potassium	K	230	Cobalt	Co	Trace
Calcium	Ca	65	Copper	Cu	Trace
Magnesium	Mg	56	Zinc	Zn	Trace
Sulfur	S	40			

a. Taken from 7,224-9,240 cm/ha of water absorbed and evapotranspirated by the crop during life cycle.
b. Taken from the air through the photosynthesis/respiration process and from water.
c. Taken from air.

Source: The Fertilizer Institute. 1976. The Fertilizer Handbook, p. 12-13, 1015 18th Street, N.W., Washington, D.C.

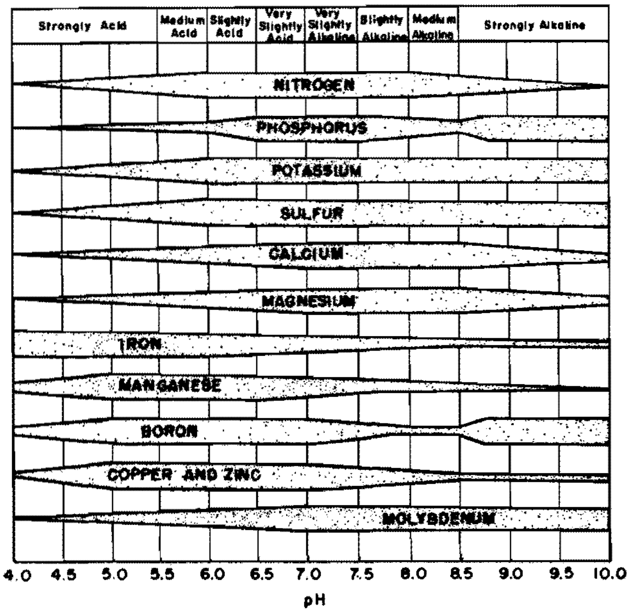
TABLE 3. CHEMICAL COMPOSITION OF ROCKS OF THE EARTH'S CRUST

	% Composition of Rocks[a]			
Constituents	Igneous[b] (95%)	Shale (4%)	Sandstone (0.75%)	Limestone (0.25%)
SiO_2	59.12	58.11	78.31	5.19
Al_2O_3	15.34	15.40	4.76	0.81
Fe_2O_3	3.08	4.02	1.08	0.54
FeO	3.80	2.45	0.30	
TiO_2	1.05	0.65	0.25	0.06
CaO	5.08	3.10	5.50	42.57
MgO	3.49	2.44	1.16	7.89
MnO	0.12	Trace	Trace	0.05
K_2O	3.13	3.24	1.32	0.33
Na_2O	3.84	1.30	0.45	0.05
CO_2	0.10	2.63	5.04	41.54
P_2O_5	0.30	0.17	0.08	0.04
SO_2		0.65	0.07	0.05
S	0.05	-	-	0.09
H_2O	1.15	4.99	1.63	0.77
Total	99.65	99.15	99.95	99.98

a. Percentages in parentheses indicate percentages of rocks in the earth's crust.
b. And metamorphic.

Source: Jackson, M. L. 1964. "Chemical Composition of Soils," IN Chemistry of the Soil, F. E. Bear, ed., p. 71-141, Reinhold Publishing Company, New York, New York.

HOW SOIL pH AFFECTS AVAILABILITY OF PLANT NUTRIENTS



Source: Sprague, H.B. 1964. Hunger Signs in Crops. N.Y., David McKay Company, p. 18.

Figure 2. Effects of Soil Reaction on Availability to Plants of Soil Nutrients (after Truog). The Width of the Bar Determines the Relative Availability of Each Element with a Change in Soil Reaction.

TABLE 4. CHEMICAL COMPOSITION OF SELECTED SOIL PROFILES[a]

Constituents	Norfolk Fine Sand, Florida, %	Sassafras Sandy Loam, Virginia, %	Ontario Loam, New York, %	Loam from Ely, Nevada, %	Hagerstown Silt Loam, Tennessee, %	Cascade Silt Loam, Oregon, %	Marshall Silt Loam, Iowa, %	Summit Clay from Kansas, %
SiO_2	91.49	85.96	76.54	61.69	73.11	70.40	72.63	71.60
TiO_2	0.50	0.59	0.64	0.47	1.05	1.08	0.63	0.81
Fe_2O_3	1.75	1.74	3.43	3.87	6.12	3.90	3.14	3.56
Al_2O_3	4.51	6.26	9.38	13.77	8.30	13.14	12.03	11.45
MnO	0.007	0.04	0.08	0.12	0.44	0.07	0.10	0.06
CaO	0.01	0.40	0.80	5.48	0.37	1.78	0.79	0.97
MgO	0.02	0.36	0.75	2.60	0.45	0.97	0.82	0.86
K_2O	0.16	1.54	1.95	2.90	0.91	2.11	2.23	2.42
Na_2O	Trace	0.58	1.04	1.47	0.20	1.98	1.36	1.04
P_2O_5	0.05	0.02	0.10	0.18	0.16	0.16	0.12	0.09
SO_3	0.05	0.07	0.08	0.12	0.07	0.21	0.12	0.11
Ignition loss	1.83	1.91	5.30	7.62	8.82	4.25	6.01	6.60
Nitrogen	0.02	0.02	0.16	0.10	0.27	0.08	0.17	0.09

a. The furrow-slice of a representative mineral soil is considered to contain approximately 2,000,000 lb of dry earth to the acre (2,242,000 kg/ha).

Source: Buckman, H. D., and N. C. Brady. 1969. The Nature and Properties of Soils, p. 24, The Macmillan Company, New York, New York.

the increase of N and S in the profile, due to the decomposition of and incorporation of fresh organic materials produced by plants growing in the soil during early stages of development. Chemical compounds in developed soil are fairly stable and rather insoluble in water. Natural rate of solubilization and release of nutrients to the soil solution is, in general, a slow process and, in most cases, will not be enough to supply the nutrient requirements for sustained production of high crop yields like those illustrated in table 2.

Soil reaction or pH is an important factor controlling nutrient availability. The relation between soil pH and the availability of some soil nutrients is shown in figure 2. The range of pH corresponding to the highest nutrient availability is not the same for all nutrients. Despite that, most nutrients present the highest or close to the highest availability within the narrow pH range of 6.5 to 7.0, which may be called the optimum pH range. The pH values above the optimum range decrease the availability of micronutrients, with the exception of molybdenum. The availability of boron decreases only up to pH 8.5, increasing after that level. Among the macronutrients, nitrogen, calcium, and magnesium decrease their availability above the optimum pH level, while phosphorus presents a pattern of availability similar to that of boron. A severe reduction in phosphorus availability occurs at pH levels below 6.0. The remaining nutrients do not present severe availability reductions until pH decreases to levels below 5.5.

Soil pH can be corrected by using soil amendments. The most commonly used soil amendments are lime or sulfur compounds, depending on whether the initial pH level in the soil is too low or too high with respect to the optimum (see chapter XX). The correction of soil pH by using soil amendments is a common practice in modern farming. Calcium carbonate (lime) is the most commonly used soil amendment to raise soil pH, while some sulfur compounds can be used to lower soil pH when it is excessively high. In both cases, the role of Ca and S as soil amendments is different from their role as soil nutrients.

The cation exchange capacity (CEC) of soil is an important chemical property with respect to nutrient availability. The CEC is the sum of negative charges of the soil colloids that can be neutralized by cations from the soil solutions. Cations occupying these negatively charged positions are loosely bound to the soil colloids, and they represent a readily available source for replenishment of the cations in the solution when they are being taken up by plants or being leached down by excessive rainfall or irrigation water. The negatively charged sites are available for storage of nutrients and, in this respect, soils with large CECs are less susceptible to rapid depletion of available nutrients than soils with low CEC values. Clay minerals produced during the soil-forming process and organic compounds produced from organic matter decomposition constitute the soil colloids and the source of negative charges giving high CECs.

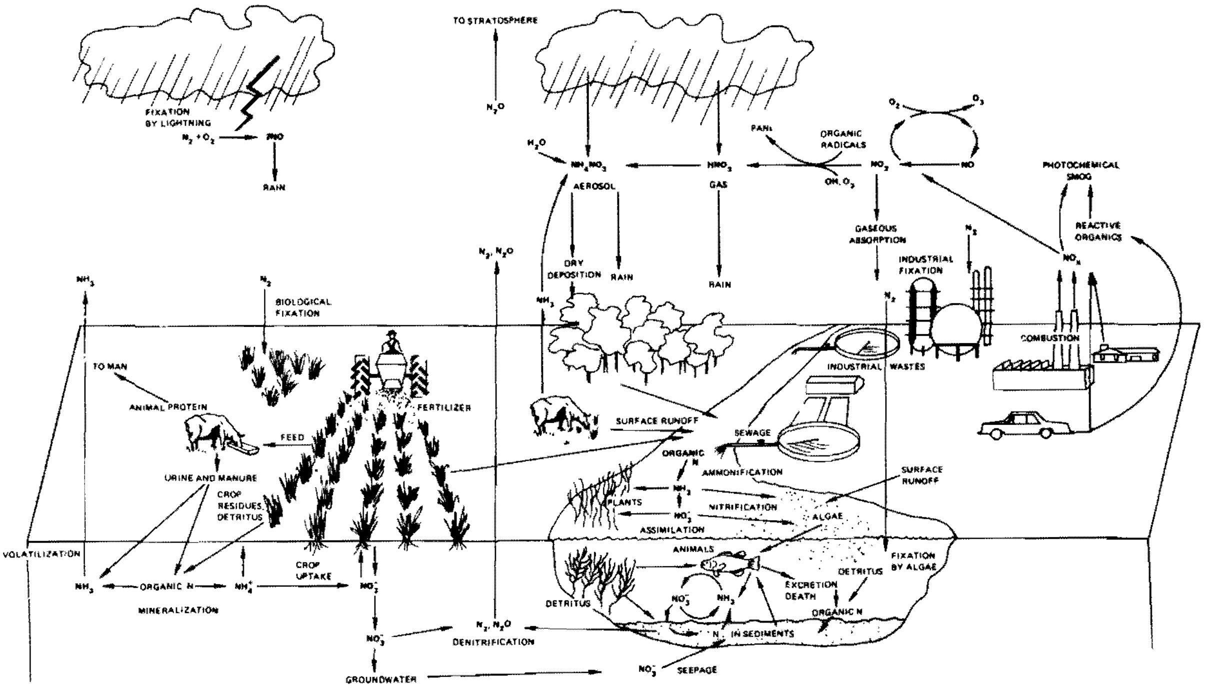
Soil Organic Matter--The organic matter constitutes a relatively small fraction of the soil components; the most common range of concentration is between 3% and 5%. Light-textured soils, as well as highly eroded soils, usually have lower organic matter concentration while organic soils and certain soils derived from volcanic ash materials may have concentrations several times higher than the norm.

Two fractions can be identified as the main components of soil organic matter. One is composed of fresh decaying material consisting of roots, stems, and leaves of dead plants; waste material of large animals, insects, and small animals living in the soil; and soil microorganisms. Enzymes produced by soil microorganisms activate the decomposition of fresh organic material with water and CO_2 produced during the process. Some of the partially decomposed and more resistant materials, together with newly synthesized compounds, form the second and more stable fraction of the soil organic matter, called humus. Another part of the decomposed fresh material is stabilized through the formation of clay-organic compounds. In these compounds, the organic matter is protected from the activity of enzymes, and further decomposition is retarded.

In spite of the relatively low concentration of stabilized organic matter in the soil, it is a very active component in relation to the principal soil functions of supplying water and nutrients for the growing plants. Colloidal humus compounds can store quantities of water and nutrients several times larger than those which can be stored by a similar weight of mineral colloidal compounds. This is because the organic colloids have higher water adsorption capacity and higher cation exchange capacity relative to the inorganic colloids.

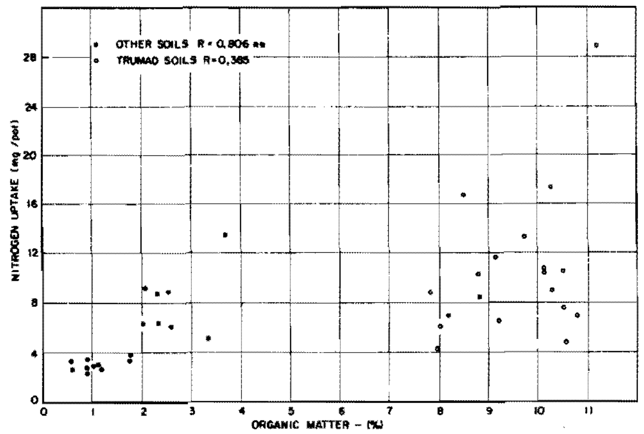
The soil organic matter is the most important source of indigenous nitrogen and sulfur for plant growth. These two elements are not present in the parent material in significant amounts and, thus, the soil nitrogen and sulfur available for plant growth proceeds almost entirely from the decomposition of organic compounds. The nitrogen and sulfur cycles are somewhat similar in nature and are among the most important cycles that operate to support life on earth. A simplified representation of the nitrogen cycle is shown in figure 3. The key aspects in managing nitrogen fertilizer for maximum efficiency are concerned with the loss mechanisms of leaching, denitrification, and NH_3 loss through volatilization.

The supply of nitrogen from the soil is not directly proportional to the amount of soil organic matter, although the relation between organic matter and total nitrogen tends to be fairly constant around the ratio of 20:1 on the average. The amount of organic nitrogen transformed into nitrogen available for crop production depends not only on the total amount of nitrogen or organic matter present in the soil profile but also on the nature of the organic matter compounds and other soil properties. Figure 4 illustrates one case where the uptake of nitrogen by



Source: The National Research Council.

Figure 3. Schematic Representation of the Nitrogen Cycle, Emphasizing Human Activities that Affect Fluxes of Nitrogen.



Source: Tejeda, H.R. 1970. "Factores Que Afectan la Mineralización del Nitrógeno en Suelos Trumaos y No-Trumaos," Santiago de Chile, Agricultura Técnica, 30 (3): 126-133.

Figure 4. Nitrogen Uptake by Corn Versus Soil Organic Matter in Samples of Two Different Soil Types.

plants grown in soils from two different origins remains within the same range, that is, when the organic matter content is 1%-4% for one group of soils and 8%-11% for the other.

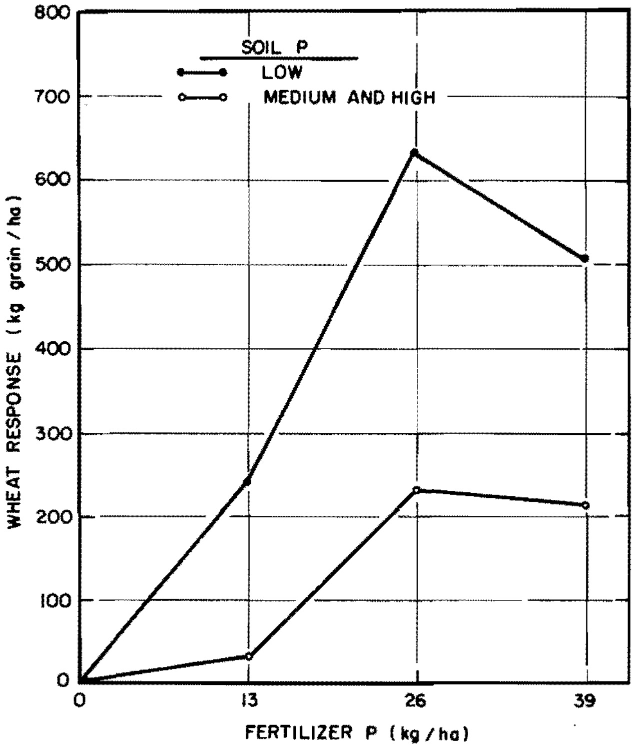
The supply of phosphorus from decaying organic matter is recognized as another important contribution to the pool of available nutrients. In some soils, up to 50% of the available phosphorus is estimated to have originated from organic decomposition. Some adverse effects from high levels of soil organic matter on the availability of micronutrients have been detected. The formation of organic-metallic compounds is considered to be the cause for strong temporary binding of soluble micronutrients in organic soils.

Another important role of organic matter in the soil is in maintaining soil structure. Some organic compounds act as binding agents by holding together the basic soil particles (clay, silt, and sand) making up the soil aggregates. The degree and form of aggregation are expressed through the classes of soil structure. Aggregation is a property that prevents the soils from becoming a solid, compact mass. The connected spaces existing within the aggregates form the pores; these pores are the channels for the movement of water and air through the soil. After the excess of water has drained to the subsoil, part of the remaining water adsorbed to the soil particles constitutes the available water for plant growth. Soils high in organic matter tend to have better structure and thus a higher water-holding capacity than poorly structured soils.

Fertilizer Nutrients

Crop yield is determined by (1) the genetic potential of the plant being cultivated; (2) the relative availability of inorganic nutrients, water, CO_2, and light energy during the growing cycle; and (3) the degree of interference from living organisms and physical factors in the production system. The objective of modern crop production technology is to bring production factors to an optimum level and to minimize the effect of all sources of interference within the bounds of the prevailing economic conditions. Assuming an ideal situation, maximum crop yield will be attained when all production factors are at the optimum level and the degree of interference is at its minimum. Under these circumstances, the maximum yield is determined solely by the genetic potential of the crop plant. In general, however, the costs of modifying all controllable factors influencing plant growth to obtain maximum yields are too high relative to the returns, and less than maximum yields are more economic. This is illustrated in the next section.

Chemical fertilizers may be economically used when the level of available soil nutrients is below the level needed for optimum economic returns. The response to a given dose of fertilizer depends, to a large extent, upon the quantities and forms of residual nutrients in the soil at the time of application. Figure 5 illustrates a typical case where the initial phosphorus status between two soils varies markedly.

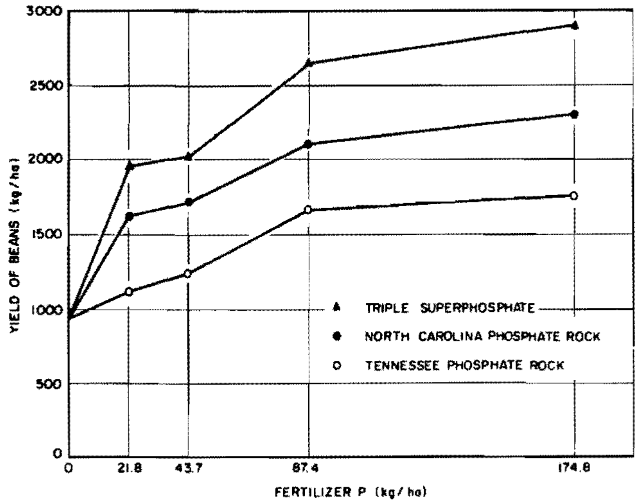


Source: Sing, B.R., L. Sing, and B.P. Sing. 1973. "Response of Dwarf Wheat (Triticum aestivum L.) to Graded Doses of P and K on Soils of Different Available P Status," Journal of Agricultural Science, 80:251-253.

Figure 5. Average Wheat Yield Response to Fertilizer Phosphorus on Nine Soils with Medium or Low Levels of Available Phosphorus and Four Soils with High Levels.

Yield responses to fertilizer application also are dependent upon the type of fertilizer material applied and the inputs of other factors influencing the production process. Figure 6 illustrates this by showing the effect of increasing application rates of three different phosphorus sources for beans. The main difference between the sources is the solubility of the phosphate compounds. The phosphate in the triple superphosphate is the most soluble source, providing the highest amount of available phosphorus to the growing crop. The phosphate in the two phosphate rocks is less soluble to plants, and this is reflected in the lower yields attained by the rates of P applied as phosphate rock as compared to yields attained by the same rates of P applied as triple superphosphate.

The method used in applying the fertilizer to the soil is another aspect to be considered. After the fertilizer is applied and it becomes incorporated into the soil, the nutrients in the fertilizer begin to solubilize. The soluble nutrients may not only be taken up by plants but also may be rendered unavailable due to secondary processes in the soil. Deep percolation, volatilization, and fixation into insoluble forms are some of the processes that



Source: Private Communication with Larry Hammond.

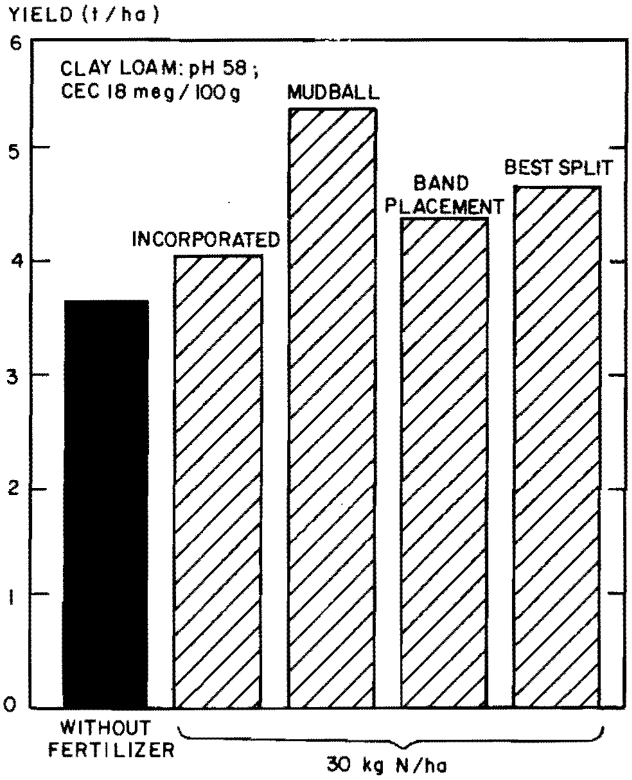
Figure 6. Bean Yield Response to Phosphorus Rates Applied in Fertilizers with Different Phosphorus Solubility.

prevent the full utilization of applied nutrients by crops. The relative importance of each of these processes is not the same in all soils nor for all fertilizers, and the predominance of one or another process will depend primarily upon the specific characteristics of the soil, water and soil temperature status in the soil profile, fertilizer source, and the particular crop grown.

The degree of physical contact between the soil and fertilizer particles and the location of fertilizer particles with respect to the root system in the soil profile are important aspects controlling the efficiency of fertilizer recovery by crops. Both aspects can be manipulated to a certain extent by the form in which the fertilizer is applied to the soil. Extensive research has been conducted to identify application procedures that will ensure the highest level of utilization of fertilizer nutrients by crops for different fertilizer materials used under different crops, soils, and climatic and management conditions. Figure 7 illustrates the average effect of four different methods of applying fertilizer nitrogen to rainfed rice grown during the 1974 wet season by Philippine farmers. The highest yield increase over the no-nitrogen treatment is produced when using the "mudball" method of application, which consists of enclosing the nitrogen fertilizer into a ball of clay, letting it dry, and finally locating the ball in the reduced zone of the soil profile. Nitrogen losses by volatilization and deep percolation are reduced; thus, there is a steady supply of nitrogen to the crop roots during the growing season. This situation contrasts with the case when the fertilizer is "incorporated" or fully mixed with the soil. The high degree of contact among the soil, floodwater, and fertilizer in the upper zone of the profile results in important nitrogen losses reflected in the small yield increase over the no-fertilizer treatment. The other two treatments represent intermediate situations between "mudballing" and "incorporating."

Effect of Crop Variety and Cultural Practices

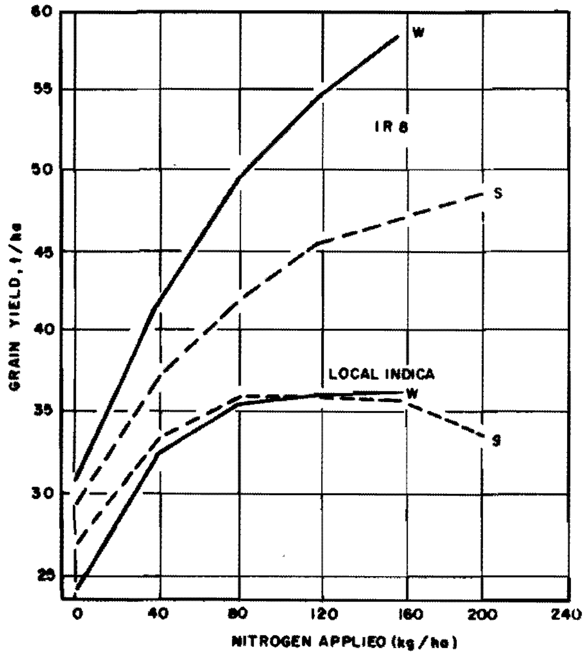
Agronomic research has shown that the effect of fertilizers on crop yield is dependent not only on the species being cultivated but also on the varieties within a given species. A variety represents a specific combination of genetic potential with respect to morphological and physiological characteristics of the plant. Some morphological characteristics of the plant, such as the length and strength of the stem in rice plants, have proved to be extremely important in relation to the response of rice varieties to nitrogen fertilizers. Tall varieties with weak stems cannot support the weight of the additional grain produced as a response to the use of nitrogen fertilizers; therefore, crop lodging occurs. Short varieties proved resistant to lodging and are thus able to produce higher yields in response to nitrogen fertilization. Physiological differences among varieties could also explain differences in grain yield response to the same rates of fertilizer applications. Using a period of 3 years, figure 8 illustrates differences in the average response to nitrogen rates of two rice varieties: the short, stiff-strawed IR-8 and the tall Indica variety. IR-8, which was one of the first high-yielding varieties developed by the International Rice Research Institute (IRRI) in the Philippines, outyielded the local Indica variety at all rates of application of nitrogen fertilizer.



Source: The International Rice Research Institute. 1974. The IRRI Annual Report for 1974. Los Banos, Laguna, Philippines, P.O. Box 933, Manila, p.167.

Figure 7. Relative Grain Yield of IR26 Rice Grown under Rainfed Conditions without Fertilizer Nitrogen and with 30 kg Nitrogen/ha as Urea under Different Methods of Application. Farmer's Field, Malayantoc, Nueva Ecija, Philippines, 1974 Wet Season.

Figure 8 also illustrates the effect of the time-of-planting or season effect, another important factor influencing yield response to fertilizer applied. While the response to nitrogen of the local variety is the same for each season, the IR-8 variety shows considerably more response during the winter season. This is because high-yielding varieties such as IR-8 have shorter and more erect leaves as compared with the long drooping leaves of the tall traditional varieties. This erect-leaf geometry allows light to penetrate deeply into the leaf canopy so that even the lower leaves receive sufficient light to carry on photosynthesis and produce the carbohydrates necessary for growth. The winter season in the tropics typically has a higher level of solar radiation than the summer because there are fewer cloudy days. Varieties which can take advantage of this high level of solar radiation are more responsive to fertilizers. Even within a given season, date of planting has a sizable effect on the response of many crops to fertilizer applications. Early planting allows



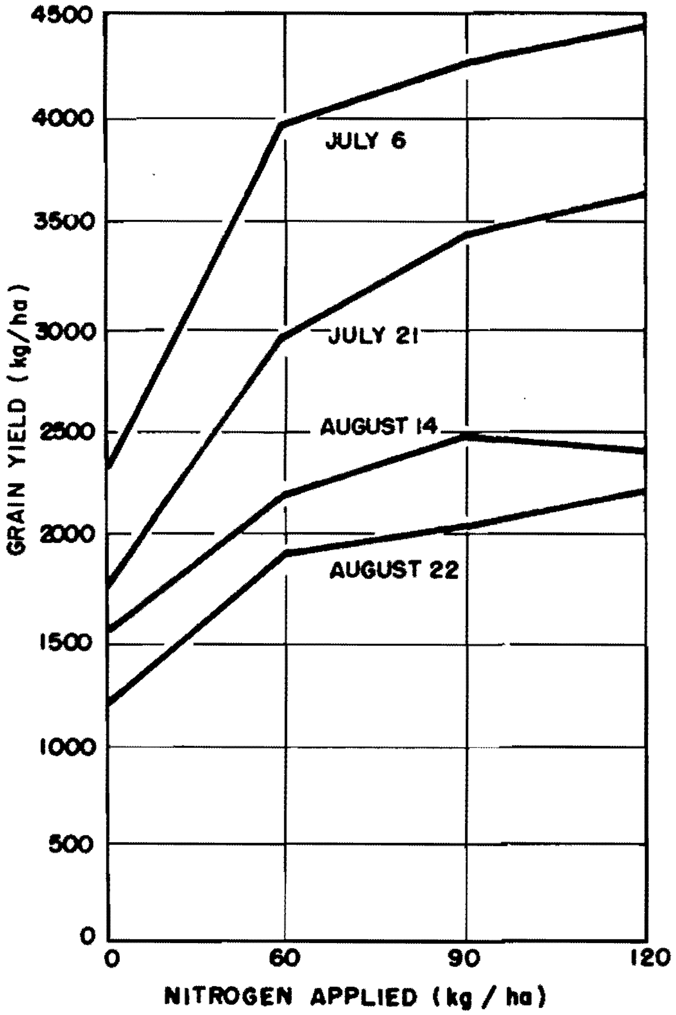
Source: Patnaik, S. 1969. "Fertilizer Use for Increasing Rice Yields in India," IN Symposium on Optimization of Fertilizer Effect in Rice Cultivation. Agriculture, Forestry and Fisheries Research Council, ed., p. 149-164, Tokyo, Japan, Ministry of Agriculture and Forestry. (Tropical Agricultural Research Series No. 3.)

Figure 8. Comparative Performance of IR8 and Local Indica Rice Varieties in Increasing Rate of Nitrogen (Average of Three Summer (S) and Three Winter (W) Seasons).

the plants to take full advantage of favorable conditions in order to achieve a complete development of the vegetative cover before entering into the reproduction and grain formation phase. This is an important favorable consequence of early planting because full vegetative development means that the plant develops maximum photosynthetic capacity relative to the other production factors. This photosynthetic capacity of the plant is one of the most important elements determining final grain yield. Figure 9 illustrates the average effect of nitrogen applications over six varieties at four different planting times. Late planting should result in less than full vegetative development since climatic factors accelerate the plant differentiation into the reproductive stages to ensure seed formation before the growing season is over. The less-than-complete vegetative development results in less photosynthetic capacity and lower grain yield.

Moisture Supply and Fertilizer Response

Water is an essential element for plant growth, and it is taken up from the soil profile by the root system. Soil water comes primarily from rainfall or irrigation, but the behavior of the water in the soil profile is essentially independent of the source. During a heavy rain, all the porous space of the soil is filled with water, and the soil is said to be at the state of saturation. After the rain ceases, part of the water in the soil drains, as it is pulled down to lower levels by the force of gravity. The water remaining in the soil after the draining corresponds to the state of field capacity (FC) and represents the main source of water for plant growth. But not all of the water stored in the soil at field capacity is available for plants. As plant roots proceed to absorb water, the remaining water is being adsorbed by the soil particles until a point is reached where the roots are no longer able to extract additional moisture. This stage of moisture in the soil is called



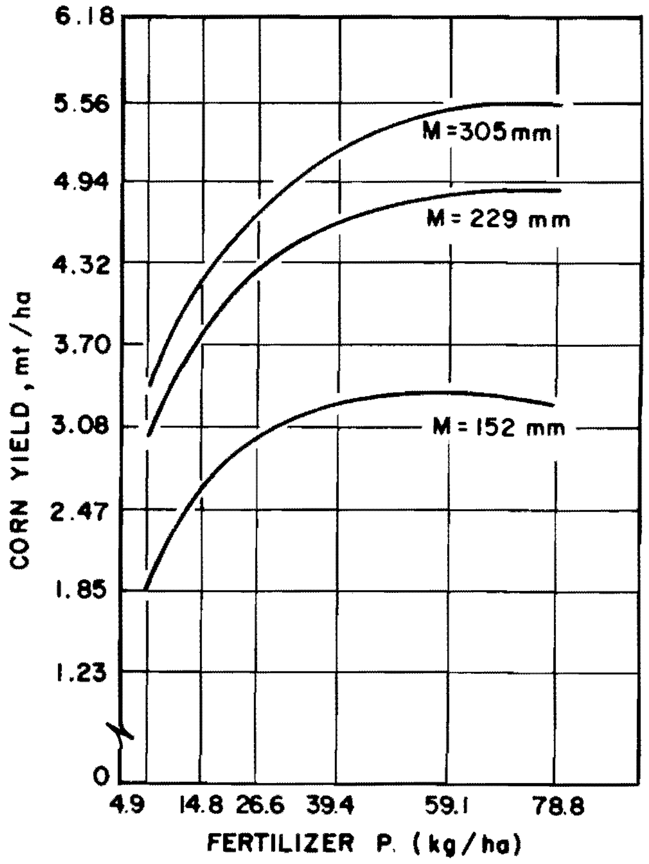
Source: Jana, R.K., and S.K. DeDatta. 1971. "Effects of Solar Energy and Soil Moisture Tension on Nitrogen Response of Upland Rice," IN International Symposium on Soil Fertility Evaluation Proceedings, Kanwar, J.S., et. al. eds., New Delhi, India, Indian Society of Soil Science, 1:487-497.

Figure 9. Effects of Level of Nitrogen on the Grain Yield (Average of Six Varieties) of Upland Rice at Four Dates of Planting, IRRI, 1969 Wet Season.

permanent wilting point (PWP) because plants subject to this soil moisture level wilt and die since they are not able to recuperate when transferred to a water-saturated environment. The forces holding water to the soil between field capacity and permanent wilting point do not increase at a linear rate, but they increase at an increasing rate as the available water becomes depleted. The specific rate of increase is a characteristic for each soil type, associated primarily with the soil texture.

Plants react to soil moisture stress by decreasing the rate of water loss from the leaves to the atmosphere. This physiological reaction is achieved by an automatic activation of the mechanism controlling the opening of the stomata. The stomata are the wall openings of the leaves, stems, and other active photosynthetic tissues through which the plant releases water vapor to the atmosphere. But the stomata are also the main devices used by plants (1) to absorb CO_2, which is utilized as a raw material in the production of organic compounds through the photosynthetic process, (2) to absorb O_2 during the process of respiration, and (3) to release to the atmosphere those gases produced during photosynthesis or respiration. Therefore, whenever the plant closes the stomata in order to decrease the rate of water loss, the rate of exchange of the other gases is also decreased. In particular, the rate of supply of CO_2 from the surrounding atmosphere to the photosynthetic organs is decreased or halted, depending on the degree of the water stress, and so is the production of new organic compounds by the plant. The overall physiological reaction to water stress has a direct effect on restricting final plant yield; the degree of the restriction depends on the intensity of the water stress, its duration, and the stage of development of the crop.

Soil moisture deficiency is a main factor in restricting the expected crop yield response when commercial fertilizer is added to the soil to increase nutrient availability to plants. A typical response interaction between water supplied and fertilizer supplied is illustrated in figure 10 for the case of phosphorus. These data were derived from the same soil over several years; thus, no soil type-moisture interaction was present. However, when the influence of water availability on crop response to fertilizer is studied across different soil types, the amount of water supplied may not correlate well with a high yield. The poor relationship between rainfall and yield response to fertilizers across different soils is a result of different soils having different moisture movement and storage characteristics. Also, the atmospheric demand for water may differ by location. Therefore, elaborate indices of water supply for crop production have been developed, but their discussion is beyond the scope of this presentation.



Source: Engelstad, O.P., and E.C. Doll. 1961. "Corn Yield Response to Applied Phosphorus as Affected by Rainfall and Temperature Variables," Agronomy Journal, 53:389-392.

Figure 10. Corn Yield Response to Applied Phosphorus at Three Levels of June Plus July Rainfall (M) at Greenville, Kentucky.

Economics of Fertilizer Use

Production Economics Aspect

The basic elements of production economics as applied to fertilizer use consist of the physical production relationships outlined above, prices of inputs and outputs, the influence of time, and the individual farmer's attitude toward making decisions. Determination of optimal fertilization rates can be carried out by several methods which are briefly described below. However, all methods are related to fertilizer response functions; thus, this concept is developed first.

A response function, as with most other physical or economic relationships, is necessarily an abstraction from reality. Inclusion of all variables which logically influence yields would result in an impossibly complicated function. Normal practice for fertilizer functions is to restrict the variable inputs to the levels of fertilizer applied with perhaps additional variables included to help isolate the effect of initial nutrient levels (soil test measures) and water supplied during the growing season (irrigation or rainfall, suitably specified). The general representation might then be

$$Y = f(X_1, X_2, \ldots X_n; X_{n+1}, \ldots X_m)$$

Where

Y = crop yield

$(X_1, \ldots, X_n)$ = inputs included within the response function as having the major influence on production;

$(X_{+1}, \ldots X_m)$ = fixed inputs and the remaining input variables which are assumed to be unimportant.

These latter factors are generally neglected, and the function is usually written

$$Y = f(X_1, \ldots, X_n).$$

A complete response relationship normally exhibits stages of increasing, diminishing, and negative returns corresponding to more than proportional, less than proportional, and negative increases in output per unit of input applied, respectively. The first and last stages of the response functions are uneconomic regions within which to produce, regardless of price relationships (21). In practice, residual nutrient levels in the soil are often high enough so that the increasing returns stage is seldom observed (except in sand or flowing culture experiments where zero nutrient levels can be obtained).

Levels of fixed factors also vary between experimental trials, between farms, and between agricultural regions. For example, when phosphorus fertilizer prices were depressed in the United States, farmers applied large amounts of these fertilizer materials to calcareous soils to build up a "fertilizer bank." This became essentially a fixed input stored in the soil. Much higher response levels were obtained from applications of nitrogen to these soils than from soils where phosphorus levels were low. Drainage of soils which are naturally poorly drained would give a similar upward shift in the response function at each application level of the variable input. If it is desired to have an estimated response function originating from the origin of the input-output axes, the individual yield estimates may be subtracted from the mean level for all observations. Most of the commonly used mathematical formulations of the response relationship described above, such as the quadratic, square root, and

Mitscherlich functions, represent only the second stage or second and third stages of the response function. The basic information supplied by the response function is the incremental output obtainable from increased levels of fertilizer use at each level of fertilizer use. This information, or some rough idea of this relationship, is essential to each of the three approaches now outlined for the determination of optimal fertilizer application levels.

Partial Budgeting--A partial budget attempts to derive a simple cost-return relationship between total returns to the farm or to an enterprise as a single input level is varied. For example, an Asian rice farmer who is currently applying 60 kg N/ha on his 2 ha of paddy land is assumed to average 3.0 tons of grain/ha. Based on his experience and that of his neighbors, he calculates that an additional 50-kg bag of urea will give him, on average, 200 kg more paddy. (This corresponds to the farmer's estimate of the slope of the response relationship in the neighborhood of the 3 ton/ha output level.) The partial budget depicting the costs and returns to this additional bag of urea would be as follows (assuming the additional fertilizer application costs are negligible):

The cost of one 50-kg bag of urea (46% N) delivered to the farm would be $10/bag.

The returns for 200 kg of paddy @ $80/ton at the farm gate would be $16; the net returns from the bag of urea would be $16 - $10 = $6; the percentage return per dollar invested would be $6 ÷ $10 = 60%.

Alternatively, the budget could be put in terms of N. One kilogram of N from urea costs $0.435 and returns 8.7 kg of paddy worth $0.696. Net returns per kilogram of N applied equals $0.261/kg (or $0.261/kg x 23 kg/50-kg bag of urea = $6.00/bag). The rate of return per kilogram of N applied is $0.261 ÷ $0.435 = 60%. A farmer generally uses the previous method based on fertilizer material applied while experimental work is carried out using the latter method based on elemental nutrients supplied.

In this example, the farmer can obtain a net return from applying the extra bag of urea. If his capital is limited, the return per dollar invested in N must then be evaluated against alternative returns that the farmer estimates he can obtain through alternative uses of his funds or against the cost of borrowing additional operating capital for purchasing the fertilizer. However, this simple example serves to emphasize the key elements in the decision--the costs, prices, and physical productivity of the fertilizer material.

Response Function Approach--The response function approach aims for a more exact measure of how much fertilizer to apply to maximize the net profit (√) from the fertilizer input.

Using the earlier notation where

X_1 = the amount of N/ha applied
Y = output/ha

the profit function is defined as

$$\surd = p_y Y - p_x X$$

where

p_y = price of paddy
p_x = price of N plus the cost of harvesting additional paddy

With unlimited funds to invest in N, the farmer would apply N until the additional returns just equaled additional cost, or Δ value = Δ cost. The equation is (marginal value product) = (marginal cost).

$$\frac{\Delta Y}{\Delta X_1} Py = Px_1$$

Alternatively, this condition may be stated as the ratio of the respective input-output prices:

$$\frac{\Delta Y}{\Delta X_1} = \frac{Px_1}{Py}$$

This condition gives a solution for the quantity of N to apply to maximize profits. The graphical solution to this problem is shown in figure 11 where the original response function faced by the farmer is shown as well as the marginal value product function obtained by multiplying the slope of the response function by output price of paddy ($0.08/kg). The partial budget example is also shown where the original application rate is 60 kg N/ha, and the additional 11.5 kg/ha of applied N gives an additional yield of 100 kg/ha.

Using the response function data, the farmer would, under a riskless situation and perfect knowledge, produce to point A by applying about 78 kg of N/ha. At this point, an additional kilogram of N produces about 5.4 kg of additional paddy worth an additional $0.435 which just equals the net cost of the additional kilogram of N applied.

Figure 11 also illustrates the difference in the two approaches up to this point. The partial budget example considered only one area of the response curve (from 3,000-3,100 kg/ha) and considered applying either 60 kg of N/ha or 71.5 kg/ha. The partial budget result found that applying the additional 11.5 kg of N/ha was profitable (the hatched area in the bottom diagram) and also indicated that additional profits could be obtained by applying even more fertilizer (net profit was positive), given that funds for purchasing fertilizer were not limited. Further, partial budgets would have been necessary to find point A which gives the additional profits shown on the cross-hatched area.

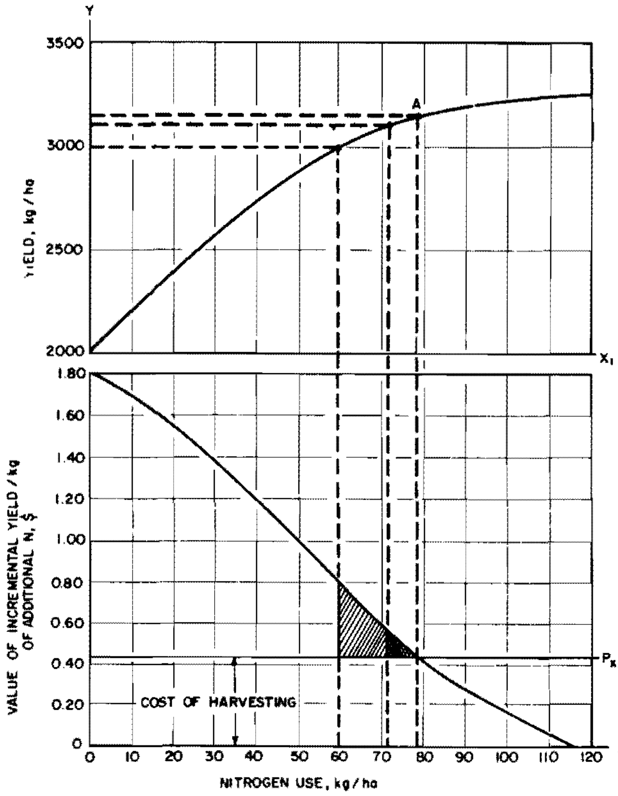


Figure 11. Response-and-Profit Relationships.

In the response function approach, the influence of additional factors such as plant density, levels of phosphorus and potassium, or irrigation water necessitates the simultaneous equating of the marginal value of each of these variables to their prices. Also, when capital for purchasing fertilizer is limited, it may not be possible to purchase enough fertilizer to get to point A in figure 11. The partial budget result indicated a return of 60% through buying the additional bag of urea, and this return has to be compared with returns obtainable from alternative uses of the money. The same principle applies using the response function approach (22).

A third approach uses mathematical programming. This technique is usually applied to whole-farm planning problems where fertilization and crop choice are often included. These models are generally not used to determine the optimal application rate of fertilizer (although the response curves can be divided into short linear segments to achieve an approximate solution to that shown above). Instead, these models make an initial estimate of the best or optimal fertilizer rate to use, and this rate is entered into the activity budget for the respective enterprise.

Returning to the previous example, the farmer may wish to consider several alternative means of utilizing the 2 ha. Budgets would then be constructed for the alternative enterprises which could utilize this land and the resource requirements for each enterprise specified. The paddy budget would have a nitrogen expense item included, and this input should be entered at the optimal level of about 78 kg/ha. The same should hold for the other fertilizer-using enterprises. The procedure would then be to select the optimum farm plan subject to the various resource constraints. The objective may be straightforward profit maximization or may take into consideration profits as well as farmer preferences and farmer attitudes to risky choices.

Some Further Topics

A number of items must be considered in the general evaluation of a large number of fertilizer materials over a wide range of crops and cropping environments. Some of these topics are now mentioned briefly.

Risk and Uncertainty--These factors were mentioned earlier and become more important the less control the farmer has over (1) the production environment within which fertilizer is applied and (2) the prices received for the output produced. In the partial budget example, the 60% rate of return could be considered an average return, but the risk associated with spending money on additional N may be so high that the farmer considers that rate of return too low to justify the risks involved. In planning fertilizer use for the coming season, the farmer must consider simultaneously the possible distribution of all input prices (including fertilizer), output prices, and yields. Based on the subjective evaluation of the possible outcomes and the risks associated with each, he makes the best decision commensurate with his individual beliefs. Extensive references exist on the procedures which have been developed to handle these aspects of risky choice (23, 24).

Time--Consideration of time enters when the influence of the fertilizer extends over several seasons and/or the crop is a long-period crop. Time may also enter when the farmer considers a single basal application of fertilizer versus split applications. Consideration of time necessitates the use of discounting or compounding through use of a discount rate to allow comparability of the alternatives at a single point in time. These tools have been used extensively in the analysis of fertilizer use, and recent extensions have been made which allow for ratooning of crops and carryover effects in crops and grasses (25, 26, 27).

Compound Fertilizers--Experimental results provide continuous response functions for fertilizer nutrients. Analysis of these response functions provides an economically optimal level for each nutrient; the ratios of these response functions do not, in general, correspond to the N:P:K ratios which are available from the various compound fertilizers available on the market. Colwell provides the procedure required to choose the best available fertilizer compound given farm-level response function estimates (28).

Fertilizer Policy Aspects

While the micro-aspects of individual farm fertilizer use represent the final payoff in terms of increased agricultural production, there also exists a complex set of interrelated factors which ultimately affect the profitability of the farm-level decisions on fertilizer use. Government policies influencing fertilizer use are felt most directly by the farmer in two areas: the relative fertilizer-crop price ratios and the agricultural infrastructure investments which influence the responses obtained from fertilizer as well as the variability of the response from season to season.

Some of the factors which have direct or indirect influences on the fertilizer price at the farm gate are:

1. Fertilizer production policy which determines local availability of fertilizer materials and their relative cost vis-a-vis imported materials.

2. Direct subsidies on fertilizer which reduce the price payable by the farmer.

3. Foreign exchange policies which influence the price at which finished fertilizers and fertilizer intermediates or raw materials can be imported.

4. The degree of protection provided local fertilizer manufacturers or fertilizer raw material producers and the extent to which higher costs are passed on to consumers.

5. The market structure of the fertilizer-producing and marketing sector which influences the extent to which market prices reflect true production-marketing costs.

6. Credit arrangements which allow the farmer to purchase promptly the required quantity of fertilizer and avoid credit charges in excess of normal commercial rates.

7. Fertilizer distribution taxes or subsidies which affect the farm-gate price level for fertilizer.

Many of these and other fertilizer policy-related issues and their implications in developing countries have been discussed by FAO and IFDC personnel (29, 30, 31, 32). One of the major issues faced by policymakers in accelerating fertilizer is choosing between fertilizer price subsidies and crop price supports as two competing alternatives to reduce real fertilizer prices. The relatively limited empirical evidence as to the better of the two alternatives is not conclusive. However, it is generally believed that output price policy is generally a more powerful factor influencing farm-level fertilizer use than is fertilizer price policy, and countries should not look upon fertilizer subsidies as a panacea for increasing food production (33). Stability of producer prices also has a major influence on fertilizer use as do innovations pertaining to fertilizer as part of a crop input package.

Land tenure arrangements can also have an important bearing on farm-level fertilizer use if some type of crop-share system is used. In many cases, the farmer pays for all fertilizer but receives only a portion of the output; thus, fertilizer use is suboptimal from the national perspective.

The influence of these factors as they affect on-farm optimal levels of fertilizer use is illustrated by Mudahar using a response function for nitrogen applied to rice in Orissa, India, estimated by Herdt and Mellor (34, 35). The response function used was $Y = 1{,}091 + 1.8N - 0.2077N^2$ where Y = paddy yield per acre and N = pounds of N applied per acre. Profit-maximizing behavior is assumed. Using this response function to generate optimal rates of N applied per acre, a number of factors which influence on-farm levels of fertilizer use are introduced. Table 5 summarizes these results and illustrates how a potentially profitable return to fertilizer use can become a marginal situation when all factors influencing fertilizer costs and returns are explicitly accounted for. Government policy to increase the efficient use of fertilizer must concentrate not only on increasing the supply of inputs which increase responses to fertilizer but must also give attention to those factors outlined in table 5 which act against the increased application of fertilizer.

As mentioned previously, the provision of inputs which allow the maximum response to be obtained from a given dose of fertilizer is crucial in expanding the profitable use of fertilizer. Public policy plays a crucial role in providing the public goods such as large-scale irrigation and drainage works, transportation networks, research services, and extension services which interact to provide large responses to fertilizer. The optimal manner to organize and finance the provision of these public goods has received much attention following reports of very high returns to publicly funded agricultural research (36). The great challenge is to design appropriate systems to allow the maximum contribution to be made by fertilizer so that this material can provide the increases in agricultural output to the developing countries that it has already provided to the developed nations.

TABLE 5. ECONOMIC ANALYSIS OF FERTILIZER RESPONSE FUNCTION FOR RICE UNDER ALTERNATIVE ASSUMPTIONS AND POLICY REGIMES[a]

		Economic Variables							
Case	Policy-Related Assumptions	P_N ¢	P_R ¢	N lb	Y lb	ΔY lb	MP lb	AP lb	r %
I	Standard	16.40	2.84	38.60	2,433.0	532.0	5.77	13.78	138.0
II	I and associated costs	19.60	2.84	35.86	2,415.6	514.6	6.90	14.35	107.9
III	II and cost of credit	22.80	2.84	33.14	2,395.3	494.3	8.03	14.92	86.0
IV	III and 20% discount for yield risk	22.80	2.84	28.30	2,261.4	360.4	8.03	12.74	58.6
V	IV and 10% discount for rice price risk	22.80	2.556	25.63	2,238.8	337.8	8.92	13.18	47.8
VI	V and 10% subsidy on fertilizer price	21.16	2.556	27.57	2,255.5	354.5	8.28	12.86	55.3
VII	IV and 10% subsidy on fertilizer price	21.16	2.84	30.07	2,275.1	374.1	7.45	12.44	67.0
VIII	IV and 10% subsidy on rice price	22.80	3.124	30.52	2,278.5	377.5	7.30	12.37	69.5
IX	III and share tenancy @ 50% of produce	22.80	2.84	13.80	2,031.6	130.6	9.03	9.47	17.9
X	III and 10% discount for rice price risk plus share tenancy @ 50% of produce	22.80	2.556	9.50	1,955.2	94.2	8.92	9.91	11.1
XI	IV and share tenancy @ 50% of produce	22.80	2.84	4.15	1,935.8	34.8	8.03	8.38	4.3

a. P_N = price of nitrogen, P_R = price of rice, N = nitrogen use per acre, Y = yield per acre, ΔY = increase in yield due to fertilization, MP = marginal product, AP = average product, and r = rate of return per dollar invested in N.

Source: Mudahar, M.S. 1978. "Needed Information and Economic Analysis for Fertilizer Policy Formulation," Indian Journal of Agricultural Economics, 33(3):40-67.

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IV General Concepts and Definitions

Fertilizers: General Definition

Broadly speaking, a fertilizer is any material, organic or inorganic, natural or synthetic, that furnishes to plants one or more of the chemical elements necessary for normal growth. The list of elements recognized as being necessary for plant growth has increased over the years and now totals 16, as shown in table 1. The first nine elements are required in relatively large amounts and are called macronutrients. Of these, carbon, hydrogen, and oxygen are supplied by air and water and are, therefore, not dealt with as nutrients by the fertilizer industry. The other macronutrients are subdivided into primary elements (nitrogen, phosphorus, and potassium) and secondary elements (calcium, magnesium, and sulfur). The remaining seven elements are required in much smaller amounts and are known as micronutrients or trace elements (see chapter XX).

TABLE 1. ELEMENTS ESSENTIAL FOR PLANT GROWTH

Macronutrients	(Available from air and water)	Carbon Hydrogen Oxygen
	Primary nutrients	Nitrogen Phosphorus Potassium
	Secondary nutrients	Calcium Magnesium Sulfur
Micronutrients		Boron Chlorine Copper Iron Manganese Molybdenum Zinc

In addition to the 16 essential elements listed above, some other elements have been shown, in certain circumstances, to be helpful in increasing crop yields or in improving the value of crops for animal or human nutrition. Examples are sodium, silicon, and cobalt.

Fertilizer Availability

A commercial fertilizer is a material containing at least one of the primary nutrients in a form assimilable or "available" to plants in known amounts. Generally, a plant nutrient is taken up by plant roots or foliage in the form of a solution in water. The primary nutrient elements form many different chemical compounds having varying degrees of solubility in water. Thus, it would seem that water solubility should provide a simple conclusive measure of the availability to plants. Unfortunately, the situation is far too complex for water solubility alone to serve as a measure of availability. All materials are soluble in water to some extent, even the most "insoluble."

Many sparingly soluble materials have been found to be available to plants and, in some cases, even more effective than readily water-soluble materials. (See Controlled-Release Fertilizers, chapter XXI.) However, some materials are so insoluble as to be virtually worthless as fertilizers. Therefore, most countries specify some degree of solubility of the nutrient content in water or other reagents or alternatively require identification and approval of the source of the material.

For example, natural organic materials may be acceptable on the basis of total N, P_2O_5, and K_2O content, provided the source of the material is identified and approved. Synthetic organic materials, if sparingly soluble, may require special methods of analysis, particularly if intended for controlled-release fertilizers. Likewise, special tests may be required for coated controlled-release fertilizers.

Since most common nitrogen and potassium fertilizers are readily water soluble, water solubility usually is accepted as evidence of plant availability, and special methods are applied to less soluble materials only when there is some evidence to indicate that the low (or controlled) solubility may be advantageous.

In the case of phosphate fertilizers, there is a wide variety of both readily and sparing water-soluble materials, and several methods are in use for evaluating their agronomic availability. The most common methods other than water solubility are based on solubility of P_2O_5 in neutral or alkaline ammonium citrate solutions or in solutions of citric or formic acid. In addition, the total P_2O_5 may be acceptable for some materials. Some examples of the basis for quality control of phosphate fertilizers are:

Federal Republic of Germany--Phosphate is expressed as the sum of P_2O_5 soluble in water and (alkaline) ammonium citrate. For superphosphate, at least 90% of the sum must be soluble in water. For compound fertilizers, at least 30% of the sum must be soluble in water.

Belgium--For TSP, only the water-soluble P_2O_5 may be guaranteed. The product must contain at least 38% water-soluble P_2O_5.

Soft rock phosphate must contain not less than 25% P_2O_5 soluble in mineral acids, of which not less than 50% must be soluble in formic acid. It must be ground to a fineness such that at least 90% passes through a 0.15-mm mesh sieve.

For compound fertilizers the P_2O_5 content may be expressed as that soluble in water, in alkaline ammonium citrate, or the sum of the two. If the compound fertilizer contains Thomas (basic) slag as the only source of phosphate, the P_2O_5 claimed is that soluble in citric acid.

United States--The guaranteed P_2O_5 content of all fertilizers is based on the "available phosphoric acid" (APA) content which is the P_2O_5 content soluble in neutral ammonium citrate including that soluble in water. There is no provision for determining or stating the water-soluble P_2O_5 content separately. The total P_2O_5 may be stated but is not included in the guaranteed APA content.

European Economic Community (EEC)--Regulations adopted December 19, 1977, specified the following permissible solvents as a basis for evaluation of phosphate fertilizers:

1. Water for those materials "where applicable"
2. Formic acid (2%) for soft natural phosphates
3. Citric acid (2%) for basic slag
4. Petermann's solution at 65°C for precipitated dicalcium phosphate dihydrate
5. Petermann's solution at ambient temperature for "disintegrated phosphates"
6. Joulie's solution for all straight and compound fertilizers in which phosphate occurs in alumino-calcic form
7. Neutral ammonium citrate solution for all fertilizer

Joulie's and Petermann's solutions are alkaline ammonium citrates containing free ammonia. Solvent compositions, extraction methods, ratios of sample to solvent, and methods for analysis are specified for each solvent.

It is beyond the scope of this manual to describe the details of analytical methods that are used for fertilizers. The development of suitable methods for analyzing fertilizers for availability has claimed the attention of agricultural chemists since the beginning of the industry. The methods are constantly being revised and improved as new knowledge and new tools become available to the chemist.

Fertilizer Regulations

Since a wide variety of natural and synthetic materials are beneficial to the growth of plants, a virtually unlimited number of products could truthfully be labeled "fertilizer" and marketed as such. The main drawback to uncontrolled marketing of fertilizer materials is the problem of the relative effectiveness of the product, and this depends on its composition. Unless the farmer can be sure that each lot of fertilizer he buys will have the same effectiveness as the preceding lot, he cannot be sure that he is fertilizing his crops in a rational manner, regardless of his stock of personal experience or advice from agricultural experiment stations.

Another drawback to uncontrolled marketing of fertilizer is the lack of a rational basis for pricing. A ton of low-analysis fertilizer is less valuable to the farmer than a ton of higher analysis fertilizer; therefore, the farmer should have a simple method for determining the best buy from the existing market.

Because of the foregoing factors, regulations (some of them in the form of laws) have been established in many parts of the world to govern the labeling and marketing of commercial fertilizers at the retail level. Since these regulations are intended for local conditions, they may vary from place to place, but the primary purposes are to ensure uniformity and to provide a simple method whereby the farmer can select the most economical product available to him.

Regulations add to the cost of fertilizer. In order to guarantee a given nutrient percentage, the manufacturer must provide some surplus, and the amount of the surplus depends on the degree of technical control during manufacture. Enforcement of regulations adds further to the cost of fertilizers. These costs, inherent in controlling fertilizer composition at the retail level, are compensated by the inherent benefits. Without basic regulations, the fertilizer trade would become chaotic. Like other regulations, care should be taken to limit them to the essentials.

Expression of Plant Nutrients--Oxide vs. Elemental Form

At present, most countries express quantities or percentages of plant nutrients in terms of elemental nitrogen (N), phosphorus pentoxide (P_2O_5), and potassium oxide (K_2O). Secondary and micronutrient elements usually are expressed on the elemental basis although calcium and magnesium sometimes are given as oxides. However, several countries have adopted the elemental basis for all plant nutrients. Recently FAO has moved toward the elemental form and during a transitional period will use both forms for phosphorus and potassium (P and P_2O_5, K and K_2O).

Conversion factors are shown in table 2.

TABLE 2. CONVERSION FACTORS OF PLANT NUTRIENTS (FROM OXIDE TO ELEMENTAL AND FROM ELEMENTAL TO OXIDE FORM)

P_2O_5	x	0.44 (0.4364)[a]	=	P
P	x	2.29 (2.2914)	=	P_2O_5
K_2O	x	0.83 (0.8302)	=	K
K	x	1.20 (1.2046)	=	K_2O
CaO	x	0.71 (0.7147)	=	Ca
Ca	x	1.40 (1.3992)	=	CaO
MgO	x	0.60 (0.6030)	=	Mg
Mg	x	1.66 (1.6582)	=	MgO
SO_3	x	0.40 (0.4005)	=	S
S	x	2.50 (2.4971)	=	SO_3

a. The figures in parentheses could be used as conversion factors for some calculations when very high accuracy is necessary (in research papers, plant nutrient balance, etc.).

Source: Handbook of Chemistry and Physics. 1973. The Chemical Rubber Company, Cleveland, Ohio.

Definition of Some Fertilizer Terms

The following definitions of terms in common use in the fertilizer industry are limited to those whose meaning might not be obvious from usual dictionary definitions.

Grade--The grade of a fertilizer is the nutrient content expressed in weight percentages of N, P_2O_5, and K_2O in that order. In most countries the grade, when used for commercial purposes, includes only that amount of nutrient found by prescribed analytical procedures, thereby excluding any nutrient present in a form that is deemed to be unavailable for plant nutrition. For example, a grade of "10-15-18" indicates a fertilizer containing 10% N, 15% P_2O_5, and 18% K_2O as found by prescribed analytical procedures.

Some countries express fertilizer grades on an elemental basis as noted above. In this case, the grade 10-15-18 would become 10-6.5-14.9. Some countries express the grade on both an oxide and elemental basis. In this manual, the oxide basis will be used unless otherwise specified.

In some cases the "grade" may be called the "analysis" or "formula." However, "formula" has another meaning (see definition).

Fertilizer--Since this manual deals with commercial fertilizer, the term "fertilizer" will be used to mean a manufactured product containing a substantial amount of one or more of the primary nutrients unless otherwise noted. The manufacturing process usually involves chemical reactions but may consist of refining or physically processing naturally occurring materials such as potassium salts or sodium nitrate.

In some countries, the terms "chemical fertilizer," "mineral fertilizer," or "inorganic fertilizer" are used to distinguish the manufactured product from natural organic materials of plant or animal origin. The latter materials are called "organic fertilizers."

Fertilizer Nutrient--One of the three primary plant nutrients N, P, and K (United States: any plant nutient).

Plant Nutrient--Any of the elements classified as essential to plant growth including N, P, and K (primary or major nutrients); Ca, Mg, and S (secondary nutrients); and Fe, Cu, Zn, Mn, B, Mo, and Cl (micronutrients).

Straight Fertilizer--Fertilizer containing only one nutrient, for example, urea or superphosphate (not United States).

Compound Fertilizer--Fertilizer containing two or more nutrients (not United States).

Mixed Fertilizer--This term will be avoided as far as possible because its meaning varies from one country to another. In the United States it means two or more "fertilizer materials" mixed together. In some other countries, it means a compound fertilizer formed by mechanical mixing without chemical reactions.

Fertilizer Material--(In the United States only) Commercial fertilizer that (1) contains only one of the primary nutrients, (2) has 85% of nutrient content in the form of a single chemical compound, or (3) is derived from plant or animal waste or a byproduct or a natural mineral and processed without adding primary nutrients from other sources. The usage of the term is arbitrary. For instance, the ammonium phosphate and phosphate-sulfate grades, 11-48-0, 13-39-0, 16-20-0, 27-14-0, and 21-53-0, are classified as "fertilizer materials," whereas 18-46-0 and all other ammonium phosphate grades are classified as "mixed fertilizers." The term will be avoided in this manual except in its obvious sense of any material used in formulating or producing fertilizers.

Complex Fertilizer--This term will be avoided. In some countries it means a compound fertilizer formed by mixing ingredients that react chemically. Some authors use the term to include only ammonium phosphates and nitrophosphates.

Nitrophosphate--A fertilizer made by a process of which one step consists of chemical reaction of nitric acid with phosphate rock. This material is also called "nitric phosphate."

Granular Fertilizer--Fertilizer in the form of particles sized between an upper and lower limit or between two screen sizes, usually within the range of 1-4 mm, often more closely sized. In general, the term "granular" does not imply any particular means for preparing the sized material; the desired size may be obtained by agglomerating smaller particles, by crushing and screening larger particles, by control of crystal size in crystallization processes, by separating a screen fraction of crushed, beneficiated potash ore, or by prilling a material. However, it is often customary to specify the method by referring to the product as "prilled," "compacted," "crystalline," etc.

Nongranular (Powdered) Fertilizer--Fertilizer containing fine particles, usually with some upper limit such as 3 mm but no lower limit.

Prilled Fertilizer--A type of granular fertilizer of near-spherical form made by solidification of free-falling droplets in air or other fluid medium.

Coated Fertilizer--Granular fertilizer that has been coated with a thin layer of some substance such as clay to prevent caking or to control dissolution rate.

Conditioned Fertilizer--Fertilizer treated with an additive to improve physical condition or prevent caking. The conditioning agent may be applied as a coating or incorporated in the product.

Bulk Fertilizer--Unpackaged fertilizer.

Bulk-Blend Fertilizer or Blended Fertilizer--Two or more granular fertilizers of similar size mixed together to form a compound fertilizer.

Liquid or Fluid Fertilizer--A general term including fertilizers wholly or partially in solution that can be handled as a liquid. This includes clear liquids, liquids containing solids in suspension, and (usually) anhydrous ammonia. However, anhydrous ammonia sometimes is referred to as a gaseous fertilizer even though it is applied as a liquid.

Suspension Fertilizer--A liquid (fluid) fertilizer containing solids held in suspension, for example, by the addition of a small amount of clay. The solids may be water-soluble materials in a saturated solution, or they may be insoluble or both.

Solution Fertilizer--Aqueous liquid fertilizer free from solids.

Fertilizer Intermediate--A manufactured fertilizer product, such as ammonia, phosphoric acid, or nongranular ammonium phosphate that is intended for further processing. Most of these "intermediates" can be, and often are, used directly for fertilizers. For example, ammonia can be used directly as a fertilizer or used as an intermediate to make urea, ammonium nitrate, ammonium phosphate, etc.

Fertilizer Application--General term for putting fertilizer in or on the soil in any one of several patterns.

Basal Application--Fertilizer applied before establishment of a crop to provide for part or all of its needs during the growing season. The fertilizer may be applied before plowing, before planting, or during planting or transplanting.

Direct Application--Use of a material, such as ammonia or phosphate rock, as a fertilizer without further processing. Also application of a straight fertilizer, such as triple superphosphate or urea, as opposed to using it to prepare a compound fertilizer.

Fertilizer Distribution--General term for transportation, intermediate storage, and marketing of fertilizer, including all operations after the fertilizer leaves the factory and before it reaches the farm.

Superphosphate--A product made by treating phosphate rock with sulfuric or phosphoric acid or a mixture of the two acids.

Single Superphosphate (also called "ordinary" or "normal" superphosphate)--Superphosphate made with sulfuric acid. The product usually contains 16%-22% P_2O_5.

Triple Superphosphate (also called "concentrated" or "treble" superphosphate)--Superphosphate made with phosphoric acid, usually containing 44%-48% P_2O_5.

Enriched Superphosphate--Superphosphate made with a mixture of sulfuric and phosphoric acids. This includes any grade between 22%-44% P_2O_5, commonly 25%-30% P_2O_5.

Available or Soluble P_2O_5--That portion of P_2O_5 which is soluble in solvents designated by government regulations for evaluating the quality of phosphate fertilizer. In the United States the term "available phosphoric acid" (APA) means the P_2O_5 content soluble in neutral ammonium citrate, including the water-soluble portion.

Chloride-Free Fertilizer--Fertilizer containing less than some specified amount of chlorine. Since the usual source of chlorine in fertilizer is potassium chloride, the term usually means a fertilizer containing potassium from some other source such as the sulfate or nitrate. However, in some cases potassium chloride may be used as a raw material and the chlorine removed in processing. Low-chlorine fertilizers may be preferred for agronomic reasons (see chapter XVIII) or in the case of some compound fertilizers containing ammonium nitrate, to avoid hazardous thermal instability (see chapter VIII under "Hazards of Ammonium Nitrate"). The maximum chloride content of "chloride-free" fertilizers may be in the range of 1.0%-2.5% depending on the type of fertilizer and country regulations.

Formula or Formulation--A list of materials, their nutrient content, and amounts needed to produce a given weight (such as a ton) of straight or compound fertilizer of specified grade.

Abbreviations--Common abbreviations of popular fertilizers that are often encountered are:

Abbreviation	Name of Product	Typical Grade or Analysis
AN	Ammonium nitrate	33%-34%N
ANL	Ammonium nitrate-limestone mixture (see CAN)	
APN	Ammonium phosphate nitrate	30-10-0 to 18-36-0
APS	Ammonium phosphate sulfate	16-20-0
AS	Ammonium sulfate	21% N
ASN	Ammonium sulfate nitrate	26% N
CN	Calcium nitrate	15% N
CAN[a]	Ammonium nitrate-calcium carbonate mixture	20.5%-28% N
DAP	Diammonium phosphate	18-46-0
MAP	Monoammonium phosphate	11-55-0
MOP	Muriate of potash--fertilizer-grade potassium chloride	60%-62% K_2O
SOP	Sulfate of potash--fertilizer-grade potassium sulfate	50% K_2O
SSP	Single superphosphate	16%-22% P_2O_5
TSP	Triple superphosphate	44%-48% P_2O_5
U	Urea	45%-46% N
UAN	Urea ammonium nitrate (solution)	28%-32% N
APP	Ammonium polyphosphate (solution)	10-34-0
KMP	Potassium metaphosphate	0-55-37
KP	Potassium phosphate (see MKP and KMP)	
MKP	Monopotassium phosphate	0-47-31
NK	Nitrate of potash (potassium nitrate)	13-44-0

a. May contain chalk, marl, dolomite, limestone, or chemically precipitated calcium carbonate. Also called calcium ammonium nitrate and ammonium nitrate limestone (ANL).

V Fertilizer Raw Materials and Reserves

The purpose of this chapter is to identify the main raw materials that are required for fertilizer production and to present general information regarding the adequacy and location of known reserves.

The major raw materials are natural gas, naphtha, fuel oil, and coal for the manufacture of nitrogen fertilizers; phosphate rock and sulfur for phosphate fertilizers; and potash ores for potash fertilizers. Natural gas, naphtha, fuel oil, sulfur, and potash are chemical substances or mixtures of chemical substances to which a clearly definable specification can be applied and which vary relatively little from place to place. Phosphate rock and coal, on the other hand, are mined products to which a specification can be applied only to a limited degree and which do vary significantly from place to place. They contain constituents, other than phosphate and coal substance respectively, which can have important effects upon the processes in which they are used to manufacture fertilizers. A process may therefore be designed to use a particular phosphate rock or coal. A change in the source of supply may adversely affect the process and lead to lower efficiency and/or to loss of output. It is therefore advisable, with these raw materials, to arrange long-term supply contracts which specify the source of supply. If a change in the source of supply becomes necessary, careful and lengthy trials of alternative materials should be made before fresh supply contracts are signed.

On the other hand, it is often desirable when constructing a plant to build in sufficient flexibility to accept phosphate rock from a variety of sources to take advantage of competitive situations or to provide for the possibility that the supply from the intended source may be cut off. Also, plant design should, as far as possible, allow for some variations in quality of both phosphate rock and coal, even when each material is taken from only one source.

Estimate of Raw Material Requirements

Table 1 sets out an estimate of the raw materials required, as divided between developed and developing countries. This estimate is based on future fertilizer consumption projections given in a report "World-Wide Study of the Fertilizer Industry: 1975-2000" which was presented by UNIDO for review by a panel of experts meeting at Vienna, November 16-18, 1976. The consumption estimates have been revised and lowered somewhat. However, the present estimates are deemed adequate for a rough estimate of raw material requirements as compared with reserves.

The estimates of ammonia feedstocks--natural gas, naphtha, fuel oil and coal, taken together--give a reasonable estimate of the total amount of energy required for nitrogen fertilizer manufacture. But the estimates of individual feedstock requirements, particularly for naphtha, fuel oil, and coal which together account for 30%-35% of the energy requirements, are subject to a large margin of error

TABLE 1. ANNUAL RAW MATERIAL REQUIREMENTS

	Developing Countries				Developed Countries			
	1980	1985	1990	2000	1980	1985	1990	2000
Natural gas (10^9 m^3)	14.1	25.3	36.5	61.3	33.0	47.5	60.0	94.5
Naphtha (million tons)	2.4	3.0	3.7	4.7	5.9	6.6	7.3	8.6
Fuel oil (million tons)	1.3	2.7	4.8	8.8	3.0	4.8	7.1	12.5
Coal (million tons)	2.8	8.6	18.3	40.3	6.5	13.9	25.0	57.6
Phosphate rock (million tons P_2O_5)	9.3	14.1	19.1	31.5	27.4	32.2	37.9	50.7
Sulfur (million tons)	6.5	10.5	14.6	24.9	19.2	23.1	27.8	38.3
Potash (million tons K_2O)	4.5	6.5	8.9	14.8	24.6	30.4	36.7	51.2

Notes for table 1

1. Ammonia feedstocks. See text for the assumed percentage of ammonia production from the different feedstocks.
2. Phosphate rock. This is equal to P_2O_5 production plus an allowance of 8% for conversion losses. It should be noted that forecasts of P_2O_5 demand exclude ground phosphate rock which has, for a number of years, accounted for about 7% of total P_2O_5 consumption. If consumption continues at this rate, the estimates of rock consumption would therefore be about 7% low.
3. Sulfur. The consumption for MAP/DAP is taken at 0.94 tons/ton P_2O_5 and for SSP and TSP 0.70 tons/ton P_2O_5, and zero for nitrophosphate (NTP). For 1980 it is assumed that production is 46% MAP/DAP, 46% SSP/TSP, and 8% NTP. From 1980 onwards it is assumed that production is 80% MAP/DAP and 20% TSP.
4. This is equal to the potash demand plus an allowance of 5% for stock increase and handling losses.

Source: "World-Wide Study of the Fertilizer Industry: 1975-2000" (Draft) November 1976, UNIDO, Vienna.

because they depend very much upon an individual assessment of the changes that are likely to take place in the use of these feedstocks up to the year 2000. Because of these uncertainties, it has been assumed that the proportion of the total nitrogen fertilizer feedstock supplied by natural gas, naphtha, fuel oil, and coal is the same in both developed and developing countries. The assumptions, and the views underlying them, are discussed under "Ammonia Feedstocks" in this chapter.

Availability and Sources of Raw Materials

Information is given in this section on the amount and geographical distribution of world reserves of fertilizer raw materials and their present production. Production rates are known with reasonable accuracy, but the same cannot be said of reserves. It is impossible to present more than a rough estimate of the reserves of any mineral deposit, particularly on a global scale, because of the difficulties involved. These fall into two broad categories.

The first difficulty arises from lack of information. Large areas of the globe either have not been surveyed at all or have been surveyed inadequately. Even when deposits are known to exist, information on their quantity and quality varies greatly. Reasonably complete data are available only for deposits being worked or for which concrete development plans exist; and, even in such cases, the data may cover only the more easily worked and accessible parts of the deposit. For deposits known to exist but not being worked, the information may be scanty. For example, deposits of potash salts have recently been discovered in Thailand and reserves are thought to be "very large indeed," but no quantitative data are available. The reason for this lack of data is simply that full exploration and evaluation of a deposit is an expensive process and only undertaken when commercial exploitation is probable. It is a commonplace of reserve estimation that, in spite of high production rates, reserves remain constant or actually increase over quite long periods of time because new deposits are being discovered as fast as existing ones are being used up.

Faced with this difficulty, some estimators confine themselves to identified deposits for which reasonably adequate information is available. Others include known but not fully explored deposits, and yet others add a "contingency" for deposits not yet discovered but which may be reasonably presumed to exist because of known geological factors.

The second difficulty is that there is no agreed definition of reserves. Some estimators include the total quantity existing in the deposit; whereas, others include only that amount which can be extracted by present mining techniques. Others, again, include only the amount which can be economically extracted at the time of writing; this depends upon the cost of mining and beneficiation in relation to market prices for the mineral. On this basis, the proportion of a deposit included in reserves would vary from one deposit to another and would also be affected by changes in market prices or in mining and extraction costs.

With these widely varying concepts of what constitutes a reserve, it is not surprising that estimates of total reserves show very large differences; for example, estimated world reserves of phosphate rock vary from 85,000 million tons to 1,300,000 million tons. In comparing various estimates, the difficulties are compounded by the fact that the definition of reserves on which the compilation is based is not always clearly stated.

It is clear, therefore, that the magnitude of national and global reserves of fertilizer raw materials is not accurately known. The estimates for crude petroleum and, to a lesser degree, natural gas are the most reliable. Because of their importance, much attention has been given to these materials and to the technology required for their estimation. The estimates for the other raw materials are much less reliable. However, the one for potash is probably the most reliable of these because the number of known deposits is relatively small and most of them have been carefully surveyed. The estimates for phosphate rock, sulfur, and coal have the greatest margin of uncertainty. These materials are widely distributed; many deposits remain to be discovered; and it is difficult to obtain representative samples from which the quality of the deposit can be assessed. Fortunately, the estimates for potash, phosphate rock, and coal show that, even when allowance is made for the inevitable inaccuracies, global reserves are more than adequate for the foreseeable future. With sulfur, total reserves are also ample; but, in time, some shift may take place to materials not at present widely used.

Ammonia Feedstocks

The feedstocks--natural gas, naphtha, fuel oil, and coal--used for ammonia manufacture differ from the other fertilizer raw materials--phosphate rock, sulfur, and potash--in that the latter find their major use in the fertilizer industry while the use of the former in this field is only a small fraction of the total consumption. The manufacture of fertilizers uses the following proportions of world production of raw materials: 85% of phosphate rock, 40% of sulfur, and 95% of potash compared with 3% of natural gas and about 0.5% of oil products and coal.

The development, structure, and economics of the industries supplying phosphate rock, sulfur, and potash are therefore closely related to the progress of the fertilizer industry. In the production of ammonia feedstocks, no such close relationship exists. In particular, the prices paid by nitrogen fertilizer manufacturers for their ammonia feedstocks are determined by their value for other uses--e.g., as fuels, as feedstocks in chemical industries, or as constituents of motor fuels--and not by their relative suitability for ammonia manufacture.

The major ammonia feedstocks in worldwide use in 1971 and 1975 and forecasts for future years are tabulated below:

	Percent of Ammonia Production					
Feedstock	1971	1975	1980	1985	1990	2000
Natural gas	60	62	71.5	71.0	69.5	68.0
Naphtha	20	19	15.0	13.0	8.5	6.5
Fuel oil	4.5	5	7.0	8.5	10.0	12.0
Coal	9	9	5.5	6.5	7.5	10.5
Total	93.5	95.0	99.0	99.0	95.5	97.0

Both the forecasts and estimates for previous years were taken from unpublished data supplied by UNIDO; however, the 1971 and 1975 estimates are not necessarily comparable with the 1980-2000 forecasts. The estimated percentage of ammonia production from coal is strongly dependent on estimates for China where about half of the world's coal-based capacity is located, mainly in over 1,000 small plants. Forecasts for future years depend on assumptions regarding the future utilization of these small plants. Another uncertainty arises from the ability of ammonia plants to use alternate feedstocks; several plants have switched from naphtha to natural gas, liquefied natural gas (LNG), or liquefied petroleum gas (LPG) recently because of high naphtha cost, and at least one plant has changed from coal to natural gas.

Despite these uncertainties, there is clearly a short-term trend toward increased use of natural gas as ammonia feedstock. A great majority of new plants planned and under construction will use natural gas, and some plants designed for naphtha have been or will be converted to natural gas feedstock including LNG. Naphtha's share will decrease because it will be too expensive. Fuel oil will account for a small but increasing share. Coal will account for a decreased percentage of ammonia production in the near future but from 1990 onward will begin to take an increasing share. However, the long-term prospect is that natural gas will remain the predominant feedstock throughout the remainder of the century. Some of the forecasted increase in use of coal is due to its assumed use as fuel in ammonia plants that use more expensive materials as feedstock.

Some minor and secondary sources of feedstocks are LPG, coke oven gas, refinery tail gas, and hydrogen from electrolysis of water or from chlorine-alkali production. Strictly speaking, we should include air and water as feedstocks since nitrogen from the air is necessary to form ammonia, and much of the hydrogen in the ammonia synthesis gas is derived from water (steam) through reaction with carbon derived from the hydrocarbon feedstock. However, in practice, air and water are taken for granted.

Some possible future sources of hydrocarbon feedstock for ammonia production are oil shale and oil or tar sands. Also, organic wastes could be a source of feedstock either by pyrolysis to produce gas containing carbon monoxide and hydrogen or by anaerobic fermentation to produce methane and carbon dioxide. In fact, it has been suggested that vegetative crops could be grown for the purpose of methane generation by anaerobic fermentation. However, for the remainder of this century, it is likely that we shall rely almost entirely on natural gas, petroleum products, and coal for ammonia feedstocks. Therefore, it seems pertinent to examine the reserves of these materials, their locations, extent, and rates of use.

Table 2 summarizes reserves of natural gas and petroleum on a regional basis as of January 1, 1977, and production in 1976. Appendix A shows reserves of these materials by individual countries.

For the world as a whole, known reserves of natural gas are equivalent to 46 years' production at the 1976 annual rate, and oil reserves are equivalent to 30 years' production. On a regional basis, gas reserves for developing areas are equivalent to 136 years' production at the current rate; whereas, North American reserves are less than 12 times the 1976 production rate.

Table 3 shows the trend of estimated reserves during the last 8 years (1971-78). The data show that reserves increased up to 1975 as more oil and gas were found than were used. Since 1975 reserves have decreased. However, the sharp decrease from 1975 to 1976 greatly exceeds production for that year and is probably caused by reevaluation of reserves. A substantial increase in natural gas reserves occurred in 1978.

TABLE 3. TRENDS IN WORLD RESERVES OF PETROLEUM AND NATURAL GAS

Year	Petroleum Reserves, Billion mt	**Natural Gas Reserves, Tcm**
1971	83.8	45.5
1972	86.7	49.1
1973	91.0	53.1
1974	85.9	57.7
1975	97.6	72.1
1976	90.2	65.7
1977	87.9	66.3
1978	88.3	71.4

Source: International Petroleum Encyclopedia, 1976, 77, and 78. Reserves are as of Jan. 1 of year listed.

There is some reason to believe that reserves of natural gas, both known and undiscovered, may be considerably greater than commonly supposed.

TABLE 2. RESERVES AND PRODUCTION OF PETROLEUM AND NATURAL GAS

	Natural Gas (billion m^3)		Petroleum (million tons)	
	Reserves[a]	Production[b]	Reserves[a]	Production[b]
Developing Regions				
Africa	5,923	46	8,299	291
Latin America	2,558	58	4,604	228
West Asia	14,543	59	50,088	1,138
East Asia	2,250	28	2,434	116
Communist Asia[c]	708	-	2,740	-
Total	25,982	191	68,165	1,773
Developed Regions				
North America	7,818	656	5,137	489
Western Europe	4,019	177	3,360	46
Eastern Europe[d]	26,906	405	11,053	618
Oceania	1,090	e	219	23
Others	60	-	4	-
Total	38,893	1,238	19,773	1,176
World Total	65,875	1,429	87,938	2,949

a. Reserves as of Jan. 1, 1977.
b. Production for calendar year of 1976.
c. Mainland China only.
d. Including U.S.S.R.
e. Included in "others."

Source: International Petroleum Encyclopedia, 1977.

Prior to 1950, there was very little exploration for gas; most gas was found while looking for oil. Until 1977 the price of natural gas in the United States was controlled at a maximum of \$0.52/thousand ft^3 (\$0.018/m^3). Previous estimates of reserves were based on gas economically recoverable at that price. Exploration was limited to those conditions in which the deposits found would probably be profitable at that price.

Now that prices of a different order of magnitude are forecast in the United States, it becomes profitable to explore in wider areas, at greater depths, and in locations where petroleum is not likely to be found. Also, substantial known resources not previously classed as economic reserves can be brought into production. The U.S. Potential Gas Committee estimates that 27.5 trillion m^3 (Tcm) of additional gas may be found in the United States, equivalent to 46 times the 1976 production (1).

The amount of methane in the earth's crust must be enormous. For example, a large zone of geopressurized aquifers in the U.S. Gulf Coast area at 2,500-8,000 m depth contains methane dissolved in hot salt water at 150°C. The amount of methane is not precisely known, but one expert estimates that it may contain 2,800 Tcm and more energy than the total U.S. coal reserves (1, 2). Opinions vary as to the economic feasibility of recovering this methane; until recently there has been no economic incentive to try.

There is also an estimated 17 Tcm of natural gas locked in "tight sands" and about 8 Tcm in coal seams for which no economical recovery means are known. Another 17 Tcm is present in shales underlying Ohio and adjacent areas. Some of this "shale gas" is already being recovered, and promising techniques for recovering more are under study (1).

While the above data relate to resources in the United States, it is likely that similar resources can be found in many countries.

World coal reserves for January 1, 1974, and production for 1973 by regions are shown in table 4. A U.S. Bureau of Mines report published in 1977 placed 1976 world coal and lignite production at 3.6 billion tons and world resources at 11,432 billion tons (3). If only half of the resources could be recovered, they represent nearly 1,600 years' supply at current production rates. Since exploration for coal has been relatively unintensive, it is likely that much more coal could be found.

Apparently petroleum and natural gas reserves are more widely disseminated than coal: 70 countries, including 45 developing countries, reported reserves of petroleum or gas or both. Only 19 countries, including 5 developing countries, reported coal reserves. However, less intensive exploration for coal may account for this difference.

The conclusions to be drawn are that ammonia feedstocks are widely distributed among both developed and developing countries, that developing countries' reserves are much larger in relation to current production rates than those of developed countries, that supplies of coal are more than adequate, but that during the period 1980-2000 the hydrocarbon feedstocks, though available in adequate quantities, are likely to become increasingly expensive.

Phosphate Rock

Phosphate rock is, with the possible exception of coal, the most variable of the raw materials used by the fertilizer industry. The deposits from which it is obtained vary widely in their concentration of phosphate and in the types and quantities of other associated materials. The quality of phosphate rock is usually defined in terms of its P_2O_5 content, the concentration normally lying between 28% and 38%. However, apart from the usefulness in determining transport and handling costs per ton of P_2O_5, the P_2O_5 concentration is an inadequate guide to the value, or suitability for fertilizer manufacture, of a particular grade or type of rock.

TABLE 4. WORLD COAL RESERVES

	Reserves, Billion Tons Identified	Reserves, Billion Tons Probable	Production (1973) Million Tons
Developing Regions			
Africa	6	15	5
Latin America	9	36	12
West Asia	1	2	6
East Asia	23	86	95
Communist Asia	300	1,011	458
Total	340	1,150	580
Developed Regions			
North America	326	2,383	547
Western Europe	150	401	283
Eastern Europe	205	4,052	657
Oceania	26	113	57
Others	32	52	85
Total	740	7,000	1,630
World Total	1,080	8,150	2,210

Source: United Nations Statistical Yearbook, 1974, quoted in "World-Wide Study of the Fertilizer Industry: 1975-2000," UNIDO, 1976. Includes black coal only. Brown coal and lignite reserves are estimated to be 340 billion tons identified and 2,630 billion tons probable.

While a complete chemical analysis of a representative sample of rock is a useful guide to its suitability for fertilizer manufacture and to the design of the plant in which it is to be used, it is only a guide. When, in a new plant, it is proposed to use a rock which is extensively used in fertilizer manufacture, the experience of other users is invaluable, but if there is little previous experience with the rock concerned, extensive trials should be made before the plant design is decided. For the same reasons, in an existing plant great care should be taken if a change in rock supply is under consideration.

World production of phosphate rock, 85% of which is used in the fertilizer industry, has practically doubled over the past 10 years and, according to the estimates of table 1, will increase a further two and one-half times between 1980 and 2000. It is likely that the best quality deposits will be gradually depleted and producers will turn to lower grade deposits leading to a reduction in the average P_2O_5 content of the marketed product and to an increase in the impurities it contains. However, it should be noted that the grade of the beneficiated product is not necessarily related to the grade of the ore. The effects of grade and of common impurities on use in various phosphate fertilizer processes are discussed in chapters XII, XIII, XIV, and XV.

The production of phosphate rock is given in table 5 for individual countries for the year 1976 (4). This table shows that though phosphate rock deposits are widely distributed (some 31 countries are producers), Western Europe and east Asia are short of indigenous resources, and three countries (the United States, the U.S.S.R., and Morocco) account

TABLE 5. WORLD PRODUCTION OF PHOSPHATE ROCK, 1976

Country	Thousands of Tons of Product	% of Total
United States	44,671	41.8
U.S.S.R.	24,200	22.6
Morocco	15,293	14.3
China	3,400	3.2
Tunisia	3,294	3.1
Togo	2,067	1.9
Senegal	1,796	1.7
Jordan	1,717	1.6
South Africa	1,639	1.5
Vietnam	1,500	1.4
Christmas Island	1,033	1.0
Israel	831	
Algeria	820	
Nauru Island	755	
Syrian Arab Republic	511	
India	510	
Brazil	463	
Korea, Democratic Republic	450	
Egypt, United Arab Republic	443	
Ocean Island	417	5.9
Australia	248	
Mexico	197	
Sahara	173	
Rhodesia	130	
Germany, Federal Republic	85	
Venezuela	80	
Curacao	54	
Sweden	25	
Uganda	15	
Peru	2	
Colombia	1	
Total	106,820	100.0

for 79% of current production. This pattern has not changed significantly over the past 10 years. From 1964 to 1973 inclusive, world production practically doubled, but over the 10 years, the United States, the U.S.S.R., and Morocco consistently supplied 75%-80% of total production. Over this period, the U.S.S.R. doubled its production, and the United States and Morocco increased theirs by about two-thirds (5).

The distribution of phosphate rock production by regions in 1976 is tabulated below:

Region	Thousands of Tons of Product
Africa	25,227
Latin America	797
West Asia	3,501
Socialist Asia	5,350
Other Asia	510
Total developing regions	35,385
North America	44,671
West Europe	110
East Europe	24,200
Oceania	2,453
Total developed regions	71,434
World total	106,819

The three major supplying countries' share of world exports is about 70%, but the division between them is very different from their share of production. The United States and the U.S.S.R., with large domestic markets, are much less dependent on exports than is Morocco. In 1976 the United States exported 20% of its production; the U.S.S.R., 23%; and Morocco, 95%. The developing countries as a group are responsible for about 60% of world exports, roughly half of which come from Morocco.

In 1974, according to FAO statistics, developing countries were responsible for about 15% of P_2O_5 fertilizer production and 20% of consumption compared with 40% of rock production. Many developing countries, including Morocco, Tunisia, Algeria, West Sahara, Togo, Jordan, Syria, Egypt, Peru, and Brazil, are increasing production or have plans for large increases; less definite plans exist for Angola, Senegal, Iraq, Colombia, Mexico, and others (6). In the developed countries, a significant change was the development of the large deposits in Queensland, Australia, which reached commercial production in 1974-75. Although production was discontinued in 1978, mainly because of falling prices, these reserves may be an important source in the future if shortages or higher prices develop. Some of the deposits, for which plans exist or are in the early stages of development, are in remote or inhospitable areas. The exploitation of these deposits will raise formidable problems of transport and infrastructure, and costs will inevitably be high. The rate of development of such deposits is likely to be slow and will depend upon the course of phosphate rock prices.

There is no agreed estimate of world reserves of phosphate rock; different authorities produce widely differing estimates ranging from 85,000 million tons (7) to 1,300,000 million tons (8). Appendix B to this chapter lists known phosphate reserves by country with a world total of about 144,000 million tons. The estimate of the requirements for the year 2000, given in table 1, corresponds to a total demand for all purposes of about 300 million tons a year. It is obvious that ample reserves of rock exist. Moreover, the rate of discovery far exceeds the rate of use.

Sulfur

Sulfur in various forms is widely distributed--it constitutes about 0.1% of the earth's crust--but the forms in which it occurs differ greatly in their value as sources. It is found as elemental sulfur, metal sulfides in coal and mineral ores, sulfates, hydrogen sulfide in natural gas, and complex organic sulfur compounds in crude oil. All of these various deposits are used as sources of sulfur, but the most important are elemental sulfur, hydrogen sulfide in natural gas, and iron pyrites.

The uses of sulfur are as varied as its sources, but about 80%-85% is used in the manufacture of sulfuric acid. About half of this acid is used in fertilizer production so that the consumption of sulfur for fertilizers is about 40% of the total. Sulfur is also used in agriculture as a pesticide and, to a comparatively small extent, as a fertilizer to overcome sulfur deficiency. In this chapter, we are concerned with sulfur solely as a raw material for the manufacture of the sulfuric acid used in the production of phosphate fertilizers. However, if sulfur deficiency were to become widespread, increasingly significant quantities would be used to overcome it, though sulfur-containing materials presently discarded by the fertilizer industry could be used for this purpose.

An unusual and important feature of the sulfur industry is its relation to the control of pollution. Probably the most common industrial pollutant is sulfur dioxide, which is produced whenever coal or oil, and sometimes natural gas, is burned and also in quite large quantities when sulfide ores are roasted for metal production. Increasingly strict and widespread regulations limiting discharge to the atmosphere of gases containing sulfur dioxide have led to the development of processes to convert this sulfur dioxide to sulfuric acid, particularly in the metallurgical industries where the effluent gases often have relatively high concentrations of sulfur dioxide. However, by far the most important contribution to sulfur production from these sources comes from the removal of hydrogen sulfide from natural gas and its conversion to elemental sulfur. In 1977 recovered sulfur mainly from natural gas amounted to 16 million tons, about half the world production of elemental sulfur and about 30% of the production of all forms of sulfur.

Sulfur is also recovered at refineries by processes which reduce the sulfur content of fuel oils and in many industrial processes using fuel oil, e.g., in the manufacture of ammonia.

The production of so large a quantity of sulfur as a byproduct of other industrial operations and, therefore, at a rate which does not respond to the demand for sulfur requires the production of sulfur from elemental deposits and from pyrites to bear the load of all fluctuations in demand. As shown below, this has led to a marked decrease in the pyrites' share of the sulfur market:

	Production (Million tons of Sulfur)	Percent of Total Production			
		Elemental Sulfur			Other
		Recovered	Other	Pyrites	Forms
1960	22.3	12	34	36	18
1974	51.6	28	34	22	16
1975	50.9	55[a]		22	27
1976	51.3	62[a]		21	17
1977	52.7	62[a]		21	17

a. Brimstone.

There are a number of reasons why pyrites have lost favor as a source of sulfur. Since they contain about 46% sulfur, freight charges are high; the capital costs of sulfuric acid plants using pyrites are much higher than those of plants using elemental sulfur; pyrites-burning sulfuric acid plants have more troublesome pollution problems than sulfur-burning plants; and the disposal of the iron oxide residues may also present problems.

Table 6 shows the production of sulfur in all forms, by countries, for 1975 (9). The developing countries have 12% of world production, totaling 6.2 million tons, as compared with an estimated 1980 demand for fertilizer production of 6.5 million tons for fertilizer production (table 1). This comparatively low production reflects the paucity of elemental sulfur deposits in these countries, with the notable exceptions of Mexico and Iraq, and also the lack of demand. As the natural gas reserves of developing countries are exploited (see table 2) and as increasing industrialization raises demand, their production of sulfur will undoubtedly increase. From 1971 to 1974, production in the Middle East increased from 0.6 million to 1.4 million tons per annum, and it is expected to increase still further to about 3 million tons per annum by 1980 (10).

TABLE 6. WORLD PRODUCTION OF SULFUR (ALL FORMS), 1975

Country	Production	
	Thousands of Tons	% of Total
United States	11,800	22.8
U.S.S.R.	9,460	18.2
Canada	7,420	14.3
Poland	5,040	9.7
Japan	2,400	4.6
Mexico	2,200	4.2
France	1,940	3.7
Spain	1,560	3.0
Germany, Federal Republic	1,070	2.1
Italy	710	1.4
Iraq	600	1.2
Finland	510	1.0
Iran	475	0.9
Germany, Democratic Republic	365	0.7
South Africa	355	0.7
Sweden	266	0.5
Norway	262	0.5
Australia	255	0.5
Others	5,157	10.0
Total	51,845	100.0

It is difficult to give a significant estimate of total world resources of sulfur because of the wide variety of forms in which it occurs and because of wide differences in the extent and efficiency of extraction from various materials. Total resources are probably about 500 billion to 750 billion tons of which more than 99% is present in coal, oil shales, and gypsum, materials which do not make a significant contribution to present production. An estimate is given below of world sulfur reserves (11) compared with the 1974 production (12).

World Sulfur Reserves and Production
(millions of tons)

	Identified	Probable	Total	Production (1974)
Elemental:				
Evaporites	580	100	680	17.6
Volcanic rocks	130	100	230	
Natural gas	155	885	1,040	15.0
Petroleum	265	1,330	1,595	
Pyrites	640	-	>640	11.0
Metallic sulfides	260	>140	>400	8.2
Subtotal	2,030	>2,555	>4,585	51.8
Tar sands	50	>1,800	>1,850	
Coal	20,000	200,000	220,000	
Oil shale		-	280,000	
Gypsum			Vast	
Total	22,000	>200,000	>500,000	

According to table 1, from 1980 to 2000 the annual consumption of sulfur for fertilizer production will increase from 25 million to 65 million tons. This increase corresponds to a total consumption from 1980 to 2000 of approximately 900 million tons, somewhat less than one-fifth of the reserves at present being used. From the table it appears that reserves in natural gas and petroleum are larger in relation to present use than are the other reserves, although those in pyrites are probably underestimated. Certainly an increasing demand for natural gas and the spread of pollution control will lead to increasing production of recovered sulfur. Elemental sulfur from evaporites and volcanic rocks will be available for a long time, but it is probable that shortages of this form of sulfur may lead to higher prices and a movement to other sources. The fertilizer industry should be able to obtain the sulfur it needs over the next 25 years, but reserves presently being used would appear to have a limited life.

It has been demonstrated that it is technically feasible to recover sulfuric acid from stack gases from combustion of coal or oil. By most estimates, the practice of removing sulfur from these stack gases by recovering it as sulfuric acid is not economically competitive with alternative methods of pollution control, but it may become so with further development or with increased cost of alternative sources.

It is also technically feasible to produce sulfuric acid (and cement) from calcium sulfate--either mineral gypsum, anhydrite or byproduct calcium sulfate from phosphoric acid production. In fact, this process is in commercial use in a few plants. The economics of producing sulfuric acid from sulfur, pyrites, and calcium sulfate will be discussed in chapter XII.

Potash

As in the case of phosphate rock, estimates of potash reserves vary widely, from 11 to over 100 billion tons of K_2O, depending mainly on how optimistic a view the estimator takes of the technical and economical possibilities of extraction.

Table 7 lists the 1975-76 production from 13 countries and their estimated reserves. More recent statistics will be given in chapter XVIII.

TABLE 7. POTASH PRODUCTION AND RESERVES

	1975-76 Production (thousands of tons of K_2O)[a]	Reserves (millions of tons of K_2O)
U.S.S.R.	7,944	15,900-24,000
Canada	4,842	18,000-66,500[b]
Germany, Democratic Republic	3,019	4,000-10,000
Germany, Federal Republic	1,950	2,000-9,000
United States	2,220	200-400[c]
France	1,720	200-270
Israel	716	500-2,000[d]
Spain	506	80-270
China	450	no estimate
Congo	278	17-70
Italy	141	200
United Kingdom	34	20
Chile	10	no estimate
Others	5	no estimate
Total	23,835	35,517-112,730[e]

a. Source of production data: British Sulphur Corp., Statistical Supplement No. 14, November/December 1976.

b. Does not include deposits in New Brunswick.

c. Does not include deposits in North Dakota and Montana.

d. Dead Sea, including Jordan

e. Other deposits not being mined and with no reliable estimate of reserves are in Brazil, Ethiopia, Iran, Laos, Libya, Morocco, Pakistan, Poland, Thailand, and Tunisia.

Only a few developing countries have potash deposits. Deposits are being worked in China and Chile; plans for exploitation exist in Jordan and Brazil (and also in Poland). Countries in which other deposits are known to exist are listed in table 7, but neither the extent nor the feasibility of exploitation has yet been determined with any accuracy. Preliminary indications are that the deposits in Thailand/Laos may be very large indeed.

The total reserves are very large when compared with the probable demand given in table 1, which is for about 1 billion tons of potash from 1980 to 2000 and consumption of 66 million tons in the year 2000. Thus, in 20 years, currently known potash reserves would be reduced by only 1%-3% depending on which estimate of the reserves is accepted. It is clear that the estimated potash requirements can easily be met from known reserves--even if these have been considerably overestimated--without taking account of possible future development of other reserves, e.g., in Thailand.

The reserves that are in production are located almost entirely in the developed countries, and it will therefore be necessary for developing countries to import most of their potash from developed countries until 1985 or possibly 1990. Thereafter, potash may become available in the developing countries. The exploitation of reserves, known or yet to be discovered, in developing countries will depend upon the comparative costs of working these resources and upon the importance attached to the savings in foreign currency which accrue from the use of indigenous resources. For a further discussion of the magnitude and character of world potash reserves, see chapter XVIII.

Other Raw Materials

As noted in other chapters of this manual, there is often a need for elements other than N, P, and K. The other essential mineral elements are Ca, Mg, and S (sometimes called secondary elements) and the micronutrients, Mo, Mn, Fe, B, Cu, Zn, and Cl. In addition, other elements not classified as essential are economically useful in some cases to increase yields or improve the nutritional quality of crops. It is beyond the scope of this chapter to discuss the types, occurrences, and distribution of raw materials for supplying these elements. However, their importance should be recognized for, when one of these elements is deficient, the effect on crop production can be as serious as the lack of one of the major elements.

Also, various nonstandard processes may require raw materials not mentioned above. For instance, the well-known Rhenania phosphate process requires sodium carbonate which may be obtained from the minerals, trona or natron, or manufactured from salt. Fused calcium magnesium phosphate utilizes magnesium minerals such as olivine, serpentine, or magnesite. Various secondary sources of hydrocarbons may be used or considered for ammonia feedstock, such as coke-oven gas, refinery tail gas, liquefied petroleum gas, byproduct hydrogen from electrolytic chlorine production, or products from processing oil shale or oil sands.

Water

The manufacture of fertilizers, particularly nitrogen fertilizers, uses large quantities of water. In the manufacture of ammonia, water is a raw material in the strict sense of the word because it is the source of more than half the hydrogen needed to make ammonia. This water is supplied to the process as steam and varies from 1.5 to 3 m^3/ton of ammonia, depending upon the process used. However, most of the water needed is used as makeup to cooling water systems. The total water requirements for an ammonia/urea plant range from 20 to 35 m^3/ton of urea. On a 1,000-tpd ammonia/1,720-tpd urea plant, this corresponds to a water supply of 150-250 m^3/hour.

These large quantities of water are not always readily available, particularly in arid climates. There are a number of ways in which this quantity can be reduced, and plant contractors can modify plant designs to give minimum water consumption though this will usually involve some increase in capital cost. Where it is available, sea water can be used; air cooling offers a prospect of substantial water savings; more efficient use of water may be possible by pumping water from a "critical" cooler to one where higher temperatures can be tolerated, and so on. However, when all practicable steps have been taken, fertilizer plants will still be large consumers of water. This may affect the decision about their location or may lead to higher costs.

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APPENDIX A TO CHAPTER V

Worldwide Reserves of Petroleum and Natural Gas

Country	Oil Reserves Jan. 1, 1977 10^6 Tons	Gas Reserves Jan. 1, 1977 10^9 m^3
WEST ASIA		
Abu Dhabi	3,973	566
Bahrain	40	85
Dubai	205	42
Iran	8,631	9,348
Iraq	4,658	764
Israel	-	1
Kuwait	9,234	898
Neutral Zone	863	142
Oman	795	57
Qatar	781	779
Saudi Arabia	20,550	1,785
Sharjah	4	28
Syria	301	34
Turkey	53	15
Total	50,088	14,544
EAST ASIA-PACIFIC		
Afghanistan	12	78
Australia	189	915
Bangladesh	-	227
Brunei	223	238
Burma	9	4
China (Taiwan)	2	23
India	411	99
Indonesia	1,438	680
Japan	4	59
Malaysia	333	425
New Zealand	26	175
Pakistan	10	448
Thailand	-	28
Total	2,657	3,399
AFRICA		
Algeria	932	3,564
Angola-Cabinda	166	42
Congo Republic	39	1
Egypt	267	79
Gabon	291	71
Libya	3,494	731
Morocco	-	1
Nigeria	2,672	1,246
Tunisia	370	187
Zaire	68	1
Total	8,299	5,923
EUROPE		
Austria	22	20
Denmark	41	19
France	7	142
Germany (West)	45	212
Greece	5	227
Italy-Sicily	43	187
Netherlands	12	1,754
Norway	775	524
Spain	60	14
United Kingdom	2,302	850
Yugoslavia	48	42
Other (Ireland)	-	28
Total	3,360	4,019
WESTERN HEMISPHERE		
Argentina	315	193
Barbados	-	8
Bolivia	33	142
Brazil	110	25
Canada	849	1,586
Chile	25	56
Colombia	113	142
Ecuador	233	340
Guatemala	3	-
Mexico	1,507	340
Peru	102	62
Trinidad and Tobago	71	97
Venezuela	2,092	1,153
United States	4,288	6,232
Total	9,741	10,376
COMMUNIST		
Bulgaria	2	2
China	2,740	708
Czechoslovakia	3	19
Hungary	43	121
Poland	11	124
Romania	294	640
U.S.S.R.	10,700	26,000
Total	13,793	27,614
Total World	87,938	65,881

Source: International Petroleum Encyclopedia, 1977. Petroleum Publishing Company, Tulsa, Oklahoma.

APPENDIX B TO CHAPTER V

World Phosphate Reserves and Resources

Country	Total Reserves and Resources, tons x 10^6	% P_2O_5 Average or Range	Ref.	Remarks
AFRICA[a]				
Algeria	1,000	30[b]	1	
Angola	120	30[b]	1	
Egypt	2,800	30[b]	1	
Liberia	1.5	28		Al-Fe phosphate
Mali	20	30	2	
Mauritania	5	23-32	2	Exploration incomplete
Morocco	40,000	30[b]		
West Sahara	16,600	30[b]	1	
Senegal				
Taiba	1,100	30[b]	1	
Thies	2,090	30[b]	1	Aluminum phosphate
Tanzania	10	27-38	3	
Togo	300	30[b]	1	
Tunisia	1,300	30	1	
Rhodesia	20	30[b]	1	
South Africa				
Palabora	1,400	30[b]	1	
Other	35	10-21	3	
Uganda	200	30[b]	1	
Upper Volta	4	27-31	2	May be much larger
Zaire	83	15	4	
Total	67,189			
WEST ASIA				
Iran	130	30[b]	1	
Iraq	660	30[b]	1	
Israel	1,000	26	5	
Jordan	1,000	15-30	6	Ore of all grades above 15% in drilled area
Lebanon	small	17-31	8	
Saudi Arabia	1,000	30[b]	1	
Syria	800	30[b]	1	
Turkey	300	30[b]	1	
Total	4,890			
EAST ASIA[c]				
China	30,000	15	5	
Christmas Is.	200	29-38	7	Includes aluminum phosphate
India	140	17.5	5	Assumes 100 at Jhamar Kotra
Korea, North	88	12.5	5	
Mongolia	1,000	20-22	7	
Pakistan	12	20-37		
Paracel Is.	20	10-27	8	Ownership disputed
Philippines				
Sri Lanka	300	30	9	
Vietnam	500	30[b]	1	
Total	17,260	(China adjusted to 15,000 million tons of equivalent 30% P_2O_5)		
OCEANIA				
Australia	2,000	30[b]	1	
Nauru	44	38.5	5	
Ocean Is.	2	40	5	
New Zealand	70	30	3	Underseas nodules
Total	2,116			
NORTH AMERICA				
Canada	50	9	3	Igneous deposits
U.S.A.				
Eastern	19,900	26	10	
Western	14,700	26	10	
Alaska	1,000	25	10	May be larger
Mexico				
Baja Calif.	1,000	30[b]	1	May be larger; does not include underwater
Zacatecas	140	30[b]	1	
Total	36,790			

(Continued)

APPENDIX B TO CHAPTER V

World Phosphate Reserves and Resources
(Continued)

Country	Total Reserves and Resources, tons x 10^6	% P_2O_5 Average or Range	Ref.	Remarks
SOUTH AND CENT. AMERICA[d]				
Aruba	10	30^b	1	Aluminum phosphate
Brazil				
Bambui	700	30^b	1	
Olinda	20	30^b	1	
Igneous	1,000	30^b	1	Carbonatites
Other	25	30^b	1	Aluminum phosphate
Colombia	600	30^b	1	
Chile	4	30	11	New discovery, may be much larger
Curacao	10	30^b	1	
Peru	6,100	30^b	1	
Venezuela	40	30^b	1	
Total	8,509			
EUROPE including U.S.S.R.[e]				
Finland				
Sakli	200	18	3	
Siilinjarva	25	10	3	
Ireland	8	25	7	
Norway	100	6-10	7	Igneous
Sweden	no estimate			Igneous
U.S.S.R.				
Kola	1,125	39.4	5	Estimated recoverable concentrate
Other	6,000	14	5	Various sedimentary deposits. Some new discoveries may not be included
Total	7,458			
World Total	144,212			

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a. Other countries that have small or unquantified deposits include Cameroon, Benin, Gambia, Niger, Gabon, Nigeria, Dahomey, and perhaps Chad.

b. Tonnage and grade stated in terms of equivalent quantity of marketable phosphate rock of 30% P_2O_5 grade or higher.

c. Also small or unquantified deposits in Cambodia, Malaysia, Taiwan, Japan, Philippines, and Indonesia.

d. Also small amounts on various islands.

e. Also small or unquantified deposits in Belgium, Bulgaria, France, Germany, Greece, and Yugoslavia.

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PART TWO

NITROGEN FERTILIZERS

VI Production of Ammonia

History of Ammonia Synthesis

As mentioned in chapter I, synthetic ammonia (NH_3) has become the principal source of all nitrogen fertilizers, particularly since 1945. At present, over 95% of all commercial fertilizer nitrogen is supplied by or derived from synthetic NH_3; only minor percentages are supplied by natural sodium nitrate, byproduct NH_3 from coke-oven gas (usually recovered as ammonium sulfate), calcium cyanamide, and other minor sources. The ammonia synthesis process was developed mainly by Fritz Haber starting in 1904, and by 1909 he demonstrated the process on a laboratory scale of 80 g of NH_3 per hour (1). Carrying out the high-temperature, high-pressure process on a commercial scale presented formidable problems with the technology and materials of construction then available. Carl Bosch, working with Haber, is generally credited with developing the process--first in a pilot plant and then on a commercial scale of 30 tpd. Production started in 1913 at Oppau, Germany.

The chemistry of the process is simple; the reaction is:

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

The reaction is exothermic; the net heat of reaction is about 11,000 cal/g-mole at 18°C (647 kcal/kg of NH_3), assuming NH_3 is in the gaseous state. The net heat released by the reaction increases with increasing temperature and may be 15%-20% higher at the usual operating conditions of 400°-500°C.

The reaction does not go to completion; equilibrium conditions are such that increase in pressure favors high conversion to ammonia, while increased temperature decreases conversion as shown in table 1 (2). Thus, it is possible to obtain about 90% conversion at 300 atm and 200°C. However, at the same pressure but at 700°C, equilibrium conversion is only 7.3%. At a constant temperature of 450°C, conversion increases from 2.1% at 10 atm to 35.8% at 300 atm and 69.7% at 1,000 atm. However, the rate of reaction is very slow at 200°C and increases with temperature; thus, a compromise must be selected between reaction rate and equilibrium values. The search for a catalyst to increase the reaction rate has received much attention both by Haber and subsequent investigators. Haber's first studies were made with an iron catalyst, which was not very active. Later, he found that osmium or uranium was much more effective, but these elements were scarce and expensive. Still later (about 1911) it was found that certain impurities increased the activity of an iron catalyst. After several thousand formulas had been tested, a doubly promoted iron catalyst was selected that was produced from magnetite (Fe_3O_4) with additions of potassium, alumina, and calcium. (The magnetite is reduced to metallic iron by the hydrogen during the operation.) This type of catalyst is still the standard material in present use although some refinements have been made.

Even with the best catalysts available, the reaction rate is a limiting factor, and a compromise must be reached between long retention time which would require a large, expensive converter and conversion efficiency. The usual compromise results in a conversion equivalent to 70%-80% of equilibrium. Since equilibrium under usual operating conditions may correspond to 25%-35% conversion, the actual conversion may be 17%-28%, for example.

In order to improve conversion, Haber originated the concept of the ammonia synthesis loop, in which the gas leaving the converter is cooled to condense most of the ammonia as a liquid which is removed from the gas. Then the remaining gas (unreacted N_2 and H_2) is reheated and returned to the synthesis converter with fresh synthesis gas. He also recognized that much of the cooling could be done by heat exchange

TABLE 1. PERCENTAGE OF AMMONIA AT EQUILIBRIUM FROM A 3:1 MOLAR MIXTURE OF HYDROGEN AND NITROGEN

	Pressure, atm						
Temperature, °C	10	30	50	100	300	600	1,000
200	50.66	67.56	74.38	81.54	89.94	95.37	98.29
250	28.34	47.22	56.33	67.24	81.38	90.66	96.17
300	14.73	30.25	39.41	52.04	70.96	84.21	92.55
350	7.41	17.78	25.23	37.35	59.12	75.62	87.46
400	3.85	10.15	15.27	25.12	47.00	65.20	79.82
450	2.11	5.86	9.15	16.43	35.82	53.71	69.69
500	1.21	3.49	5.56	10.61	26.44	42.15	57.47
550	0.76	2.18	3.45	6.82	19.13	31.63	41.16
600	0.49	1.39	2.26	4.52	13.77	23.10	31.43
650	0.33	0.96	1.53	3.11	9.92	16.02	20.70
700	0.23	0.68	1.05	2.18	7.28	12.60	12.87

Source: From A. T. Larson and R. L. Dodge (1923). Journal of the American Chemical Society, 45:2918; and A. T. Larson, Ibid. (1924), 46:367-72.

between the cool gas entering the converter and the hot gas leaving it.

Thus, the basic principles of the ammonia synthesis process were well known to Haber and his coworkers and serve as the basis of the modern ammonia production industry.

Data from the Haber-Bosch work did not become available outside Germany or outside their company (BASF) for many years because of company secrecy and the 1914-18 war. A Haber process plant built during the war at Sheffield, Alabama, U.S.A., by U.S. Army Ordinance was based on information obtained by U.S. Intelligence. However, the information on the ammonia synthesis catalyst was not complete, and the plant did not operate (3). After the war, the U.S. Government established the Fixed Nitrogen Research Laboratory to develop the necessary information, and in 1921 the first synthetic ammonia plant was built in the United States by the Atmospheric Nitrogen Corp., now Allied Chemical Co. By 1932 there were 10 ammonia plants in the United States with a total design capacity of 287,000 tons of N per year.

During the early years of World War II, the U.S. Government realized that, if the United States became involved in the war, its fixed nitrogen supply would be inadequate to meet the demand for munitions. As a result, 10 more plants were built with a total N capacity of 595,000 tpy. During the late years of the war and the years following, the output of these plants was diverted to fertilizer, primarily ammonium nitrate. The demand for fertilizer increased rapidly, and by 1958 there were 58 plants in the United States with an estimated annual capacity of 3.8 million tons of N. Major improvements in ammonia production technology were (1) the use of natural gas or naphtha as feedstock in the late 1940s and 1950s and (2) the development of centrifugal compressors in the 1960s. These developments, in combination with increased scale, progressively lowered the cost of ammonia and of nitrogen fertilizer (up to 1972) and increased the demand. In 1974 world N production capacity was estimated at 62.5 million tons, and forecast capacity for 1981 was 107.2 million tons (4). Allowing for operation at less than full capacity and for nonfertilizer uses, the nitrogen fertilizer supply was estimated to increase from 41 million tons in 1974 to 62 million tons in 1981 (3). Actual production of N for fertilizer use was estimated to be about 46 million tons in 1977 (5).

Most of the plants built before 1945 were based on coke. In the original Haber process coke was used in a water-gas generator which operated in a cycle of "blow" and "make." In the blow cycle the coke was burned with air until the temperature of the coke was increased to a suitable level (above 1000°C). Then the air was turned off and steam was blown through the hot coke bed forming CO and H_2 by the water-gas reaction:

$$C + H_2O \rightarrow H_2 + CO$$

The reaction is endothermic and quickly cools the coke bed to the point that it must be reheated by another blow cycle. The "make" gas typically contained 50% H_2, 40% CO, 5% N_2, and 5% CO_2. To provide the necessary nitrogen separate gas producers which also used coke were blown continuously with air to obtain producer gas containing 62% N_2, 32% CO, 4% H_2, and 2% CO_2. The two gases were collected separately in gas holders and mixed in the proper proportions to give an N_2:H_2 ratio of 1:3 in the final synthesis gas. As an alternative, the gas producer could be blown continuously with a mixture of oxygen-enriched air and steam to produce gas of the desired composition. In some later plants, such as the TVA plant built in 1942, a semiwater gas process was used in which the "make" gas was partially oxidized with secondary air thus obviating the need for separate air-blown gas producers. In this case the "make" gas contained 36.3% H_2, 21.8% N_2, 36.2% CO, and 5.5% CO_2. The nitrogen content could be adjusted to that stoichiometrically required by adding some of the blow gas. Extensive cleaning of the gas was required to remove dust, sulfur, and other impurities. The gas was compressed in several stages with purification steps in between. The first step was the "shift reaction" of conversion of CO and steam to H_2 and CO_2:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The next step was CO_2 removal at about 25 atm by water scrubbing. A third step was removal of residual CO by scrubbing with "copper liquor" (copper acetate and formate solution) typically at about 200 atm. The final stage was the ammonia synthesis step described previously, which was carried out at various pressures from 200 to 1,000 atm, depending on the process.

The total energy consumed by the coke-based process for fuel, feedstock, and mechanical energy was 88 GJ per ton of NH_3 as compared with about 36 GJ for a modern natural gas-based plant (1). The labor requirement was about 1,800 men versus 60 for the modern plant, and the investment cost was nearly three times as great. Also, the expense of the coking operation was considerable.

Direct use of coal or lignite as feedstock was begun as early as 1926 using the Winkler gasifier. Partial oxidation of heavy fuel oil was developed, and steam reforming of natural gas and light hydrocarbons was used commercially in 1940 but did not become popular until the 1950s. At present, steam reforming of natural gas and naphtha is estimated to account for over 80% of all ammonia production. Some other feedstocks such as liquefied petroleum gas (LPG) and refinery tail gas are treated by steam reforming; therefore, the total ammonia production by this method may be as much as 85%. The great majority of new ammonia plants that are planned or are under construction will use natural gas; therefore, the short-term trend will be toward greater use of this feedstock. However, the amount of natural gas in the world is limited, and eventually other feedstocks will become important as discussed in chapter V.

The technological improvements mentioned above and other improvements too numerous to mention, coupled with increase in scale, have resulted in a steady decline in ammonia production cost from over \$200/ton in 1940 to about \$30/ton in 1972. After 1972 the trend was reversed and costs have risen, mainly because of increased cost of feedstocks and a sharp increase in plant construction cost. The increased construction cost was caused primarily by increased material and labor costs and partly by more complicated heat and energy recovery equipment which became necessary to conserve expensive fuel. More stringent pollution control regulations also were a factor.

Further technological improvements are expected, but none are foreseen of such magnitude as to reverse the present upward cost trend due to rising fuel, feedstock, and construction costs. Only minor economies can be achieved by further increase in scale above the current standard of 1,000-1,200 tpd, and any economies in scale are likely to be offset by increased distribution costs. The world's largest single-train ammonia plant is rated at about 1,600 tpd. Designs are available for 2,000-tpd plants, but the economic benefits are doubtful.

Steam-Reforming Processes

Thermochemical Data

Since steam-reforming processes account for over 80% of the world's ammonia production, this type of process will be described in more detail than the others. Figure 1 is a block flow chart of the steam-reforming process using natural gas feedstock. It shows the principal chemical reactions and typical pressure levels. The overall approximate chemical reaction may be written:

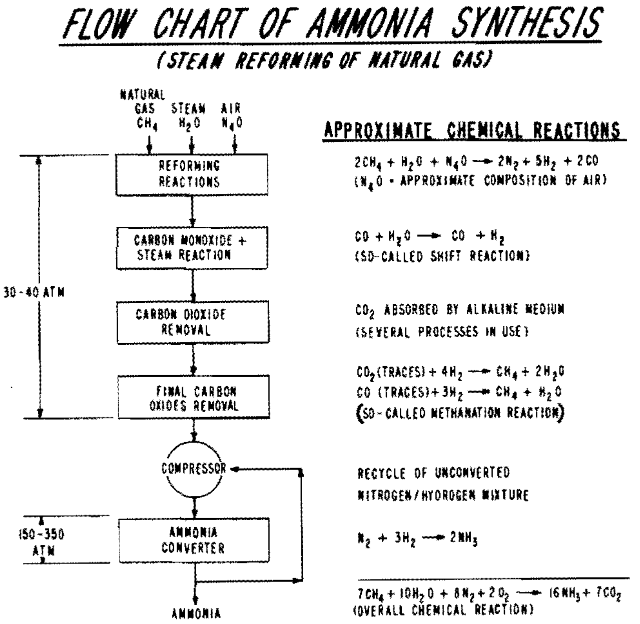

Figure 1. Flow Chart of Ammonia Synthesis (Steam Reforming of Natural Gas).

$$7CH_4 + 10H_2O + 8N_2 + 2O_2 \rightarrow 16NH_3 + 7CO_2$$

Using the standard heats of formation, the heat of the overall reaction may be calculated as follows:

Reactants	kcal/g mole		kcal, Total for Above Equation
$CH_4(g)$	-17.89 x 7	=	-125.23
$H_2O(l)$	-68.32 x 10	=	-683.20
$N_2(g)$	0		0
$O_2(g)$	0		0
Total reactants			-808.43
Products			
$NH_3(l)$	-16.06 x 16		-259.96
$CO_2(g)$	-94.05 x 7		-658.35
Total products			-918.31
Net heat of reaction			-109.88

Thus, the overall reaction is exothermic to the extent of about 110 kcal for the equation shown above, assuming NH_3 in the liquid state or about 30 kcal for NH_3 in the gaseous state. Since the reaction, as written, produces 17 x 16 = 272 g of ammonia, the net heat released by the reaction amounts to about 404,000 kcal/ton of liquid ammonia or 110,000 kcal/ton of gaseous ammonia. At first thought, this may seem contrary to the general conception that ammonia production consumes a tremendous amount of heat. However, if the same amount (7 g-moles) of CH_4 were burned to CO_2 and H_2O, about 1,343 kcal (LHV) would be released which is equivalent to about 5 million kcal/ton of NH_3 (about 21 GJ).[1] Therefore, production of ammonia consumes energy in the sense that it uses as feedstock a material that could otherwise be used as fuel.

The various steps of ammonia production are carried out at different temperature levels ranging from 0° to 1200°C; thus, fuel must be used to heat the reactants. While much of the heat is recovered, a substantial portion is lost. As a result, natural gas-based ammonia plants with the most efficient heat recovery systems require about 8.6 million kcal (36 GJ) for fuel and feedstock (6). This requirement is based on the low heating value (LHV) of methane, which does not include the heat of condensation of water vapor that is formed in the combustion of methane. In addition, a substantial amount of electrical energy is required (20-50 kWh/ton) even though most of the mechanical energy is supplied by turbines driven by steam that is generated by heat recovery in the process. Marginal improvement in heat recovery is possible but at the expense of increased capital cost. Table 2 shows typical temperature levels in the steps of NH_3 production by steam reforming of natural gas, the main reaction occurring in each step, and the standard heats of the reactions. It will be noted that all the reactions are exothermic except the steam reforming of methane. Also, there is a wide difference in temperature level for the various steps. Therefore, heat-exchange equipment comprises a large proportion of the ammonia plant cost.

Feedstocks for Steam-Reforming Processes

Natural Gas--As mentioned previously, natural gas is the principal feedstock for ammonia production; it currently accounts for over 70% of the world's ammonia production (6). Natural gas is classified as "associated" or "nonassociated." Associated gas occurs with crude oil; it is liberated from the oil when the pressure is released in the oil-gas separator plant. Its composition varies with the pressure at which the separator is operated. Since methane is the most volatile, it can be released at a relatively high pressure. By releasing gas at successively lower pressures, a separation can be made in which methane is released first and the less volatile gases, ethane, butane, and propane, are collected separately.

The higher hydrocarbons usually have a higher value for petrochemical production or for sale as liquefied petroleum gas (LPG) than methane. Therefore, in most cases, these products are sold separately, and the term "natural gas" usually refers to the fraction that contains mostly methane with only small percentages of ethane and higher hydrocarbons. For use as ammonia feedstock, methane is preferable to the higher hydrocarbons since all carbon in the feedstock is converted to carbon dioxide or monoxide which must be removed from the ammonia synthesis gas. Therefore, the lower the carbon:hydrogen ratio in the feedstock, the smaller and less expensive the purification units in the synthesis gas preparation will be.

In ammonia-urea complexes, where all of the ammonia is used to make urea, the amount of CO_2 derived from methane feedstock may not be sufficient for the urea plant needs. Urea requires a $CO_2:NH_3$ ratio of 1:2; whereas, the production of ammonia by

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[1] LHV = Low heating value, which does not include the heat of condensation of water formed in the reaction.

TABLE 2. CHEMICAL REACTIONS, TEMPERATURES, AND HEAT OF REACTION IN PRODUCTION OF AMMONIA FROM METHANE

Step	Reaction	Typical Temp., °C	ΔH°, kJ/g-mole[a]
Steam reforming[b]	$CH_4 + H_2O = CO + 3H_2$	790-820	+206.2
Secondary reforming[b,c]	$CH_4 + 1/2O_2 + (2N_2) = CO + 2H_2 + (2N_2)$	900-1200	-35.6
Shift reaction	$CO + H_2O = CO_2 + H_2$	200-450	-91.8
Carbon dioxide removal	(Physical separation)	70-105	-
Methanation	$CO + 3H_2 = CH_4 + H_2O$ $CO_2 + 4H_2 = CH_4 + 2H_2O$	250-450	-206.2 -165.0
Ammonia synthesis	$3H_2 + N_2 = 2NH_3$	300-500	-91.8
Ammonia condensation	$NH_{3(gas)} = NH_{3(liquid)}$	30 to -30	-21.0

a. Heat of reaction taken from reference (1); + sign indicates heat absorbed; - sign indicates heat released. To convert to kcal, multiply by 0.239.

b. For simplicity, a single reaction is shown for the reformer step which represents the predominant net reaction. However, the chemistry is much more complex. In particular, a significant amount of CO_2 is formed in these steps.

c. Completion of reaction 1 also takes place in secondary reforming.

reforming pure methane produces a CO_2:NH_3 ratio of 7:16 according to the approximate equation given earlier. In this case it would be advantageous if the natural gas contained enough higher hydrocarbons to supply enough CO_2 for urea production. This is often the case as shown by the example of natural gas composition given in table 3. As an alternative, extra CO_2 can be obtained from stack gas during the combustion of fuel in the reformer furnace, but this alternative is relatively expensive.

TABLE 3. COMPOSITION OF TYPICAL NATURAL GAS

Constituent	% by Volume	
	At Well-Head	As Delivered by Pipeline
CH_4	75.9	93.3
N_2		2.0
Argon		0.4
CO_2	7.3	0.01
H_2S	8.9	<5 ppm
Hydrocarbons		
C_2H_6	3.3	3.3
C_3H_8	1.2	0.9
C_4H_{10}	0.8	0.2
C_5H_{12}	0.5	0.01
C_6H_{14}+	2.3	

In the past, associated natural gas has often been regarded as an unwelcome byproduct of petroleum production, and this is still the case in some countries where there is no means for economical recovery or use. In such cases the gas may be pumped back into the oil-bearing formation to "pressurize" it and, thus, augment the flow of oil, or it may be "flared," i.e., wasted by burning in open air. The amount of natural gas that is flared is substantial. Efforts are being made to utilize it by establishing ammonia, methanol, or other petrochemical plants or energy-intensive industries such as aluminum production or by liquefying the gas for shipment. However, these efforts involve much time and capital and often entail enormous difficulties because of the remote locations and hostile environments ranging from desert areas and tropical jungles to arctic regions.

Both associated and nonassociated natural gases vary widely in composition; the example in table 3 is only an illustration. Gas from some nonassociated deposits may be nearly pure methane. In other deposits gas may contain higher percentages of H_2S, CO_2, or both. Other, usually minor, constituents are N_2 and sometimes He (helium). The CO_2 and H_2S usually are removed by scrubbing before delivery by pipeline to avoid corrosion of the pipeline; the H_2S may be converted to elemental sulfur which may be a profitable byproduct in some cases.

Methane from Sources Other than Natural Gas-- Obviously methane from any source could be used as feedstock for ammonia production; some of these sources have been mentioned in chapter V. One promising source is anaerobic decomposition of waste organic material or of "biomass" (vegetable cellulosic materials) such as forest waste or vegetative crops. Several projects are in operation or under construction in the United States to produce methane from manure or urban waste (7). Anaerobic fermentation produces a gas containing about 55% CH_4; the remainder is mainly CO_2 which can be readily removed by scrubbing with monoethanolamine (MEA) or other solvents. In several cases, methane from these sources is sold to natural gas pipeline distributors for mixing with natural gas at prices ranging from \$1.30-\$1.90/1,000 ft^3 (\$46-\$67/1,000 m^3). It has been estimated that methane from such sources could supply 20% of the present U.S. consumption of natural gas (8). Since ammonia feedstock amounts to only 1%-2% of U.S. gas consumption, it is evident that "biogas" could supply enough methane for present and probably future ammonia needs. In most of the projects the cost presumably is partially borne by waste disposal, but by some estimates biogas produced from vegetative crops would be competitive or cheaper than alternate ammonia feedstocks such as coal or naphtha. Methane is produced in many small bio-gas pits in India; in China it is reported that over 400,000 marsh gas pits produce methane from night soil, grass, stalks, waste water, garbage, etc. (9). The methane is used for rural cooking and for some industrial uses such as fuel for small cement plants, fuel to drive water pumps, etc. While it is not known to be used for ammonia production, obviously the gas could be used for this purpose if enough gas could be collected at one location for an economical scale of operation. In this connection, it has been estimated that 5 million ft^3/day (142,000 m^3/day) of crude gas containing about 60% methane can be collected from a sanitary landfill at Mountain

View, California, for 8-10 years (7). No doubt, urban waste from larger cities could be used to generate enough methane for even a 1,000-tpd ammonia plant. However, much development work is needed to establish the technical and economical feasibility of large-scale production of methane from urban waste and to dispose of the residue, which may be useful for fertilizer.

Liquefied Petroleum Gas--LPG which contains mainly butane and propane has been used as ammonia feedstock in Japan and reportedly will be used in Norway. Liquefied natural gas (LNG) also is used in Japan. These materials are relatively expensive but often less expensive than naphtha. Synthetic natural gas (SNG) is practically pure methane produced from coal and may be considered for future use in ammonia production.

Naphtha--In those areas of the world where natural gas is unavailable, naphtha became a favored feedstock for ammonia production by steam reforming, particularly in the period of 1950-74 when naphtha was relatively cheap. In many countries the amount of naphtha produced in oil refining exceeded the demand. Naphtha is the lighter fraction of hydrocarbons, boiling from about 40° to 130°C with an average molecular weight of about 88 and an H:C atomic ratio of about 2.23. Straight-run naphtha is preferred to naphtha produced from higher hydrocarbons by cracking or "hydrocracking" because the latter usually contains sulfur compounds that are difficult to remove. The composition and properties of a typical naphtha are given in table 4. Since 1974 the price of naphtha on the world market has risen more rapidly than that of other feedstocks because of the demand for naphtha for use in the manufacture of motor fuel and petrochemicals (ethylene, propylene, etc.). Therefore, several plants originally designed to use naphtha have switched to other feedstocks such as natural gas, LNG, or LPG. As a result, few new plants are being built to use this feedstock.

TABLE 4. COMPOSITION AND PROPERTIES OF TYPICAL NAPHTHA

Constituent or Property	Average Value
Specific gravity at 15.5°C	0.686
Initial boiling point, °C	41
Final boiling point, °C	131
Unsaturates, % (volume)	1
Aromatics, % (volume)	4
Saturates, % (volume)	95
Total sulfur as (ppm by wt)	368
H_2S	2
RSH	146
R_2S_2	119
R_2S	80
S	1
Unreactive S	20
C, %	84.4
H, %	15.7
Mol wt	88
Heating value, kcal/kg	10,500

The process for steam reforming of naphtha was developed mainly by Imperial Chemical Industries (ICI) in England and has been widely used in Europe, Japan, and many developing countries. The main technical problem was to avoid carbon formation on the reforming catalyst without excessive steam consumption. This problem has been solved by modifications of the catalyst composition.

Refinery Gases--Petroleum refineries and petrochemical operations produce a variety of byproduct gases that can be used as fuel or feedstock or both. The composition of refinery tail gas varies widely; it usually contains H_2, CH_4, and higher hydrocarbons and can be used as ammonia feedstock by steam reforming. The amount of tail gas available is likely to be insufficient for an economical scale of ammonia production unless the refinery is a very large one. Another drawback is that the volume and composition of the tail gas may vary according to the demand for the various refinery products, and these variations can cause difficulties in the ammonia plant operation. Also, refineries often have a use for the components of the tail gas. For instance, the hydrogen can be separated and used in "hydrocracking" (production of light hydrocarbons by hydrogenating and cracking heavier fractions).

In the production of ethylene (by cracking naphtha), a byproduct gas stream containing mainly methane and hydrogen is produced. Several other petrochemical processes produce byproduct gases that are usable as ammonia feedstock either by steam reforming or cryogenic separation of hydrogen.

Only a few ammonia plants in Europe and Japan use refinery tail gas.

Coke-Oven Gas--Coke-oven gas contains about 55% H_2, 25% CH_4, 8% CO, 6% N_2, plus minor amounts of higher hydrocarbons, CO_2, and various impurities. Presumably, it could be used for ammonia production by steam reforming after purification, but the usual practice is to separate the hydrogen by a cryogenic process involving a liquid nitrogen wash. Many steel-producing plants have an air separation unit to supply oxygen for use in steel production, thus the liquid nitrogen is available from this source. The cryogenic process produces a nitrogen-hydrogen gas mixture suitable for ammonia synthesis, and the remaining gas mixture of CO, CH_4, and heavier hydrocarbons is used as fuel. The main drawback is similar to that of refinery tail gas; the amount of coke-oven gas depends on coke production which, in turn, depends on steel production. Only a few plants use coke-oven gas for feedstock.

Heavy Oil--Liquid hydrocarbons heavier than naphtha are used for ammonia feedstock by partial oxidation processes which will be discussed in a later section of this chapter. However, there has been some interest in applying the steam-reforming process, and Toyo Engineering Corp. has recently reported successful development on a pilot-plant scale (10). Successful operation of the pilot plant was reported when using crude oil from several sources or heavy residual oil. Little detail is available about the process, but it involves use of two newly developed catalysts in the primary and secondary reformer. Both catalysts are unaffected by sulfur. The primary reformer catalyst is effective in heavy oil gasification without carbon deposition at 900°-1000°C, while the secondary reformer catalyst is effective in reforming the methane remaining in the gas from the first reformer. The gas from the reformers still contains all of the sulfur (as H_2S) that was present in the feedstock, which would have to be removed in a subsequent purification step as in partial oxidation processes. Potential advantages of the process compared with partial oxidation processes are lower investment cost (an air separation plant is not required) and lower energy consumption.

Other Feedstocks--Methanol or ethanol can be used as feedstock in steam-reforming processes, but no commercial use has been reported. Other feedstocks such as electrolytic hydrogen, coal, and fuel oil will be discussed separately under applicable process headings.

Feedstock Prices[2]--Prices of feedstocks are often controlled by governments. The price of crude oil on

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[2] Based on mid-1978 situation.

the world market is controlled by the Organization of Petroleum Exporting Countries (OPEC), and the world market price of crude oil derivatives such as naphtha is indirectly controlled by the price of crude oil. The domestic prices of crude oil and naphtha in oil-producing countries are often controlled by the governments at a lower level than world market prices. Even in oil-importing countries, governments may exercise control of feedstocks such as naphtha by subsidizing refinery operations.

Natural gas prices in the United States as of July 1978 are controlled at a maximum of $1.43/1,000 ft^3 ($50.53/1,000 m^3). This is the price for gas from new sources delivered to an interstate pipeline. The price of gas delivered to customers via interstate pipeline is also controlled and will be increased by a transport cost and will vary depending on the mix of "old" and "new" gas, transport distance, amount and pattern of use, and whether the contract is for "firm" or "interruptible" gas. Even "firm" gas is subject to curtailment when the supply is not adequate. Legislation is pending (1978) in the United States to increase the maximum price of interstate natural gas gradually and perhaps to remove the controls eventually.

"Intrastate" gas is not controlled in the United States at present (1978). Prices to industries are subject to contract negotiations and are usually not publicly announced. Most new ammonia plants in the United States are located in gas-producing states such as Texas, Louisiana, and Oklahoma where the supply is more reliable and not subject to Federal Government control. Prices may range up to $1.90/1,000 ft^3 ($67/1,000 m^3).

Natural gas prices in some European gas-producing countries may be $0.80/1,000 ft^3 ($23/1,000 m^3). Prices in some developing countries that have ample supplies of natural gas reportedly range from $0.20 to $0.60/1,000 ft^3 ($5.66-$16.98/1,000 m^3) depending on cost of collection and purification, length of pipeline transport, and government policy.

Heavy fuel oil in oil-importing countries may be priced somewhat below crude oil at the refinery, particularly in the case of high-sulfur oil that cannot be used for fuel without expensive pollution control.

The price of coal varies widely depending on its quality, cost of mining, and transport cost. Future coal costs in the United States for 1980-2000 are estimated to range from $13 to $25/ton at the mine, but present costs are higher, particularly for low-sulfur coal which is in short supply and may cost as much as $50/ton (11).

The effect of type and cost of feedstocks on ammonia plant capital cost and ammonia production cost is discussed in a later section of this chapter.

LNG prices in the United States and Japan typically are about $3.00/1,000 ft^3 ($106/1,000 m^3) at the receiving terminal. A recent publication shows a range of $1.22 to $3.37/1,000 ft^3 ($43-$119/1,000 m^3) for present and future U.S. LNG projects; the lower prices are for contracts negotiated several years ago (12). LNG is not known to be used in the United States for ammonia feedstock, but its use in Japan has been reported.

The world market price for naphtha is typically about $135/ton and is related to the price of crude oil, which is currently about $95/ton. The prices of both materials are likely to be controlled by the government. For instance, the price of U.S. domestic crude oil is $8/bbl (about $58/ton).

Feedstock Requirements--In nearly all ammonia plants the same material is used as both feedstock and fuel. The fuel requirements may be 40% of the total or more, depending on the extent to which heat recovery equipment is utilized. In previous years when fuel was inexpensive, many ammonia plants were built with minimum heat recovery facilities. Buivadas, et al., give an example of how the fuel requirement (natural gas) was decreased by 34% through more efficient energy use, mainly high-pressure steam generation and preheating combustion air to the reformers (13). The decrease in total fuel plus feedstock requirement was about 15%. The increase in fuel efficiency was obtained at the expense of about 6% increase in plant investment cost.

The following requirements for fuel plus feedstock assume efficient heat recovery (13).

Feedstock and Fuel	Assumed Heating Value[a]	Requirements per ton of NH_3	
		Quantity	Million kcal
Natural gas	8,015 kcal/m^3	1,073 m^3	8.6
Naphtha	10,556 kcal/kg	0.89 t	9.4
Fuel oil	9,722 kcal/kg	1.00 t	9.7
Coal	6,333 kcal/kg	1.97 t	12.5

a. All values are low heating values (LHV).

In a natural gas-based plant 34% of the gas is used for fuel and 66% for feedstock; in a naphtha-based plant about 38% of the naphtha is used for fuel and 62% for feedstock (13). These values are for plants equipped with good energy recovery systems. Fuel requirements do not include electric power generation or steam generation other than that connected with heat recovery. Modern ammonia plants are self-sufficient in steam supply, and much of the mechanical power is supplied by steam rather than electricity. However, in developing countries, a captive electric generating plant usually is considered essential for a dependable supply of electricity. Also, if a urea plant is associated with the ammonia plant, additional fuel will be required to supply the steam needed for urea production. Therefore, total fuel requirements may be larger than those mentioned above.

When a high-cost feedstock is used for ammonia production, it may be advantageous to use a lower-cost fuel for heating and for producing steam and electricity. Likewise, when the supply of feedstock (such as natural gas) is inadequate for both fuel and feedstock, a different material may be used as fuel. Several plants in the United States that use natural gas feedstock are equipped to use a light fuel oil for heating the reformer. In cases where the fuel oil is more expensive than natural gas, the fuel oil system may be used only when the natural gas supply is limited.

Use of heavy oil or coal for fuel could be considered for plants using expensive or scarce feedstocks. However, these fuels cannot be used to heat reformer furnaces unless some extensive modifications are made. Impurities in heavy oil or coal would adversely affect the reformer tubes by causing corrosion or erosion unless design modifications were made. Deane and Browne have described a naphtha-based flowsheet in which a "non-premium fuel" is used for preheating the feedstock and the air to the secondary reformer (14). Obviously, there would be no technical problem in using coal for steam and electric power in units designed for that purpose. Direct use of coal for heating the reformer furnace would present serious difficulties, but indirect use such as byproduct gas derived from coal may be technically and economically feasible in some cases.

Technology of Steam-Reforming Process

A simplified flow diagram for production of ammonia by steam-reforming natural gas or naphtha is shown in figure 2. In the following discussion, each of the steps will be discussed in the sequence in which they occur.

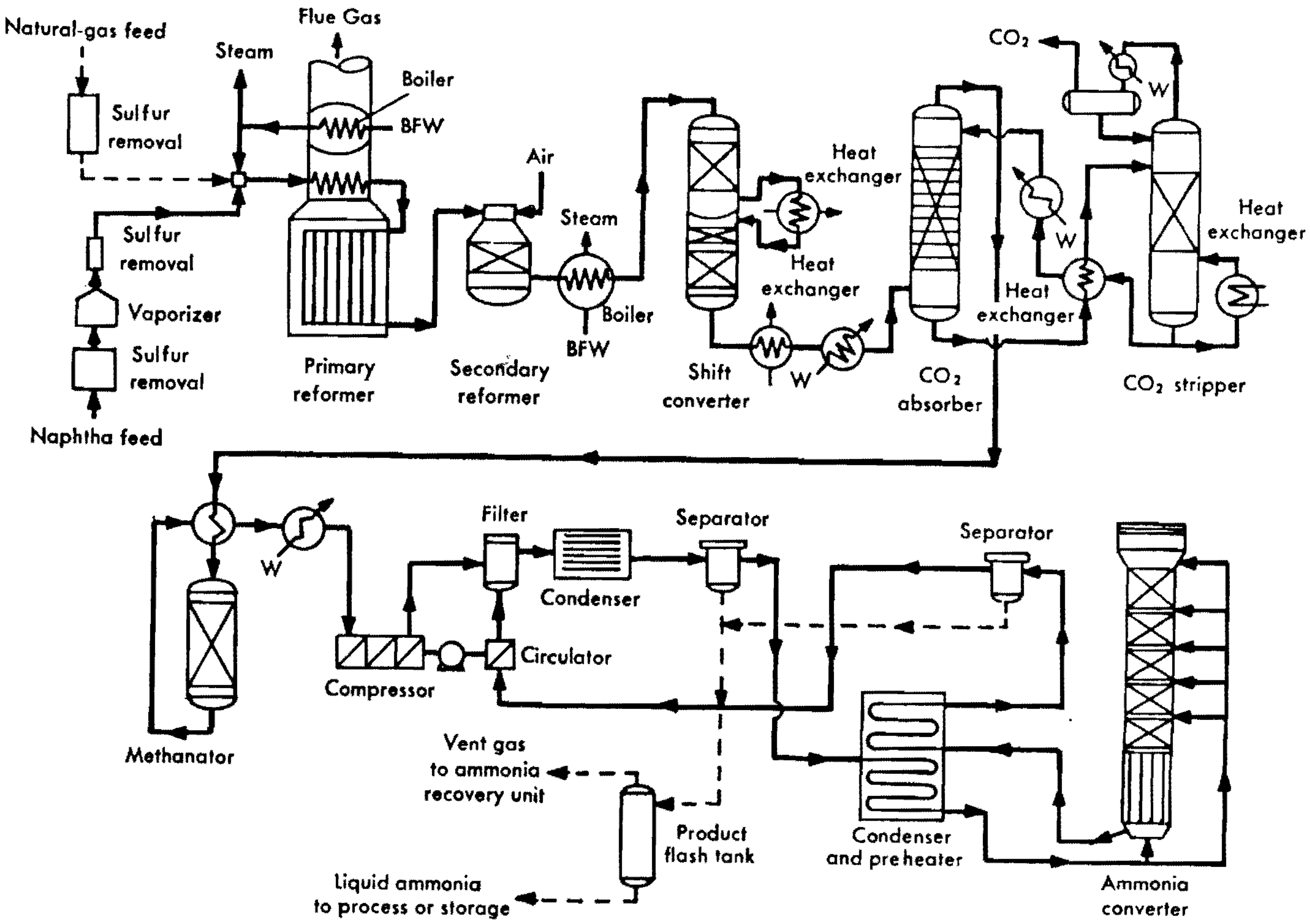

Figure 2. Flow Diagram for Production of Ammonia by the Steam-Reforming Process.

Feedstock Preparation--As mentioned previously, most natural gas requires some purification, particularly the removal of CO_2 and H_2S, which may be done by the natural gas producer if the gas is transmitted by pipeline. If the gas is taken directly from wellheads, the user (ammonia producer) may have to purify the gas. Depending on the source, natural gas may contain entrained dust or droplets of liquid (oil or water) which should be removed by separators, filters, etc.

After the initial purification, natural gas is compressed to reformer pressure, if not already at that pressure, and preheated. Then, any remaining sulfur is removed to avoid poisoning of catalysts. The sulfur may be removed by adsorption on activated carbon at ambient temperature or by absorption by hot zinc oxide (290°-400°C) after the gas has been preheated. In some cases both treatments may be used. Some natural gas may contain significant amounts of chlorides which can poison catalysts particularly the low-temperature shift catalyst. Catalysts or absorbents are available for removal of chlorides. Quartulli describes a pretreatment system for removal of both chloride and sulfur from natural gas or naphtha (figure 3) (15). The preheated gas or vaporized naphtha is mixed with a small amount of hydrogen (recycled synthesis gas) and passed through a "hydrotreater" containing a catalyst which converts sulfur compounds to H_2S and chlorides to HCl. The catalyst has a nickel-molybdenum or cobalt-molybdenum composition. The hydrotreated feedstock is then passed through one or more guard vessels containing layers of chloride removal catalyst (a copper-based material) and sulfur removal catalyst (zinc oxide). This system will effectively remove sulfur in "nonreactive" forms (such as thiophenes) which cannot be removed by zinc oxide without hydrotreating. Since naphtha usually contains unreactive sulfur, hydrotreating or hydrodesulfurization is commonly used in naphtha-based plants. The catalysts (absorbents) used in the guard beds are expensive and cannot be regenerated. Therefore, if the feedstock contains much sulfur or chloride, some means for removing most of these impurities as a pretreatment should be considered. In the case of natural gas, absorption in an alkaline solvent such as monoethanolamine or potassium carbonate, which can be regenerated, is commonly used for removing most of the sulfur.

Sulfur and chlorides (and other catalyst poisons) can enter the ammonia plant in the steam or in the air to the secondary reformer; thus, precautions should be taken to eliminate such impurities insofar as is practical. In addition, a layer of guard absorbent may be placed on top of the catalyst, particularly in the case of the low-temperature shift catalyst.

Primary Reforming--The purpose of the primary reforming step is to convert the bulk of the hydrocarbon feed to H_2 and CO by reaction with steam so that the remainder of the reaction can be carried out in the secondary reformer with the heat available from the introduction of air which burns part of the gas

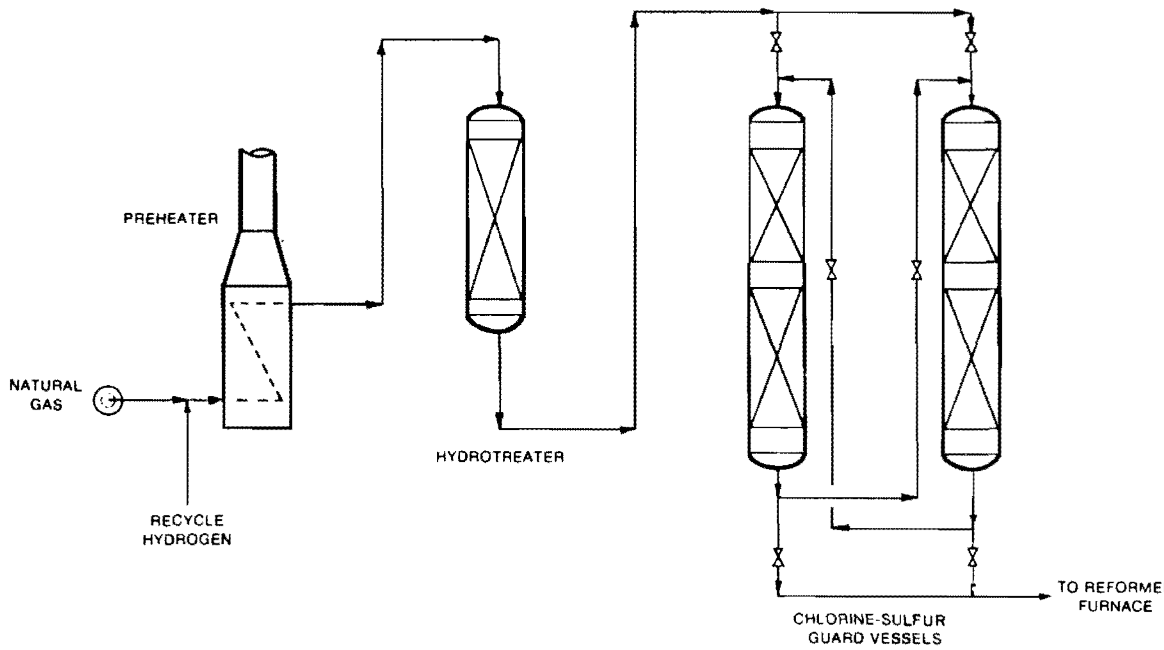

Figure 3. Natural Gas Treating System for Chlorine and Sulfur Removal.

and supplies the required amount of nitrogen for ammonia synthesis.

The preheated feedstock and high-pressure steam at or above reformer pressure (35-50 atm) are mixed and passed through a large number of tubes (50-400) which are externally heated in a reformer furnace by the combustion of a fuel which is usually but not always the same as the feedstock (natural gas or naphtha). The usual mole ratio of steam to carbon in the feedstock is 3.5-4.0:1.0. The reformer tubes are usually centrifugally cast stainless steel containing 25% Cr and 20% Ni. They range from 7.5 to 20 cm in diameter with a wall thickness of 0.6-2.5 cm and a length ranging from 3 to 14 m (16). The tubes are packed with catalyst containing nickel on a calcium aluminate base, usually in the shape of a ring about 16 mm in diameter by 16 mm long. The nickel content typically is 14%-16%. Promoters such as potassium may be added, and the composition of the base may be varied to increase its strength, durability, and porosity. The temperature of the gas leaving the reformer tubes may be 800°-900°C, and the temperature of the tube wall may be 900°-1000°C or more. This high temperature and the high pressure constitute severe conditions that require expensive materials of construction and careful design and operation. The heat in the combustion gas leaving the reformer is used successively to produce steam, to preheat the incoming feedstock-steam mixture, and, where fuel economy is important, to preheat combustion air.

There are many designs of reformer furnaces, all of which aim at efficient heat transfer by radiation, convection, and even heat distribution to prevent overheating or underheating any of the tubes or portions of the tubes. The fuel burners may be placed at the top, sides, or bottom of the furnace. Various means are used to cope with the difficult problem of connecting the tubes to the inlet and outlet gas connections in such a way that thermal stress will not cause failure of the tubes or their connections. Some designs permit the isolation of a tube or tubes that have failed. This arrangement permits the plant to continue operation even after some of the tubes have failed. During scheduled shutdowns, tubes that have failed or that are in poor condition can be replaced.

The gas leaving the primary reformer usually contains 5%-15% methane (dry basis). The gas temperature usually is in the range of 800°-900°C.

Secondary Reforming--The object of the secondary reforming step is to complete the conversion of methane to H_2, CO, and CO_2 and to supply the required proportion of N_2 for NH_3 synthesis. This is done by adding air to the amount required to give an N:H atom ratio of 1:3 in the synthesis gas after the shift conversion step. This means that the mole ratio of $N_2:(H_2 + CO)$ should be 1:3 in the gas leaving the reformer unless more N_2 or H_2 can be added in some subsequent step of the process. The oxygen accompanying the nitrogen in the air burns part of the combustibles (H_2, CO, and CH_4) in the partially reformed gas, thereby raising the temperature high enough for rapid completion of the reforming.

Although most processes involve the use of air alone, in some cases oxygen-enriched air is used to supply more heat and, thereby, take some of the load from the primary reforming step. In fact, it is possible to add enough oxygen so that the reforming process becomes "autothermal" and the primary reforming step can be omitted entirely. On the other hand, less air can be used than required for nitrogen supply, and part of the nitrogen can be added separately, preferably at a later step in the process. This arrangement places more load on the primary reformer but decreases the amount of feedstock required. This can be an advantage when the feedstock is expensive (or in short supply) and a less expensive fuel is used in the primary reformer.

In the usual case when air to the secondary reformer is the sole source of nitrogen, the heat input is limited to that generated by combustion reactions plus the sensible heat in the preheated air and in the gas from the primary reformer.

A typical secondary reformer is a cylindrical, refractory-lined, insulated vessel. The upper part is empty and serves as a combustion chamber in which the gas from the primary reformer is partially oxidized by preheated air. The lower part is filled with a catalyst similar to that in the primary reformer. The air should be free from dust that might clog the catalyst bed and from catalyst poisons (S, Cl, and As). The air is filtered, compressed to reformer pressure, and mixed with the gas in a burner at the top of the vessel. The combustion causes the temperature to rise to about 1200°C in the combustion chamber. As the hot gas descends through the catalyst bed, it is cooled by the endothermic reforming reactions and leaves the reformer at a temperature of about 950°-1000°C. The gas at this point contains, on a dry basis, about 56% H_2, 12% CO, 8% CO_2, 23% N_2, plus argon, and usually less than 0.5% CH_4. It also contains excess steam ranging from one-third to one-half of the total gas volume.

Carbon Monoxide Conversion--Gas from the secondary reformer is cooled (generating steam) to about 375°C which is the usual temperature for the shift conversion reaction:

$$CO + H_2O \rightarrow H_2 + CO_2$$

The reaction is exothermic; therefore, it is usually carried out in two steps with heat removal between steps. The rate of reaction is more rapid at high temperatures, but equilibrium is more favorable at low temperatures. Thus, it is common practice to operate the first step at a higher temperature than the second so that most of the CO is converted in the first step, and in the second step the CO is reduced to less than 1% (often as low as 0.2%).

Prior to 1960, the same type of catalyst was used in both steps. This catalyst is mainly iron and chromium oxides, about 55% Fe and 6% Cr. It is active only at relatively high temperatures (350°-430°C) and is known as a high-temperature shift (HTS) catalyst. About 1960 a new copper-based catalyst came into use which is active at lower temperatures (200°-260°C) and is known as low-temperature shift (LTS) catalyst. Most LTS catalysts contain zinc and alumina in addition to copper.

The LTS catalyst is much more expensive than the HTS catalyst and is more susceptible to poisoning; thus, it has a shorter useful life. Its advantages are that (1) it is active at a lower temperature range, where equilibrium is more favorable, thus more CO reacts with the steam to form H_2, and (2) less excess steam is required.

It is generally agreed that the advantages of the LTS catalyst outweigh its disadvantages; thus, it is commonly used in the second step of CO conversion. Some precautions that may be taken to extend the life of the LTS catalyst are (1) scrubbing the air to the secondary reformer with water or dilute alkali solution to remove catalyst poisons, (2) more rigorous purification of feedstock and boiler feedwater, and (3) insertion of guard beds between the high- and low-temperature shift converters to remove S and Cl from the gas. Figure 4 shows a typical arrangement of a sequence of HTS converter cooler, ZnO guard, LTS converter, cooler, and CO_2 removal. An alternative, but more expensive, arrangement is to use HTS catalyst in both converters with CO_2 removal after each converter. Removal of CO_2 after the first conversion step provides more favorable equilibrium conditions so that the CO content can be decreased to a low level in the second step even with the less active HTS catalyst. With either arrangement the CO content can be lowered to about 0.2% or less.

Carbon Dioxide Removal--After leaving the shift conversion step, the gas may contain 18% CO_2 or more depending on the feedstock composition. It is then cooled, if necessary, to a temperature range which depends on the requirements of the absorbent used in the CO_2 removal step. Absorption in water was commonly used in pre-1940 plants. Its disadvantages were high energy consumption and loss of H_2 and N_2 which are appreciably soluble in water at the high pressure used. Recovery of CO_2 having adequate purity for urea production was difficult. Between 1940 and 1960, a 20% solution of monoethanolamine (MEA) was favored. After 1960, the majority of new plants used potassium carbonate solution with various additives to promote absorption and inhibit corrosion. Its main advantage is lower heat requirements for stripping the CO_2 from the solvent. However, there are several other solvents in use, mainly organic liquids, some of which have a proprietary composition.

The potassium carbonate system operates mainly on pressure differential--CO_2 absorption at high pressure and CO_2 release at low pressure. In the absorption step the pressure is typically about 30 atm (reformer pressure minus pressure losses), and the temperature may be 100°C. The CO_2 is absorbed chemically by the conversion of potassium carbonate to bicarbonate. When the solution is regenerated by releasing the pressure to about atmospheric pressure, CO_2 and water vapor escape. In some cases, CO_2 release may be assisted by stripping with low-pressure steam or air. The regenerated solution is returned to the absorber at a temperature of 85°-90°C and is heated by the gas from the LTS shift converter. In this way some or most of the heat required by the CO_2 removal process is derived from the heat in the incoming gas.

In contrast MEA absorption-regeneration operates on a temperature differential with absorption at a relatively low temperature, 27°-60°C, and regeneration at 100°-140°C. Thus, it is necessary to cool the incoming gas to the absorber and to heat the MEA solution in the regenerator with steam. The MEA process has been improved by the addition of promoters and corrosion inhibitors, thereby lowering heat requirements.

Much attention has been given in recent years to methods for removal of acid gases (mainly CO_2 and

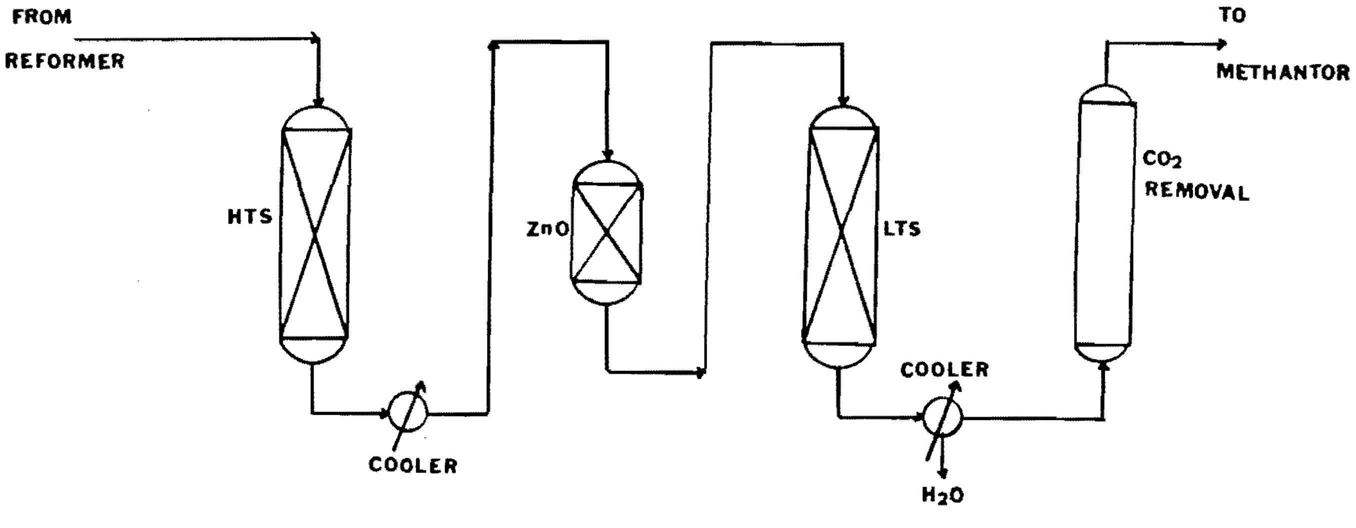

Figure 4. Carbon Monoxide Conversion System Using High Temperature Shift (HTS) and Low Temperature Shift (LTS) Catalysts.

H_2S), not only from ammonia synthesis gas, but also from natural gas, synthesis gas for products other than ammonia, and fuel gas produced by coal gasification or carbonization. Numerous processes have been developed, and the choice of process for an ammonia plant may depend on a balance between energy costs, capital costs, and other factors. Since partial oxidation of heavy oil or coal yields gases containing H_2S as well as CO_2, the acid gas removal process for this use must be capable of removing and separating these impurities and converting the H_2S to S or other nontoxic compounds. Some partial oxidation processes produce gas containing small percentages of HCN which must be removed and converted to nontoxic compounds.

A complete discussion of CO_2 removal processes is beyond the scope of this manual. However, table 5 taken from Quartulli briefly summarizes the characteristics of 20 major processes (15).

TABLE 5. PROCESSES FOR REMOVAL OF ACID GASES (CO_2 AND H_2S)

System	Solvent	Characteristics (Low or High Temp)	Solution Circulation	Acid Gas Content In Treated Gas	Heat Requirements	General Comments
REACTION TYPE SYSTEMS						
MEA	20% Mono-Ethanolamine	LT Absorption HT Stripping	Medium	Less Than 50 PPM	High	CO_2 pickup excellent High operating costs due to high utility consumption Requires extensive use of alloy materials to combat corrosion Intermediate size vessels required High exchanger costs
Promoted MEA	25-35% Mono-Ethanolamine Plus UCAR Amine Guard	LT Absorption HT Stripping	Medium	Less Than 50 PPM	Medium	Additive reduces corrosion and permits increase in circulation for increased CO_2 pickup Heat requirements lower than 20% MEA system
DGA	60% 2-(2-Amino-Ethoxy Ethanol-Amine) Diglycol Amine	LT Absorption HT Stripping	Medium	Less Than 100 PPM	Medium	Limited experience with this solvent for synthesis gas treatment Principally used for natural gas treating for CO_2 and H_2S removal High acid gas pickup Operates in similar manner as MEA system
Vetrocoke	K_2CO_3 Plus As_2O_3	Essentially Isothermal	High	500-1000 PPM	Low	Excellent performance Low utility consumption Use of arsenic additive presents disposal and pollution problems Considerable experience
Vetrocoke	K_2CO_3 Plus Glycine	Essentially Isothermal	High	500-1000 PPM	Low	Experience not as extensive as arsenic-based process Requires somewhat greater steam for stripping than arsenic system
Carsol	K_2CO_3 Plus Additives	HT Absorption and Stripping	High	500-1000 PPM	Low	Excellent performance and low utility costs Can be used as a single stage or two stage system Used in NH_3 plants up to 1500 ST/D capacity
Catacarb	25-30% K_2CO_3 Plus Additives	HT Absorption and Stripping	High	500-1000 PPM	Low	Excellent performance – low operating costs Has been used in ammonia plants up to 1700 ST/D capacity
Benfield	25-30% K_2CO_3 Plus Diethanol-Amine and Additives	Essentially Isothermal	High	500-1000 PPM	Low	Used extensively for ammonia hydrogen town gas manufacture Low operating costs Extensive experience as both single stage and two stage systems
Lurgi	25-30% K_2CO_3 Plus Additives	HT Absorption and Stripping	High	500-1000 PPM	Low	Low utility costs Used in several installations in Germany and other areas
Alkazid	Potassium Salt of Methyl-Amino Propionic Acid	LT Absorption HT Stripping	Dependent on Service			Other Alkazid solutions available depending on application acid gas constituents, and degree of selectivity All systems are water solutions of Amino Acids Has been used with partial oxidation process
COMBINATION REACTION – PHYSICAL TYPE SYSTEMS						
Sulfinol	Sulfolane, Di-isopropanol-Amine Sol'n	LT Absorption HT Stripping	Medium	Less Than 100 PPM	Low	Excellent performance Process can be used for CO_2 and H_2S removal applications in synthesis gas and natural gas services Chemicals cost relatively high but CO_2 pickup is good Vessel sizes relatively small but exchanger costs are high
TEA/MEA	Triethanol-Amine and Monoethanol-Amine	LT Absorb/Stripping (For TEA), and LT Absorption HT Stripping (For MEA)	High (TEA) Low (MEA)	Less Than 50 PPM	Low	Used in several NH_3 installations with excellent performance Requires two absorption stages in series operation A stripping system is required for each solvent
PHYSICAL ABSORPTION SYSTEMS						
Purisol (NMP)	N-Methyl-2 -Pyrrolidone	LT Absorption	Medium	Less Than 50 PPM	Low	Expensive heat exchange equipment eliminated with this process Used in high pressure processes such as partial oxidation based plants Excellent acid gas cleanup Solvent is non-corrosive
Rectisol	Methanol	LT Absorption (with Refrigeration)	Medium	Less Than 10 PPM	Low	System circulates refrigerated methanol Several columns required Can be used for CO_2 H_2S and COS removal in many applications High investment but performance is excellent Specified for many partial oxidation based processes Can be used also in coal gasification processes Solvent non-corrosive
Fluor Solvent	Propylene Carbonate	LT Absorption LT Stripping	Dependent on Pressure		Low	Has high degree of solubility for CO_2 Acid gas desorbed by release of pressure without application of heat Requires intermediate flash operation Process works to best advantage at high pressure
Selexol	Propylene Glycol Dimethyl Ether	LT Absorption	Dependent on Pressure		Low	Suitable for high pressure absorption services Can operate at low pressure but residual gas content increases Can also be employed for natural gas treatment

Source: Developments in Ammonia Production Technology, no date, p. 18-19, The M. W. Kellogg Company, Houston, Texas.

Methanation--The gas leaving the CO_2 absorption step still contains about 0.3% CO and 0.2% or less CO_2. These oxides must be removed before the ammonia synthesis step because they would decrease the activity of the ammonia synthesis catalyst and cause deposition of ammonium carbamate in the synthesis loop. The methanation reactions are:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

These reactions are the reverse of the reformer reactions, and a similar nickel-based catalyst is used. It will be noted that each molecule of CO and CO_2 consumes three and four molecules of H_2, respectively. Therefore, it is necessary to efficiently remove CO and CO_2 to the minimum practical level.

The methanation step is usually carried out with a gas inlet temperature of 300°-350°C; therefore, the gas must be preheated to that temperature. Since the reactions are exothermic, the temperature may rise to 320°-400°C at the gas outlet, depending on the CO + CO_2 content of the gas. A heat exchanger is commonly used to preheat the incoming gas and cool the exit gas.

Compression--The synthesis gas leaving the methanation step typically contains about 74% H_2, 24% N_2, 0.8% CH_4, and 0.3% Ar, dry basis. The gas must be compressed to the pressure required by the synthesis step. Before centrifugal compressors came into general use, reciprocal compressors were used. These reciprocal compressors often involved as many as five stages of compression with the various gas purification steps at intermediate pressures. Synthesis pressures varied widely from 100 to 800 atm depending on the process. Reciprocal compressors are still used for small plants (less than 500 tpd), but centrifugal compressors are now used in the great majority of new plants having capacities of 600-1,500 tpd. Synthesis pressures in these new plants usually are in the range of 150-250 atm, although some of the larger plants may operate at 300-350 atm. It was previously considered that the use of centrifugal compressors was applicable only to plants of 550-tpd capacity or more, but process designs using centrifugal compressors are now offered for plants having capacities as low as 300 tpd (15).

Centrifugal compressors are driven by steam turbines using high-pressure steam generated mainly from hot process gas leaving the secondary reformer. The steam is exhausted at a lower pressure and used in the reforming process and other process steps.

Reciprocating compressors are driven by electric motors. They are more efficient than centrifugal compressors; typical efficiencies are reported to be 87% for reciprocating compressors as compared with 70% for the centrifugal type. However, reciprocating compressors are more expensive, especially for large plants. The power consumption in plants using reciprocating compressors may range from 600 to 900 kWh/ton of ammonia as compared with 20-35 kWh in plants using steam-driven centrifugals. However, this high electric power requirement is offset by lower fuel requirement. Where electricity is cheap or can be generated onsite with low-cost fuel such as coal and when the ammonia feedstock is expensive, there may be some saving in operating cost from using reciprocating compressors, especially in small plants. The largest plant with reciprocating compressors is reported to produce 670 tpd of ammonia.

Centrifugal compressors usually are built with two or three casings, often with interstage cooling. Compressor design is highly specialized, and the details of design, arrangement, and operation are complex. A typical simplified diagram of a synthesis gas loop is shown in figure 5. Cooling and compressing the gas condenses nearly all of the water vapor remaining in it. The compressed gas enters the synthesis loop at various points depending on process design.

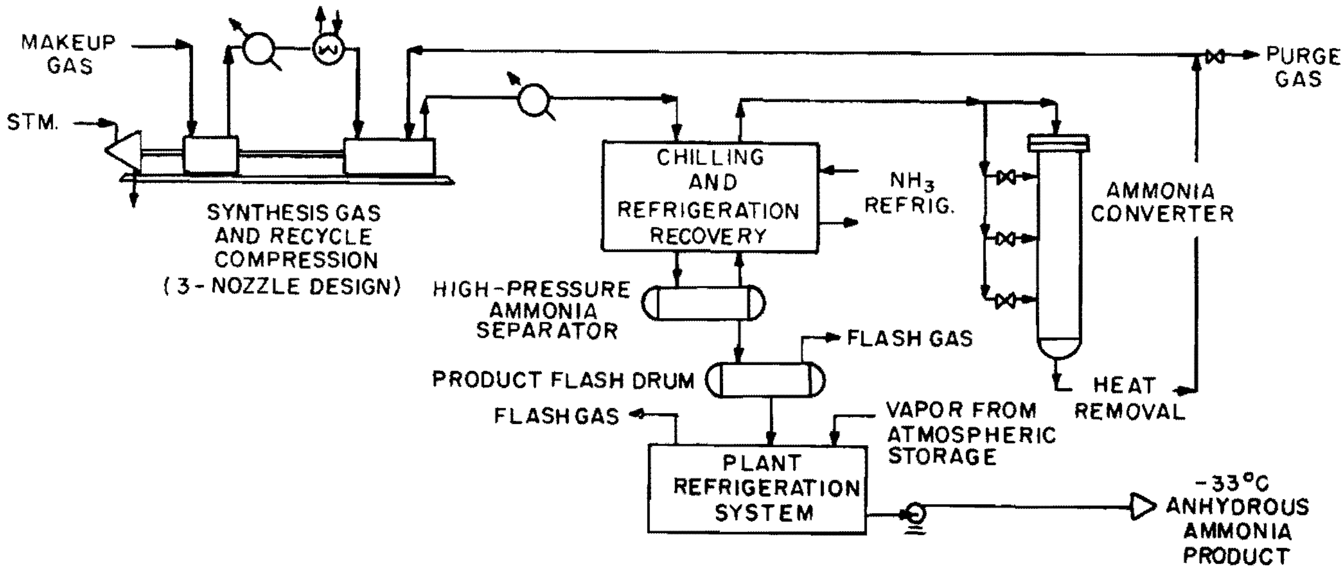

Figure 5. Typical Ammonia Synthesis Loop.

Ammonia Synthesis--As mentioned previously, ammonia synthesis is commonly carried out at 400°-450°C, using an iron catalyst promoted with potassium and alumina. The gas entering the converter consists mainly of gas circulated in the loop with a relatively small amount of fresh synthesis gas called "make-up" gas. The gas entering the converter contains N_2 and H_2 in a 1:3 ratio plus 10%-14% "inerts" and about 2% NH_3. The "inerts" consist mainly of methane, argon, and sometimes helium if the natural gas feedstock contains that element. (Methane is not, strictly speaking, an inert gas, but the term is used in ammonia synthesis context since it does not participate in the reaction.) Since the inert gas concentration tends to increase as the N_2 and H_2 are removed, it is necessary to vent a side stream of "purge gas" to keep the inert gas concentration at a tolerable level.

Ammonia synthesis converters are of two types: (1) those having a multiple catalyst bed with provision for "quenching" the gas between beds, for removing heat by steam generation, or for preheating the incoming feed gas and (2) those having a continuous catalyst bed in which a heat exchanger removes the heat of reaction. "Quench" converters may inject cool feed gas at several points between catalyst beds to keep the temperature in the desired range, 400°-450°C, for example. The gas leaving the converter will contain 12%-18% NH_3, depending mainly on the pressure; conversion per pass increases with pressure. The gas is cooled first by heat exchange with the incoming gas, then by air or water, and finally by refrigeration to condense most of the ammonia as a liquid. The degree of cooling required depends on the pressure. At high pressures much of the ammonia can be condensed at temperatures obtainable by water cooling. At lower pressures (150-200 atm) increased reliance must be placed on refrigeration. If the ammonia is to be delivered to atmospheric pressure storage, it must be further cooled to -33°C (chapter VII). The gas remaining after ammonia condensation is recycled to the converter by means of a compressor.

The purge gas may be used as supplemental fuel in the primary reformer with or without prior recovery of its ammonia content by water scrubbing. In some cases it may be worthwhile to separate the purge gas components cryogenically (after NH_3 recovery). The CH_4 and H_2 can be returned to the process, and the argon can be sold where there is a market for it.

Another means for utilizing purge gas is a purge gas conversion unit (PGCU) made by Kellogg. The unit consists essentially of a second ammonia synthesis loop in which the purge gas is compressed, passed through a converter containing ammonia synthesis catalyst, and then cooled to recover additional ammonia. After ammonia recovery, a relatively small purge stream is drawn off for use as fuel and the remainder is recycled to the converter. The unit can be added to an existing ammonia plant. Since it converts 75% of the hydrogen in the purge gas to ammonia, ammonia production is increased by about 5% without increasing feedstock requirements. The ratio of additional investment and operating cost to incremental ammonia recovery is said to be quite favorable.

Partial-Oxidation Processes Using Hydrocarbon Feedstock

Hydrocarbons heavier than naphtha can be used as feedstocks for ammonia production by partial oxidation processes. Natural gas and naphtha also can be used, but since the plant cost for the partial oxidation process is considerably higher than that for steam reforming, the lighter feedstocks seldom are used. However, the partial oxidation process does offer the advantage of wider choice of feedstock with greater tolerance for impurities. The main disadvantage is the higher capital cost since an air separation plant is required to supply oxygen to the gasification step and nitrogen in a later step.

Crude petroleum can be used as feedstock, but the most common feedstock is heavy residual oil from petroleum refining processes which has had the more valuable lighter fractions removed. Such oil may contain 3.5% S, depending on the sulfur content of the crude oil and the refining process. Using such oil for fuel or power generation would involve expensive equipment for pollution abatement in most countries; therefore, it is often available at a relatively low cost.

The feedstock requirement typically is about 0.74 tons of heavy oil per ton of ammonia (17). In addition, about 0.23 tons of oil or the equivalent in other fuel is required for generation of steam and electricity. In contrast with the steam-reforming process where most of the fuel is used in the reforming furnace, which requires a premium grade of fuel, the auxiliary fuel for a partial oxidation process is used in a separate unit which can use coal, for example.

The principal partial oxidation processes are known as the Texaco, Shell, and Koppers-Totzek processes. The Koppers-Totzek process is also used for coal and will be described under that heading. The Shell and Texaco processes are generally similar. Figure 6 is a simplified flow diagram of the partial oxidation process.

The gasification pressure in partial oxidation processes has been gradually increased to a range of 60-90 atm which helps save energy for compression. Lembeck describes a flowsheet using Texaco's partial oxidation technology in which gasification and purification are carried out at 72-90 atm (17). Heavy fuel oil is preheated and pumped into the gasifier together with high pressure steam and preheated oxygen from an air separation unit. The reaction takes place at a high temperature (1200°-1500°C), and no catalyst is required. The chemical reactions involved are complex and not completely understood. However, it is generally believed that the oil is cracked to form carbon and methane and other hydrocarbon gases; these products are partially oxidized to CO, CO_2, and H_2O, and partially converted by steam to CO and H_2. A typical composition of the resulting gas is 46% H_2, 47% CO, and 4% CO_2 dry basis with small percentages of H_2S and N_2. A considerable amount of soot (carbon) remains suspended in the gas.

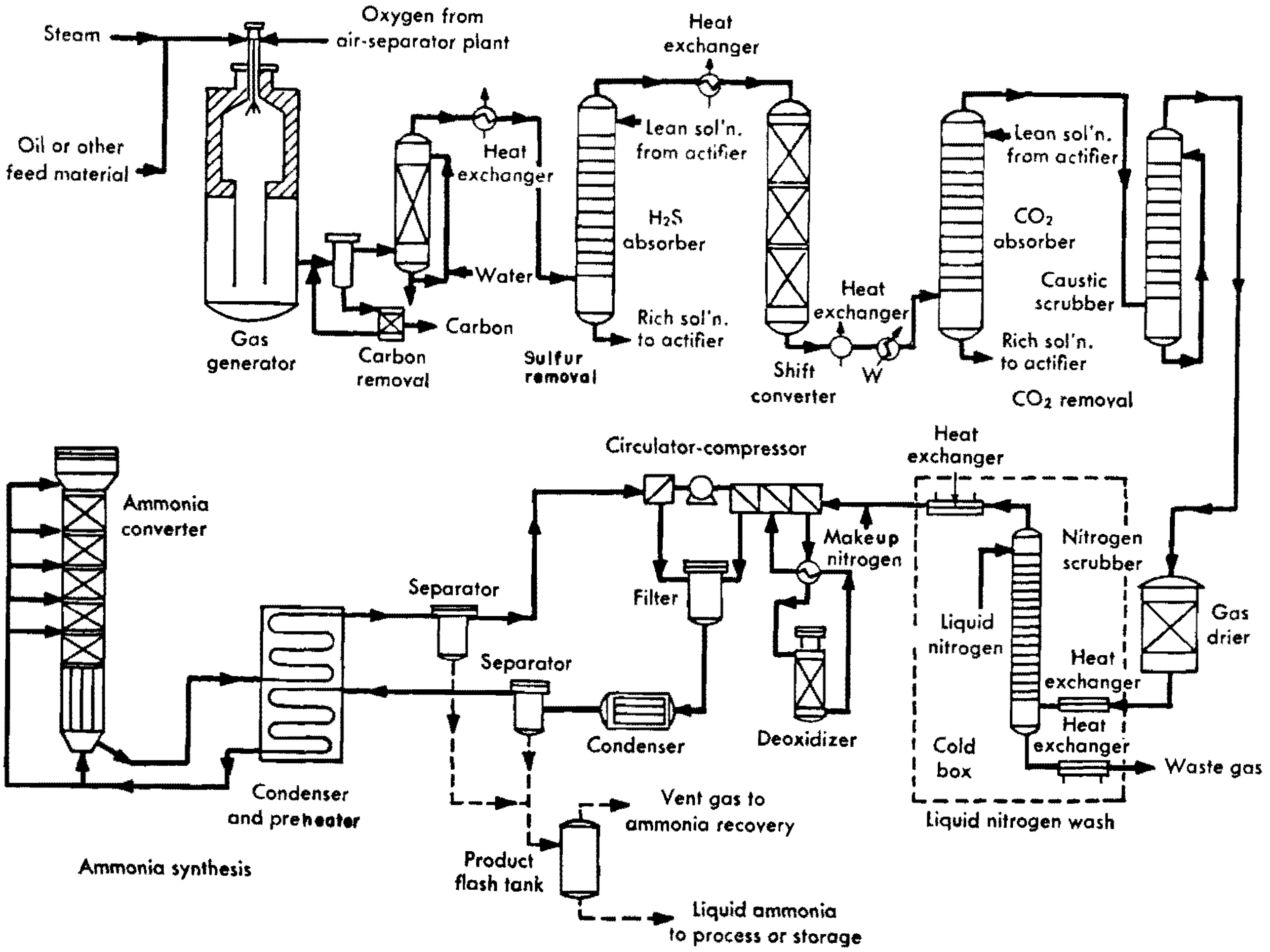

Figure 6. Flow Diagram for Production of Ammonia by a Partial Oxidation Process.

The hot gas is quenched with process water to the inlet temperature of the shift conversion step (about 300°C), and most of the soot is removed in the water which goes to a soot recovery unit. The soot is eventually recycled in the oil feedstock or used as fuel for steam generation, and the water from which the soot was recovered is recycled to the quench step. The quenching step also vaporizes some of the water into the gas stream, which supplies water vapor needed for the shift reaction.

The shift reaction is carried out with a recently developed cobalt-molybdenum catalyst; thus, the CO content of the gas is reduced to about 1%. The next step is removal of CO_2 and H_2S by a Rectisol scrubbing process using methanol as the solvent. The H_2S is recovered separately and sent to a Claus process unit for conversion to elemental sulfur. Since the CO_2 is of adequate purity for urea production and is available at 2.5 atm and 40°C, compression costs are lowered.

The final purification step is a liquid nitrogen wash process which uses liquid nitrogen from the air separation plant. This process removes CO and also lowers the CH_4 and argon content to a very low level. These impurities leave the process in a gas stream which is useful as fuel in steam generation.

Prior to the nitrogen wash, residual CO_2 must be removed by caustic scrubbing and water is removed by silica gel or other desiccant to prevent freezing of these gases in the nitrogen wash column.

After purification, nitrogen is added to adjust the N_2:H_2 ratio to the stoichiometric 1:3 ratio, and the gas is compressed to 230 atm for ammonia synthesis. This step is similar to that described under steam-reforming processes. However, it is claimed that, because of the efficiency of the nitrogen wash step in removing impurities and inerts, the synthesis step can be operated without gas purge and, consequently, with higher efficiency. Also the gas purity contributes to long life of the synthesis catalyst.

It should be noted that the total fuel and feedstock requirement is 0.97 tons of heavy oil per ton of ammonia. This amount represents enough fuel to generate all of the steam and electric power required by the process including the air separation plant.

Supp describes an ammonia plant built in and operated by VEBA Chemie (Germany) in 1972. This plant uses heavy residual oil (2.5% S) which is gasified by the Shell partial oxidation process (18). The plant is capable of producing simultaneously 1,215 tpd of ammonia and 450 tpd of methanol but has sufficient flexibility to produce variable proportions of the two products up to a maximum of 1,400 tpd of ammonia or 600 tpd of methanol. Either unit can be operated independently. A second ammonia plant which will produce 1,600 tpd of ammonia is under construction for the same company (19).

The process is generally similar to that described above with some exceptions that relate to the coproduction of methanol. However, one basic difference is that H_2S and CO_2 are removed before the shift conversion step by a Rectisol scrubbing step, and CO_2 formed in the shift conversion is also removed after shift conversion by Rectisol scrubbing. Final purification is performed by liquid nitrogen wash as in the previous example. The low impurity content of the ammonia synthesis gas is illustrated by the analysis that shows less than 10 ppm of CH_4, less than 30 ppm of Ar, and less than 1 ppm of CO and all other impurities.

The Shell gasification process differs from the Texaco process mainly in that a waste-heat boiler follows the gasifier and a different method is used for collecting and recycling the soot.

Banquy has also described a high-pressure, partial oxidation process with gasification at 80 atm and synthesis at 300 atm (20). In comparing the economics of this process with steam reforming of natural gas, he concluded that partial oxidation appears attractive when the price of heavy oil is 80% or less than that of natural gas on a calorific basis. However, the comparison was made in 1970 when both feedstocks were relatively inexpensive, and plant construction costs were relatively low. A later section of this chapter will discuss the economics of ammonia production in more detail.

Processes for Production of Ammonia from Coal

About 10% of the world's ammonia production is based on coal, coke, or lignite. About half of the coal-based capacity is in the People's Republic of China where there are over 1,000 small plants with productions ranging from 3,000-10,000 tpy (9). It was reported that 1,100 small coal-based ammonia plants were built between 1966 and 1974 and 100 more per year were being added in 1975 (21). The technology of one of these plants has been described (21). The feedstock was lump anthracite or semianthracite although it was reported that briquetted coal or lower grade coal was used in some plants. In general, the process is similar to the original Haber process which was described previously. The coal was gasified in a semiwater gas producer blown alternately with air and steam. Gas purification sequence was water scrub, H_2S removal, shift conversion, CO_2 removal by water scrubbing, and copper liquor scrubbing for CO removal. The gas was compressed in six stages by reciprocating compressors with the purification steps between various stages. The product from the small plants is often used to make dilute ammonia solution (16%-25%) or ammonium bicarbonate for local use, although some of the larger plants make ammonium nitrate.

Several large modern ammonia plants have been constructed recently in China which are based on natural gas, and more are under construction. However, it is planned to continue operation of the small plants and to build more small and medium-size plants (50,000-100,000 tpy). These smaller plants will supply local fertilizer needs in areas where transportation facilities are not adequate.

Staege lists 13 plants built since 1950 for direct use of coal in India, Greece, Turkey, South Africa, Pakistan, Thailand, India, and Zambia (22). Most of them are small (40- to 340-tpd capacity), and some of them have been converted to other feedstock. However, the list included three large plants (900-1,000 tpd) of which two in India are not yet in operation or are in an early stage of startup. The third one is in South Africa; its operation has been described by Waitzman (23). There has been much interest and discussion in the United States about producing ammonia from coal, and one plant has been tentatively planned to produce 1,360 tpd of ammonia in a proposed project partially financed by the U.S. Government (24). In addition, TVA will convert its natural gas-based demonstration-scale plant (200 tpd) to use coal to supply part of the feedstock on an experimental basis (23).

Coal gasification processes for ammonia production can be classified according to the method of gasification as fixed-bed (Lurgi), fluidized bed (Winkler), or entrained bed (Koppers-Totzek and Texaco). The so-called fixed bed gasification is more accurately called a moving bed. Lump coal (5-30 mm) is charged at the top and descends countercurrently to the gas stream. As it descends, it is first dried and preheated, then carbonized, and finally gasified by the oxygen and steam entering the bottom. The coal ash is discharged from the bottom through a grate, or in one modification, as a slag. Because the countercurrent method of operation results in good heat exchange, this method requires less heat and, hence, less oxygen than the other methods. Also, the expense of drying and fine grinding of the coal is avoided.

The Lurgi moving bed gasifier usually is operated at 30 atm. It requires the least amount of oxygen--one-half to one-third as much as entrained coal gasifiers. It is not necessary that the oxygen be of high purity; 90% is satisfactory. The gas leaves the top of the gasifier at about 450°C and is cooled and washed to remove tar, liquid hydrocarbons, dust, etc. The washed gas contains CO, H_2, CO_2, CH_4, and other hydrocarbons. It is treated by a series of steps including steam reforming, CO shift conversion, CO_2 and H_2S removal, liquid nitrogen wash, steam reforming of the methane that is separated by the nitrogen wash, nitrogen addition, and compression to produce ammonia sythesis gas (25).

Some limitations of the fixed or moving bed gasification process are that the coal must be in the form of lumps (5-30 mm), the coal must be of the noncaking variety or pretreated to prevent caking, and various byproducts are formed (tar, phenolic compounds, light oils, etc.) that must be collected and utilized or disposed of. In preparing the sized coal feed, fines are formed that can be burned in an auxiliary plant to generate the steam and electricity requirements of the process. Tar can also be burned or injected into the gasifier at a point where the temperature is high enough to gasify it.

In the fluidized bed gasification process, of which the Winkler process is the main example, coal or lignite is ground to less than 15-mm particle size and introduced into the fluidized bed through feed screws near the bottom. Steam and oxygen are injected near the bottom of the fluidized bed. In contrast to the gradual increase in temperature of the coal in the moving bed process, the fluidized bed is essentially isothermal (about 1000°C). Consequently, there is neither tar nor other liquid byproducts, and the gas contains mainly H_2 and CO with less than 1% CH_4. A substantial amount of ash is entrained in the gas stream. The hot gas is cooled by waste-heat boilers and scrubbed to remove ash and then purified in a sequence of steps similar to other processes. The process produces a char containing 6%-12% of the carbon in the feed. About 90% of this char is removed from the bottom of the gasifier in a dry state; the remainder is recovered by wet scrubbing of the gas. This char can be burned in an auxiliary boiler to supply steam and electricity.

The Winkler gasifier is widely used to make producer gas for industrial and domestic use, but few have been used for ammonia production. Its advantages are that it will work with almost any grade of coal or lignite and that it is adaptable to high-capacity units. Disadvantages for ammonia production are low pressure (1-3 atm), which increases compression costs, and the ash content of the gas, which requires an electrostatic precipitator for final cleanup.

Entrained coal gasifiers are typified by the Koppers-Totzek (KT) and Texaco processes. Most of the present coal-based ammonia plants (except in China) use the KT process. The process is essentially a partial oxidation process as are most coal gasification processes. At least two KT ammonia plants have been built to use either coal or heavy oil although only one (in Finland) is known to have used both feedstocks. However, any entrained gasification units presumably could be readily adapted to heavy oil or lighter hydrocarbons including natural gas.

In the KT process coal is dried and finely ground to about 75% through 200-mesh (Tyler). The powdered coal is picked up by streams of oxygen and blown into the gasification chamber through two burners facing each other. More recently, four-burner units have been used. Steam enters through annular openings around the burners. The gasification is complete in about one-tenth of a second at temperatures in the range of 1000°-1200°C. Part of the ash is fused and removed from the bottom of the gasifier, and part is entrained in the gas. The gas typically contains 56% CO, 31% H_2, 11% CO_2, and less than 0.1% CH_4. After being cooled in waste heat boilers, the ash is removed by wet scrubbing and electrostatic precipitation. The remainder of the ammonia synthesis gas preparation is similar to that described under partial oxidation of fuel oil.

Disadvantages of the process are the need for fine grinding of coal, operation at low pressures (1-3 atm), and higher oxygen consumption than other coal gasification processes.

The Texaco coal gasification process is the newest one and has not yet been applied to ammonia plants although extensive development work has been done on the gasification process, and it will be used in the TVA demonstration plant (23).

The Texaco process differs from the KT process in that the finely ground coal is mixed with water to form a thick slurry containing about 45% water. The slurry is preheated and fed, together with oxygen, into a gasifier which can operate at pressures as high as 180 atm. The process as applied to ammonia production has been described by Mitzer and Moe (24). In this case the gasifier is operated at 58 atm and about 1300°C. Fused ash is quenched with water in a chamber at the bottom of the gasifier and removed as a slurry. The hot gas is quenched to 1000°C by a combination of water and cool gas recycle. It then passes through a waste-heat boiler and is cleaned to remove soot and fly ash in a venturi scrubber. The sequence of the remaining steps of synthesis gas preparation is CO shift conversion, removal of H_2S and CO_2 by Rectisol wash (cold methanol), and liquid nitrogen wash. As in other partial oxidation processes, the H_2S is converted to elemental sulfur. The proposed plant would produce 1,360 tpd of ammonia and about 100 tpd of sulfur using 2,360 tpd of bituminous coal containing 14.6% ash and 4.2% S. The estimated plant construction cost is $185 million as compared with $103 million for a natural gas-based plant (24). With coal at $22.50/ton, the estimated ammonia selling price would be $173/ton with profit based on 12% discounted cash flow. This would break even with a natural-gas based plant using gas at about $90/1,000 m^3 ($2.55/1,000 ft^3).

Brown compared six ammonia-from-coal processes and concluded the best choice would be between a modified slagging Lurgi gasifier and a Texaco gasifier (26). He estimates capital costs for a 1,000-tpd plant at $115 million, $110 million for the two processes, and ammonia costs at $131 and $127/ton including 33.3% annual capital charges, assuming the coal cost to be $5.50/ton. He suggests that coal would be a more economical feedstock than natural gas when the cost of gas is three to four times the cost of coal on a calorific basis. Brown's estimated capital costs presumably are for a battery-limits plant.

Waitzman estimates the plant costs for a 900-tpd "grass roots" plant using the Texaco coal gasification process at $140 million compared with $75 million for a natural gas-based plant. He estimates that the ammonia sales price, allowing for a 14% after-tax return on investment, would be $160/ton using coal at $27.50/ton or gas at $100/1,000 m^3. Thus, on a calorific basis, coal would be economically competitive when gas cost is more than three times that of coal.

All of the above economic comparisions are based on U.S. or European conditions and are not directly applicable to a developing country.

Ammonia from Electrolytic Hydrogen

Several ammonia plants have been built to produce ammonia from hydrogen that is produced by the electrolysis of water. These plants have been located where low-cost hydroelectric power is available in Norway, India (Nangal), Egypt (Aswan), Peru (Cuzco), Iceland, and Canada (Trail, British Columbia). The technology of the electrolytic process has been described by Mrochek and Grundt (27, 28). Purified water is the feedstock; potassium hydroxide is added to increase the conductivity, but it does not participate in the reaction. Commercial cells vary somewhat in efficiency, but a typical power consumption is 4.3 kWh/m^3 of H_2, which corresponds to about 8,600 kWh/ton of ammonia (28). Additional energy is required for an air separation plant to produce the nitrogen required for ammonia production. Energy also is required for compression of the hydrogen and nitrogen and recirculation of the gas mixture through the synthesis loop. The total energy requirement is about 10,200 kWh/ton of ammonia. This energy is equivalent to about 8.8 million kcal/ton of ammonia, which is about the same as for natural gas-based ammonia plants. However, if fuel were used to generate electricity, nearly three times as much thermal energy would be required since the efficiency of conversion of thermal energy to electrical energy is seldom more than 38%.

The estimated cost of production of ammonia from electrolytic hydrogen in a 300-tpd plant (100,000 tpy) with electricity at 5 mills/kWh would be about \$124/ton, according to Grundt (28). Increasing the scale to 900 tpd would decrease production cost only slightly to \$116.50/ton. However, increasing the cost of electricity to 10 mills (\$0.01) or 20 mills/kWh would increase the ammonia production cost to \$175 or \$277/ton, respectively. Grundt's estimate of production cost for a 300-tpd plant is summarized below:

Item	\$/ton of NH_3
Capital charges (15% of \$40 million)	60
Maintenance, labor, utilities, etc.	13
Electricity--10,200 kWh at \$0.01	102
Total	175

The process generates one volume of oxygen per two volumes of hydrogen or about 0.7 ton of O_2/ton of NH_3; thus, a credit for byproduct oxygen can be taken if there is a use for it. For example, the oxygen can be used in an iron and steel industry. A small additional amount of oxygen would be available from the air separation unit. Another potential byproduct is heavy water (deuterium oxide, D_2O). Pure water contains about 0.0135% D_2O. The hydrogen is electrolyzed more rapidly than its isotope, deuterium; thus, the concentration of D_2O in the electrolyte builds up and can be recovered at a rate of 70 g/ton of NH_3 (28). Heavy water is used in some types of nuclear reactors.

The bulk of the investment cost for an ammonia plant based on electrolytic hydrogen is for the electrolyzers. One Norsk Hydro electrolyzer with 235 cells will have a capacity equivalent to about 3.75 tpd of ammonia although smaller or larger ones can be built. Larger plants normally use a number of identical electrolyzers; for instance, a 200-tpd plant would require about 53 electrolyzers in operation. Extra units usually are supplied so that some of the units can be shut down and cleaned without interrupting or decreasing ammonia production.

Since the electrolytic process does not produce CO_2, ammonia cannot be used to make urea unless CO_2 is available from another source. It can be used to make ammonium salts (sulfates, phosphates, or nitrates), or ammonia can be applied to the soil directly either in the anhydrous form or in aqueous solution (chapter X).

Since the desired capacity of the electrolysis plant is obtained by installing the required number of units, there is little economy of scale. Figure 7 taken from Grundt indicates that, for plants of less than 250-tpd capacity, the electrolytic plant would cost less than a natural gas-based plant. For example, a 100-tpd electrolytic plant would cost about \$20 million as compared with roughly \$25 million for a natural gas-based plant or over \$40 million for a plant using partial oxidation of fuel oil (late 1976 prices).

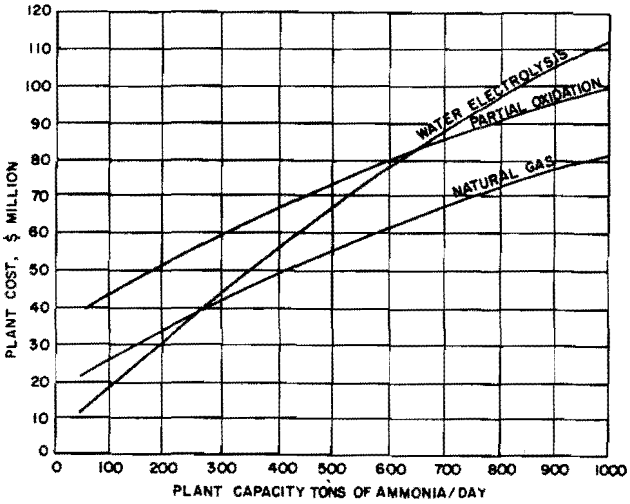

Figure 7. Comparison of Ammonia Plant Costs for Electrolytic Hydrogen, Natural Gas, and Partial Oxidation Processes Based on Ref.(28).

The cost of production of ammonia by the electrolytic process is not greatly dependent on plant size but, of course, it is strongly dependent on the cost of electricity. Thus, if low-cost electricity is available, the electrolytic plant would be competitive with plants using other processes, particularly for small plants.

A particular advantage in developing countries would be the fact that ammonia production from electrolytic hydrogen is a much simpler process than those using other feedstocks.

Hydrogen is also produced as a byproduct of electrolytic production of chlorine and caustic soda, and several small ammonia plants have used this byproduct for ammonia production either as the only feedstock or as a supplementary source. The amount of hydrogen available from chlorine-caustic plants is too small to supply a significant portion of the ammonia needs in most situations.

Economics of Ammonia Production

Capital Requirements

Since ammonia production is highly capital intensive, it is especially important that the estimated or assumed capital cost be as accurate and realistic as possible. When the process, feedstock, and location have been selected, an accurate estimate of the capital requirements can be made although even then the actual cost often exceeds the estimate by a substantial amount or, less frequently, is less than the estimate.

For the purposes of this manual, no specific cations will be assumed and, therefore, investment ost estimates illustrate only an order of magnitude. is hoped that the estimates will be useful as a uide, particularly for comparative purposes, to idicate the effect of such factors as location, choice nd price of feedstock, scale of operation, and ercentage of capacity utilization on production costs.

Ammonia plant construction costs increased harply in the period of 1967-74; the 1967 UN manual hows a battery-limits cost of about $11 million for a 00-tpd natural gas-based plant at a U.S. location 29). A similar plant was estimated to cost about 50 million in 1974 (13). Since 1974 cost increases ave been minor; a 1978 estimate was about the same $50 million), implying that cost-saving techniques in he ammonia plant engineering and construction ndustry have offset rising labor and material costs 30). However, it is unlikely that greater efficiency vill continue to offset rising construction costs in the uture.

Types of Estimates--There are three common types of estimates which differ in what they include. The most common type is for a "battery-limits" plant, which consists of the process equipment erected and ready to operate when supplied with specified feedstock and utilities. There is some variation in what facilities are included in the battery limits; for instance, cooling towers for recirculating cooling water and facilities for boiler feedwater treatment may or may not be included. In partial oxidation processes a separate boiler for generating steam and (often) electricity is included; whereas, in steam-reforming processes, sufficient steam is generated in the process to supply process needs for steam and most of the mechanical energy but not electricity. Thus, a battery-limits estimate should have a definition of what is or is not included.

A "turnkey" plant estimate includes not only the battery-limits unit or units but also all supporting and auxiliary facilities necessary for plant operation. It may include roads and railroads within the plant; distribution systems for electricity, water, compressed air, and fuel; offices; laboratories; site preparation; storage for raw materials and products; maintenance shops, etc. Usually it does not include roads or railroads leading to the plant. Here again, there may be considerable variation in what is included depending on the plant site. A "green field" or "grass roots" location is one where there is no existing related facility; whereas, an addition to an existing production facility will require less extensive supporting facilities. "Site preparation" requirements are likely to vary widely depending on location. For instance, a marshy location may require landfill and piling; whereas, a mountainous location may require extensive earth and rock moving to create a reasonably level plant site.

A "project cost" estimate includes the "turnkey" plant plus additional expenses such as a feasibility study; training of operating, maintenance, and supervisory personnel; startup expense; interest on money spent during construction; and working capital. In developing countries the project cost may include training of marketing personnel and many items of infrastructure such as roads, railroads, harbors, piers, and waterways; housing, recreation, cultural, and religious facilities for employees; guest house; commissary, etc. There is some question as to whether all of these improvements in infrastructure should be charged to the plant operation since they generally contribute to the development of the country and the welfare of its people. Housing, for example, usually is at least partially self-supporting from rental to employees. Transportation infrastructure often is utilized for many purposes not directly connected with fertilizer production.

In the present discussion, investment costs will be based on the battery-limits cost for an industrial location in a developed country. To arrive at the total cost, 50% of the battery-limits cost will be added except when otherwise stated.

In the last 15 years process designs have been developed and gradually improved for ammonia production by steam reforming of natural gas, naphtha, and other light hydrocarbons in plants using centrifugal compressors. Standard designs have evolved for three capacities--550, 900-1,040, and 1,360 mt/day (600, 1,000-1,150, and 1,500 short tons/day). The great majority of new plants built in the last decade have been designed for one of these three capacities even though the capability exists for design of plants using a centrifugal compressor over a range of 270 to 2,700 tpd. Recent (1978) information from an engineering construction firm provided the following rough estimates for natural gas-based battery-limits plants for a U.S. Gulf Coast location:

Capacity, Metric Tons/Day	Battery-Limits Cost, $ Million	Cost per Annual Ton of NH_3 Capacity, $[a]
550	35	193
1,040	48	140
1,360	69	154

a. Annual capacity = 330 x daily capacity.

These costs are shown in figure 8. Even though a straight line is shown connecting the three points, the points do not fall on the line, and it should not be inferred that the data can be safely extrapolated to higher or lower capacities or even interpolated to intermediate capacities.

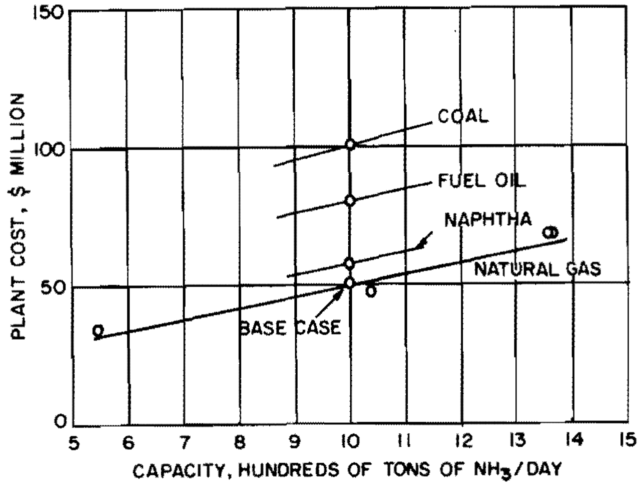

Figure 8. Estimated Investment Cost for Ammonia Plants as Related to Capacity and Type of Feedstock.

Basis: Battery Limits, Developed Country, Industrial Location.

The majority of new plants built or ordered in the last decade have been in the 900- to 1,040-tpd capacity range. Since development costs have been spread over a larger number of plants, the investment cost is lower per annual ton of capacity, and this capacity range is generally regarded as the economic optimum scale in most cases. A capacity of 550 tpd usually is regarded as the economic minimum scale for plants using centrifugal compressors, and plants of this size are selected when the market is limited or when the amount of available feedstock is limited. The 1,360-tpd size is sometimes used in locations where site development costs are high; the total project cost may be lower per annual ton of capacity. However, in some cases where site development costs are high, it may be preferable to locate two or more smaller plants at the same site as has been done in Indonesia and South Korea, for example.

Relatively few plants have been built to produce ammonia by partial oxidation of heavy oil or coal; thus, process and equipment design has not been standardized to the same extent as for steam-reforming processes. Therefore, there is no reason to suppose that 1,000 tpd is an economic optimum for these processes. In fact, there is some reason to believe that the economic optimum scale may be higher for oil- and coal-based processes. For example, Supp implies that 1,600 tpd may be near optimum for ammonia production by partial oxidation of heavy fuel oil when the market is not a limiting factor (18).

For the purpose of further discussion, an investment cost of $50 million will be assumed for a 1,000-tpd battery-limits natural gas-based ammonia plant located in an industrial site such as the U.S. Gulf Coast, and a total turnkey plant cost of $75 million will be assumed for the base case. This is in line with recent TVA estimates (23, 31). The total plant cost includes land, product storage, site preparation, and auxiliary and support facilities (31).

The usual assumption that total plant cost is 1.5 times battery-limits cost does not seem appropriate in the case of plants larger or smaller than 900-1,040 tpd because of the unusual relationship between battery-limits plant costs and capacity. For the purposes of the present estimate, the 50% allowance for additional plant costs will be applied only to the base case (1,000 tpd); for other plant sizes the additional plant costs will be assumed to vary as the 0.6 power of the capacity. This assumption leads to the following total plant costs:

Cost of Natural Gas-Based
Ammonia Plants, U.S. Location

Capacity	550	1,000[a]	1,360
Battery-limits cost, $ million	35	50	69
Other plant costs	17.5	25	30
Total plant costs	52.5	75.0	99.0

a. Base case.

Working capital will not be included, but an allowance of 5% will be made in the operating cost estimate for "administrative and miscellaneous" cost which includes interest on working capital.

For feedstocks other than natural gas, the capital cost will be estimated by applying the following factors:

Feedstock	Plant Cost Factor	Assumed for Base Case, $ Million[a]
Natural gas	1.00	75.0
Naphtha	1.14	85.5
Heavy oil	1.60	120.0
Coal	2.00	150.0

a. Total plant cost, battery limits x 1.5.

These factors are a compromise between estimated costs from several sources and are approximately in line with relative costs given by Nichols and Blouin (31). The factor for naphtha-based plants presumably can be applied with some degree of confidence to standardized plant sizes (550 and 1,360 tpd) that are lower and higher than the base case. For other feedstocks there is insufficient experience to indicate how the plant costs would vary with capacity. Therefore, the estimated costs are shown on figure 8 as a single point with a short line indicating a probable trend. Comparisons of the estimated production costs as affected by factors other than the scale of operation will be based on 1,000-tpd capacity, with the exception of electrolytic hydrogen-based ammonia plants which have been discussed in a previous section of this chapter.

It should be emphasized that the investment estimates are not total project costs. Some items that the estimates do not include are:

1. Escalation of costs beyond 1978.
2. Interest on capital during construction.
3. Feasibility studies.
4. Training programs and other startup expenses.
5. Contingencies.
6. Electric power generation, except in the case of plants based on coal or heavy fuel oil.
7. Emergency electric-generating facilities to serve as backup for regular power supplies.
8. Import taxes or custom duties.
9. Any unusual expense to ensure water supplies such as dams, reservoirs, long pipelines, or desalination of seawater.
10. Infrastructure such as housing, roads, or railroads outside the plant; harbor improvement; piers; jetties; airport facilities, etc.
11. Unusual site preparation expenses.

Production Cost and Gate Sale Price Estimates

The following simplifying assumptions are made to arrive at comparative estimates for production costs and gate sale prices:

1. Labor costs--$8/man-hour for operating labor only.
2. Overhead--100% of labor, includes administration, fringe benefits, etc.
3. Chemical control--20% of labor, includes laboratory personnel and supplies.
4. Miscellaneous supplies--$1.00/ton.
5. Electricity--$0.027/kWh.
6. Cooling water--$0.01/$m^3$ on a once-through basis (actual requirement may be about 5% of once-through requirement when recirculation through cooling towers is used).
7. Boiler feedwater--$0.26/$m^3$.
8. Depreciation--6.67% of plant cost (15-year straight line).
9. Maintenance--5% of plant cost, including labor and materials.
10. Taxes and insurance--2% of plant cost per year.
11. Interest--4% of plant cost per year which may be viewed as 8% interest on one-half of plant cost.[3]
12. Return on investment (ROI)--10% of plant cost/year with no provision for income taxes.[3]

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[3] If the depreciation allowance is used to decrease the capital investment, the average plant investment over a 15-year period would be one-half of the initial investment.

13. Administrative and miscellaneous costs--5% of the total of other production costs, which include allowance for interest on working capital, startup expense, etc.

The base case for 1,000-tpd ammonia plants will assume the following conditions:

Fuel and Feedstock	Heating Value[a]	Cost, $/Unit (Base Case)
Natural gas	8,015 kcal/m^3	0.053/m^3
Naphtha	10,556 kcal/kg	130/t
Fuel oil	9,722 kcal/kg	80/t
Coal	6,333 kcal/kg	25/t

a. Low heating value (LHV).

Fuel and Feedstock	Requirements per Ton of NH_3		
	Quantity	Million kcal[a]	Cost, $
Natural gas	1,073 m^3	8.6	56.87
Naphtha	0.89 t	9.4	115.70
Fuel oil	1.00 t	9.7	80.00
Coal	1.97 t	12.5	49.25

a. From reference (13).

For the base case, a 1,000-tpd plant operating at about 90% capacity (300,000 tpy) using natural gas at $0.053/$m^3$, the estimated production cost is about $115/ton of NH_3, and the gate sale price is $140 (see table 6). For comparison the world market price is about $117/ton of NH_3 (Fertilizer International, July 1978). This is slightly higher than the estimated production cost but considerably lower than the estimated gate sale price. During the period of January 1976 to July 1978, the world market price of ammonia ranged from $90 to $135/ton. Some factors that might lead to a price lower than that estimated in table 5 are: (1) the average feedstock price may be less than $0.053/$m^3$, (2) the return on investment may be less than 10%, and (3) the majority of plants were built at a time when plant construction costs were lower than at present and are partially depreciated, thus the capital investment is lower. It will be noted that capital-related costs are about 38% of the production cost and 49% of the gate sale price.

The effect of scale of operation for natural gas-based plants is shown in table 7 for the range of 550 to 1,360 tpd. Increasing the scale from 550 to 1,000 tpd decreases the production cost by about

TABLE 7. EFFECT OF SCALE OF OPERATION ON PRODUCTION COST AND GATE SALE PRICE OF AMMONIA FROM NATURAL GAS

	Capacity, tpd		
	550	1,000[a]	1,360
Capacity, thousand tpy	165	300	408
Plant cost, $ million	52.5	75.0	109.0
	$/ton of NH_3		
Natural gas	56.87	56.87	56.87
Catalysts, chemicals, and supplies	1.75	1.75	1.75
Utilities	3.69	3.69	3.69
Labor-related costs	4.03	3.17	2.80
Capital-related costs	56.22	44.18	42.88
Subtotal	122.56	109.66	107.99
Adm. and misc. expense, 5%	6.12	5.49	5.40
Production cost	128.68	115.15	113.39
ROI, 10%	31.82	25.00	24.26
Gate Sale Price	160.50	140.15	137.65

a. Base case.

TABLE 6. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA

Feedstock--Natural gas (base case)
Capacity--1,000 tpd; Capacity utilization--90%
Annual production--300,000 tons
Location--U.S. Gulf Coast
Plant cost--$75 million

Item	Quantity	Unit Price, $	$/ton of NH_3
Natural gas	1,073 m^3	0.053	56.87
Catalysts and chemicals			0.75
Misc. supplies			1.00
Electricity	33 kWh	0.027	0.89
Cooling water	220 m^3	0.01	2.20
Boiler feedwater	2.3 m^3	0.26	0.60
Labor	0.18 man-hour	8.00	1.44
Overhead	100% of labor		1.44
Chemical control	20% of labor		0.29
Maintenance	5% of plant cost		12.50
Taxes and insurance	2% of plant cost		5.00
Depreciation	6.67%		16.68
Interest	4.0%		10.00
Subtotal			109.66
Adm. and misc. expense, 5%			5.49
Production cost			115.15
ROI, 10%			25.00
Gate sale price			140.15

$13/ton and the gate sale price by $20/ton. Further increase in scale to 1,360 tpd decreases costs only marginally.

The cost of natural gas fuel and feedstock for the base case is $0.053/m^3 or $6.61/million kcal. This is about 52% of the production cost. As noted previously natural gas prices vary widely and may be as low as $1.00-$1.50/million kcal in some locations and as high as $12 (for imported LNG).

Unfortunately, low-cost natural gas is available only in remote locations where construction costs are high. A grass-roots plant in an industrial location of a developed country is estimated to cost $75 million (base case); whereas, the same plant in a developing country is likely to cost 25%-50% more. Perhaps more importantly, it is usually necessary to provide more auxiliary and supporting facilities, since services and supplies that are readily available in developed countries may be unavailable. Also, infrastructure improvements are likely to be needed; it may be debatable how much of the infrastructure improvements should be charged to the plant. However, the fact remains that the plant could not function efficiently without them.

Whatever the reasons, it is not uncommon for the total project cost in a developing country to be twice as much as in an industrialized developed country.

The effect of increasing the plant cost by 50% and 100% and the effect of natural gas cost on production cost and gate sale price of ammonia are shown in figures 9 and 10. In constructing these figures, only capital-related costs and natural gas costs were assumed to vary. Other costs were assumed to be constant except administrative and general costs which were assumed to be 5% of the sum of all other costs; this allows for increase in interest on working capital as the product cost increases. Figure 10 indicates that a plant costing $150 million and using natural gas at $4/million kcal would be competitive with a $75 million plant using $12 gas, but neither would be competitive with world market prices. If gas were available at $2/million kcal, the plant capital cost would have to be about $95 million (about 27% above the base case) to produce ammonia at a gate sale price in the middle of the range of 1976-78 world market price. Developing countries may be able to obtain loans on concessional terms which would lower the ammonia price required for profitable operation. The comparison does not include shipping costs; if ammonia is produced for export, each plant would have some advantage within its region compared with more distant plants. If ammonia is produced for domestic use, a comparison should take into account the delivered cost of imported ammonia plus the cost of converting it into an acceptable end product (see chapter XI).

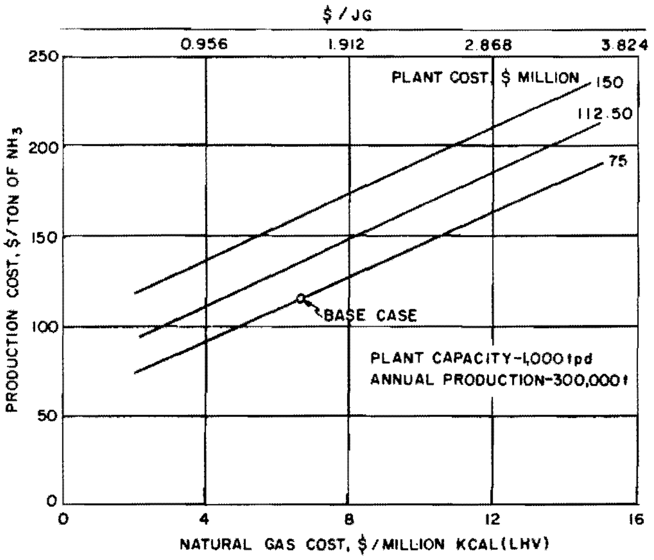

Figure 9. Effect of Plant Investment Cost and Natural Gas Cost on Production Cost of Ammonia.

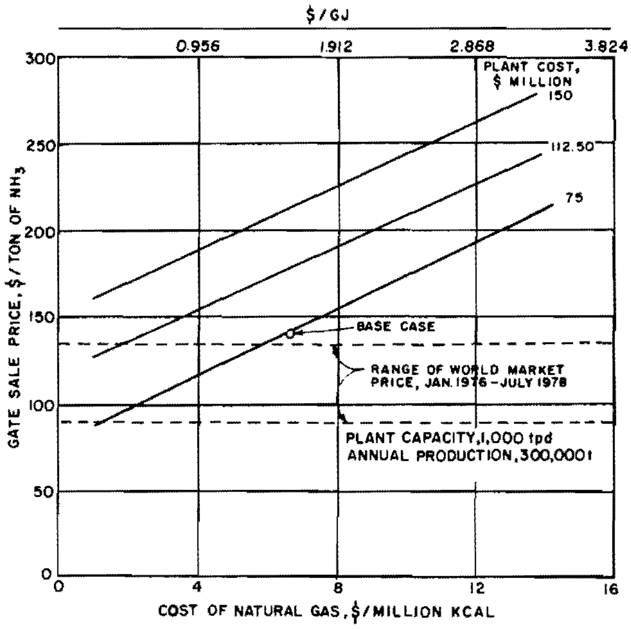

Figure 10. Effect of Plant Investment Cost and Natural Gas Cost on Gate Sale Price of Ammonia.

The previous comparisons have been based on a capacity utilization of about 90% (annual production = 300 times daily rated capacity). Some plants have achieved several-year records of 100% capacity utilization, which is generally assumed to be 330 times daily capacity, or even higher, but many plants do not attain 90% annual capacity utilization for a variety of reasons such as interruptions in feedstock supply, lack of market demand, or technical difficulties. In particular, many ammonia plants in developing countries have operated well below 90% of rated capacity even when fertilizer was in short supply. There are some outstanding exceptions, and the average for developing countries is improving.

Since ammonia production is highly capital intensive, the percentage of capacity utilization has an important effect on production cost and profitability. For example, operating at 100% rather than 90% of capacity would decrease the production cost for the base case by $4.42/ton and the gate sale price by $6.92. However, operating at 75% rather than 90% capacity would increase the production cost by $8.84/ton and the gate sale price by $13.84. For higher cost plants, the effect is proportionately larger. Thus, the advantage of locating a plant where low-cost feedstock is available can be lost by a combination of higher capital cost and lower capacity utilization.

Even though minimizing the capital cost is important, it should not be done at the expense of reliability. In general extra money spent in improving plant reliability will be repaid in improved capacity utilization, lower production cost, and greater profitability. In locations where feedstock costs are low, some saving in capital costs can be made by less elaborate heat and energy recovery facilities. The extra equipment that is required to improve efficiency is important when feedstock costs are high but much less important where low-cost natural gas is available. In addition, the extra equipment tends to complicate plant operation and increase maintenance cost. Some other means for reducing capital costs are to (1) choose a standard design, (2) select reliable and capable contractors, and (3) minimize construction time.

The choice of feedstock affects the production cost in that it affects plant cost, as previously discussed, by influencing raw material costs and other operating costs. The choice of feedstock may also affect plant reliability, although there are no precise data on this point. Coal-based plants have a poor record for reliability although production rates up to 90% of capacity have been reported. If production of ammonia from coal becomes popular, it is likely that equipment design will be improved and standardized so that more dependable operation can be expected.

Estimated production costs and gate sale prices for a 1,000-tpd ammonia plant located in a developed country using naphtha, fuel oil, and coal are shown in tables 8, 9, and 10, and in figures 11 and 12. The results of the estimates are summarized below:

Fuel and Feedstock	Assumed Price	$/ton of NH_3 Production Cost	Gate Sale Price
Natural gas	$0.053/m^3	115.16	140.16
Naphtha	130/ton	185.10	213.60
Fuel oil	80/ton	168.90	208.90
Coal	25/ton	158.41	208.41

The production cost and gate sale price of ammonia for each of the four feedstocks as related to the feedstock price are shown in figures 11 and 12. The effect of type of feedstock on production cost may be expressed in terms of the price of feedstock required to produce ammonia at given cost levels as follows:

Production Cost, $/ton of NH_3	Required Feedstock Cost, $/Million kcal Natural Gas	Naphtha	Fuel Oil	Coal
100	4.70	3.50	1.20	Negative
150	10.50	8.70	6.30	2.40
200	16.00	13.80	11.20	6.80

Under the conditions assumed in the estimate, a $100/ton ammonia production cost can be attained with natural gas at $4.70, naphtha at $3.50, or fuel oil at $1.20/million kcal; this production cost cannot be attained with coal. A $150/ton production cost can be attained with natural gas at $10.50, naphtha at $8.70, fuel oil at $6.30, or coal at $2.40/million kcal.

A similar comparison using the estimated gate sale price follows:

Gate Sale Price, $/ton of NH_3	Required Feedstock Cost, $/Million kcal Natural Gas	Naphtha	Fuel Oil	Coal
120[a]	4.50	3.40	Negative	Negative
150	7.70	6.20	2.30	Negative
200	13.00	11.00	7.30	3.30

a. Approximate present world market price.

The above comparisons are based on estimated capital investment costs for a developed country. If the investment cost in a developing country were 50% higher, production costs and gate sale prices would be substantially higher. In the case of a coal-based plant, for example, increasing the investment cost by 50% would increase the ammonia production cost by about $44/ton and the gate sale price by $69/ton.

It is probably not realistic to assume that a coal-based ammonia plant can be operated at the same percentage of rated capacity as a natural gas- or naphtha-based plant, and this factor should be taken into account. However, there is not enough

TABLE 8. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA MADE FROM NAPHTHA

Feedstock--Naphtha (base case)
Capacity--1,000 tpd; Capacity utilization--90%
Annual production--300,000 tons
Location--Developed country
Plant cost--$85.5 million

Item	Quantity	Unit Price, $	$/ton of NH_3
Naphtha	0.89 tons	130	115.70
Catalysts and chemicals			1.00
Misc. supplies			1.00
Electricity	50 kWh	0.027	1.35
Cooling water	288 m^3	0.01	2.88
Boiler feedwater	1.9 m^3	0.26	0.49
Labor	0.20 man-hour	8.00	1.60
Overhead	100% of labor		1.60
Chemical control	20% of labor		0.32
Maintenance	5% of plant cost		14.25
Taxes and insurance	2% of plant cost		5.70
Depreciation	6.67% of plant cost		19.01
Interest	4% of plant cost		11.40
Subtotal			176.30
Adm. and misc. expense	5% of subtotal		8.81
Production cost			185.11
ROI, 10%			28.50
Gate sale price			213.61

TABLE 9. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA MADE FROM HEAVY FUEL OIL

Feedstock--Heavy fuel oil (base case)
Capacity--1,000 tpd; Capacity utilization--90%
Annual production--300,000 tons
Location--Developed country
Plant cost--$120 million

Item	Quantity	Unit Price, $	$/ton of N
Fuel oil	1.00 ton	80.00	80.00
Catalysts and chemicals			0.50[a]
Misc. supplies			1.00
Electricity	Self-sufficient		-
Cooling water	352 m^3	0.01	3.52
Boiler feedwater	1.6 m^3	0.26	0.42
Labor	0.27 man-hour	8.00	2.16
Overhead	100% of labor		2.16
Chemical control	20% of labor		0.43
Maintenance	5% of plant cost		20.00
Taxes and insurance	2% of plant cost		8.00
Depreciation	6.67% of plant cost		26.68
Interest	4% of plant cost		16.00
Subtotal			160.87
Adm. and misc. expense	5% of subtotal		8.04
Production cost			168.91
ROI, 10%			40.00
Gate sale price			208.91

a. No provision is made for removal of SO_x or NO_x from stack gases from combustion of fuel oil in steam/electric generating unit.

TABLE 10. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA MADE FROM COAL

Feedstock--Coal (base case)
Capacity--1,000 tpd; Capacity utilization--90%
Annual production--300,000 tons
Location--Developed country
Plant cost--$150 million

Item	Quantity	Unit Price, $	$/ton of NH_3
Coal	1.97 tons	25.00	49.25
Catalysts and chemicals			0.50[a]
Misc. supplies			1.00
Electricity	Self-sufficient		-
Cooling water	308 m^3	0.01	3.08
Boiler feedwater	1.9 m^3	0.26	0.49
Labor	0.52	8.00	4.16
Overhead	100% of labor		4.16
Chemical control	20% of labor		0.83
Maintenance	5% of plant cost		25.00
Taxes and insurance	2% of plant cost		10.00
Depreciation	6.67% of plant cost		33.35
Interest	4% of plant cost		20.00
Subtotal			151.82
Adm. and misc. expense	5% of subtotal		7.59
Production cost			159.41
ROI			50.00
Gate sale price			209.41

a. No provision is made for removal of SO_x or NO_x from stack gases from combustion of coal in steam/electric generating unit.

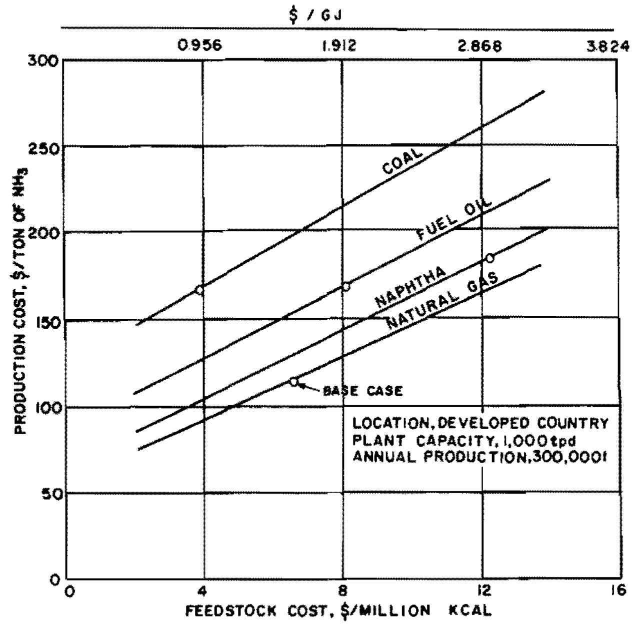

Figure 11. Effect of Price and Type of Feedstock on Production Cost of Ammonia.

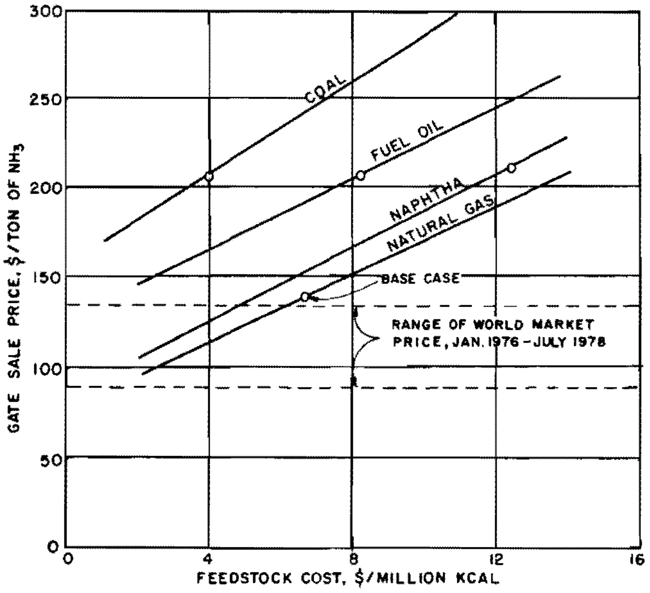

Figure 12. Effect of Type and Price of Feedstock on Gate Sale Price of Ammonia.

experience with coal-based plants to establish what average capacity utilization can be expected. If it were assumed that the coal-based plant would operate at an average capacity utilization of 10% less than a gas-based (80% versus 90%, for example), the production cost differential would be increased by about $9/ton and the gate sale price by $13/ton.

From the preceding comparisons, it seems unlikely that coal-based ammonia plants using present technology can produce ammonia at or near the world market price. In the past, coal-based plants have been built in situations where coal was the only indigenous feedstock and where the advantages of domestic production (security, foreign exchange savings, etc.) outweighed the higher cost. In the future, some developed countries may undertake ammonia production from coal as their natural gas supplies become exhausted, particularly if improved technology becomes available.

In developing countries as a group, natural gas reserves are equivalent to 136 years' use at current production rates (6). While the production rate is increasing, more reserves are being discovered. Moreover, gas and oil reserves seem to be more widely distributed than coal; 70 countries including 45 developing countries reported reserves of natural gas or petroleum or both, while only 19 countries including 5 developing countries reported coal reserves. It appears, therefore, that natural gas is likely to be the dominant feedstock on a worldwide basis for the remainder of the 20th century, probably well into the 21st century, and possibly throughout the 21st century depending on the rate of discovery.

Economics of Small-Scale Ammonia Plants

Evaluation of the economics of small ammonia plants (100-300 tpd) is difficult because relatively few of them have been built in recent years and because their advantages depend on specific conditions that are hard to generalize. Some situations in which a small plant can be considered are:

1. When there is a local market that would be difficult or expensive to supply from larger, distant plants.
2. When the location is such that it would be difficult to transport large heavy equipment to the plant site or to erect it.
3. When there is a limited supply of feedstock at a favorable cost, such as a small pocket of natural gas or a small supply of byproduct hydrogen.

The battery-limits cost of a 200-tpd ammonia plant using natural gas feedstock in a U.S. location was estimated by TVA to be $18 million (32). This estimate was based on December 1974 prices with escalation to 1978. The cost per annual ton of ammonia was about 61% more than that estimated for a 1,000-tpd plant on the same basis.

Recently, a plant rated at 181 tpd (200 short tons per day) was completed at Columbus, Mississippi (United States). The reported cost was $16 million (33). One of the advantages of the location was a long-term supply of privately owned natural gas. The location is also a considerable distance from inland waterways or ammonia pipelines and hence presumably has some cost advantages for local distribution.

Another example of a project involving a small ammonia plant is in New Zealand where a project to produce urea and ammonium sulfate was announced recently (34). The project included an ammonia plant to produce 92,000 tons of N per year (presumably about 340 tons of NH_3 per day). The cost of the ammonia plant was reported to be NZ $14.7 million which is equivalent to about US $15.6 million. The plant will use natural gas from indigenous reserves and supply New Zealand's nitrogen fertilizer requirements which are presently being imported.

Assuming that the capital cost of a 200-tpd plant is 60% greater per ton of capacity than that of a 1,000-tpd plant, the capital-related production costs would be about $27/ton greater, using the standard method of calculation used in this chapter. This cost differential could readily be offset by lower-cost feedstock, more reliable supply of feedstock, and savings in import or distribution cost.

There have been numerous proposals for small ammonia or ammonia-urea plants in developing countries, especially for remote countries or remote regions of larger countries. For example, Snamprogetti has proposed 150-tpd integrated urea-ammonia plants (see chapter IX) and estimated that 10 such plants would cost about 46% more than one 1,500-tpd plant (35). However, it was estimated that the delivered cost of the urea at the farm level would be substantially less.

A proposal for numerous small plants rather than one large one would involve the question of feedstock supply. There are not many countries where feedstock is available at a large number of locations. However, the feedstock problem could be solved if processes for production of methane from organic wastes can be developed successfully on a scale sufficiently large for a small ammonia plant.

Small ammonia (and urea) plants are available in a standardized design consisting of skid-mounted preassembled units that can be set up and connected with relatively little onsite construction labor (36). Thus, the construction time can be quite short. As a result, there is less interest on capital during construction and less escalation of costs during construction. In addition, shortening the period from inception to completion would help to minimize the uncertainties that are inherent in long-range planning.

Maintenance costs for small plants could be minimized by use of a standardized design with interchangeable spare parts so that spare parts could be quickly obtained from a central location.

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VII Transportation and Storage of Ammonia

Introduction

Much of the world's ammonia production is shipped from the plants where it is produced to other locations for further processing into finished fertilizers, for direct use as fertilizer, or for use as a raw material for nonfertilizer products. Some idea of the magnitude of ocean transport of ammonia can be gained by a recent ISMA report that lists 153 maritime ammonia terminals throughout the world including 18 that were under construction when the report was issued (July 15, 1977). The aggregate storage capacity of these 153 terminals was 2,734,000 tons, and individual capacities ranged from a few hundred tons to 121,000 tons (1). The list did not include inland terminals that can be reached only by barges on inland waterways, by pipelines, or by rail. Total world trade in anhydrous ammonia between countries in 1976 amounted to about 3,050,000 tons and increased to 4,033,000 tons in 1977 (2). The leading ammonia exporting country in 1976 was the Netherlands with about 569,000 tons. Other countries that exported more than 100,000 tons in 1976 were Austria, Belgium, France, U.S.S.R., Hungary, the United States, Canada, Trinidad, Venezuela, and Kuwait.

Another ISMA report dated July 1978 lists 192 ships that are suitable for transportation of anhydrous ammonia, including 33 of more than 10,000-ton capacity, ranging up to 46,500-ton capacity (3). These ships also carry other liquefied gases, especially liquefied petroleum gases (LPG). In general, equipment that is suitable for transporting LPG is also suitable for transporting anhydrous ammonia. Such facilities (trucks, rail tankers, barges, and ships) often are used interchangeably for transport of the two materials.

Ammonia is almost invariably transported in the liquid state; therefore, it must either be compressed or refrigerated or some combination of the two. Ammonia storage tanks may be classified as fully refrigerated, semirefrigerated, or pressurized, and a similar classification can be applied to transport equipment. Fully refrigerated storage tanks are equipped to maintain a temperature of about -33°C at which the vapor pressure of ammonia is atmospheric (see figure 11, chapter X). In semirefrigerated storage tanks, the ammonia is kept at a moderately low temperature, such as 0°-5°C, at which the gauge pressure is only 3-4 atm. This permits the use of much lighter steel tanks than if the temperature were uncontrolled. Unrefrigerated pressure storage tanks usually are designed for pressures up to about 18 atm which should be adequate for any ambient temperature normally encountered in most climates.

The metallurgy of the steel used for storage tanks, transport vessels, and pipelines is important but rather too complex for detailed explanation here. However, two points should be noted. Each type of steel has a transition temperature below which it is subject to brittle fracture. The brittle fracture is initiated at a notch or crack, usually near a weld where a stress occurs. Once initiated, a fracture may spread rapidly. Therefore, it is important that a vessel or pipeline should not be operated at a temperature below its transition temperature unless it has been thermally stress relieved after fabrication. Stress relieving is expensive and sometimes impractical. For this reason pressure vessels and pipelines should not receive refrigerated ammonia; the ammonia should be warmed to a temperature above the transition temperature of the steel used in the vessel.

Another problem is corrosion cracking of pressure vessels which may occur over a wide range of temperatures and pressures. The cause of stress corrosion cracking is not fully understood, but it is much less likely to occur if the ammonia contains a small amount of water. For this reason, addition of a minimum of 0.2% of water is required if the ammonia is to be transported in pressure vessels.

Storage and transport of ammonia at the retail level will be described in chapter X. The present chapter is concerned mainly with large-scale transport and storage.

Ammonia Storage

Pressure storage including semirefrigerated storage is economical for quantities up to about 2,000 tons; in the upper portion of this range, spherical semirefrigerated storage tanks may be used while in the lower portion of the range, horizontal cylindrical tanks with hemispherical ends are used.

Even when all of the ammonia is used at the plant site where it is produced, it is common practice to have facilities for storage of at least 15 days' production so that interruptions in operation of downstream facilities will not necessitate interruption of the ammonia plant operation. In an ammonia-urea complex, for example, when the urea plant must be shut down for repairs, the ammonia plant can continue to operate with the ammonia going to storage. When the urea plant resumes operation, it can utilize the current output of the ammonia plant plus an additional small percentage from storage provided that the urea plant has sufficient capacity. For this reason it is common practice to design the urea unit of an ammonia-urea complex to have 5%-10% more capacity than would be required to utilize the daily ammonia plant output.

A simplified diagram of a refrigerated ammonia storage facility is shown in figure 1. In this case liquid ammonia under pressure is received from the ammonia plant synthesis loop (see chapter VI). As the pressure is reduced in the flash tank to nearly atmospheric, part of the ammonia evaporates; the negative heat of evaporation reduces the temperature of the remaining liquid to about -33°C at which temperature it goes to the storage tank. The ammonia vapor is liquefied by compression and water-cooling and returned to the flash tank. Ammonia received from the ammonia plant contains

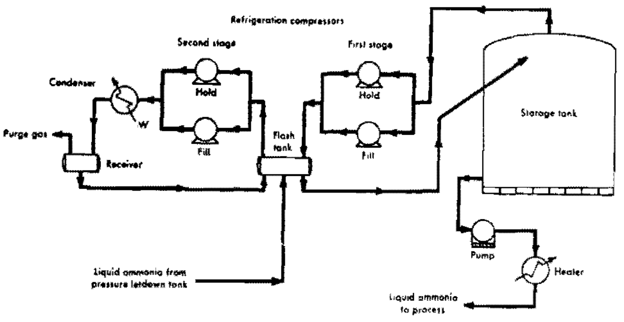

Figure 1. Simplified Diagram of Refrigerated Ammonia Storage Facility.

small amounts of dissolved gases, H_2, N_2, Ar, and CH_4; these gases, called "flash gases," are not condensed and must be purged from the second-stage compressor loop. When the storage tank is not being filled, a relatively small amount of ammonia evaporates as heat is conducted into the tank through the insulation. This heat is removed by evaporation of ammonia, and the relatively small amount of ammonia vapor is compressed by a small compressor, liquefied by water cooling, and returned to the storage tank. When the tank is being filled, a larger quantity of ammonia vapor is formed, requiring the use of a larger compressor. Liquid ammonia withdrawn from the tank to processing or to shipment may optionally be warmed. If it is loaded into a refrigerated carrier (ship or barge), the ammonia is pumped through insulated pipes at storage temperature. When the downstream process requires that the ammonia be heated or vaporized, this may be done by recirculated warm water from the cooling water system.

Refrigerated ammonia storage tanks are of two types. One type is of double-wall construction with the annular space between the walls filled with loose perlite insulation and kept slightly above atmospheric pressure with dry air, nitrogen, or inert gas. The other type of tank is of single-wall construction, insulated on the outside with foam glass, styrofoam, polyisocyanurate foam, or polyurethane foam. Although the investment cost for the double-wall tank is greater than for single-wall construction, maintenance costs usually are lower.

Semirefrigerated storage tanks are also well insulated; the ammonia is held at the desired temperature, usually 0°-5°C, by allowing it to evaporate at a controlled pressure. The vapor is compressed and liquefied by water cooling, and the liquid is returned to the tank. Thus, the system is similar in principle to fully refrigerated storage, but the refrigeration system is much less sophisticated and relatively inexpensive.

Terminals for shipping or receiving liquid ammonia are similar in principle to the in-plant storage facility although there may be important differences. Obviously, a terminal to receive or discharge shipments to ocean-going vessels or barges must be at a location that is accessible to such vessels. Harbors suitable for receiving large ships are not plentiful, and terminal sites adjacent to such harbors may be scarce and expensive. In some locations considerable expense may be involved in harbor improvement, construction of a pier, and preparation of a terminal site. To minimize port time, ships must be loaded or unloaded rapidly with minimum vaporization of refrigerated ammonia. Thus, high-capacity pumps and large, well-insulated pipelines are needed. Assuming that the ammonia plant is not adjacent to the port, considerable expense may be involved in transport of ammonia to the port. For example, a 25-cm cryogenic pipeline suitable for transport of ammonia from a ship to a terminal or vice versa may cost \$650/m. Extra refrigeration capacity may be required to cool the ammonia as it is received. If ammonia is received at a terminal for use in manufacturing a fertilizer product such as ammonium nitrate or diammonium phosphate, the manufacturing facility should be as close to the terminal as feasible to minimize transport cost from the terminal to the plant. For the above reasons the investment and operating costs of an ammonia terminal are likely to vary widely and usually are greater than that of an in-plant storage facility. Estimated capital costs for refrigerated storage facilities are shown in figure 2.

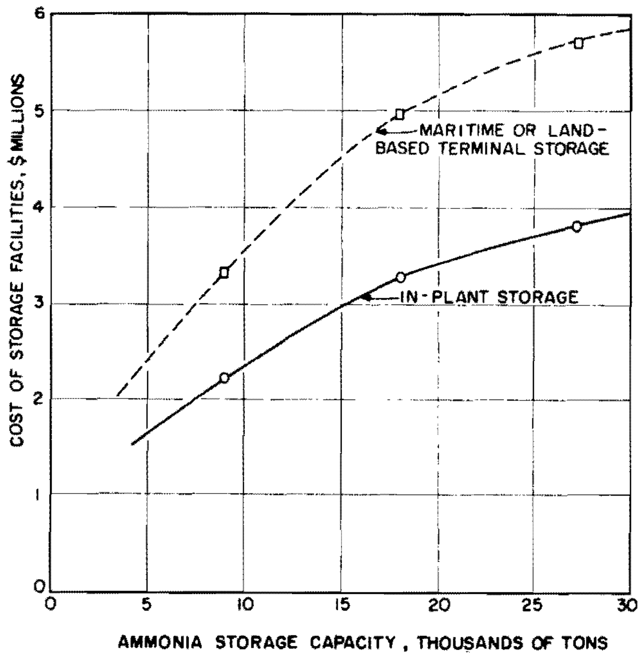

Figure 2. Estimated Capital Costs for Refrigerated Ammonia Storage Facilities.

The cost of in-plant storage includes only the storage tank, its foundation, and refrigeration equipment required for normal in-plant storage and use. Maritime terminals or land-based terminals for receiving and distributing ammonia are likely to cost roughly 50% more than in-plant storage, especially if they are remote from any manufacturing facility.

The operating cost of a storage facility consists mainly of fixed charges. Assuming that a maritime terminal of 30,000-ton capacity costs \$6 million, the annual operating cost can be estimated roughly as follows:

	Annual Cost, \$
Depreciation, 6.67% (15 years)	400,000
Maintenance, 5%	300,000
Taxes and insurance, 2%	120,000
Utilities	80,000
Labor and overhead	60,000
Total annual cost	960,000
Cost/ton of capacity	\$32

If such a facility were to receive 100,000 tpy, the cost per ton of throughput would be \$9.60. Similar calculations indicate that the annual operating cost of terminals of 10,000- and 20,000-ton capacity would be about \$55.00 and \$41.50/ton of capacity, respectively.

The size of a marine terminal depends mainly on the capacity of ships that are expected to serve it and should be 25%-50% larger than the ship's capacity to allow for delays in scheduling shipments and delays due to storms, strikes, etc. The estimated terminal costs for receiving 100,000 tpy in terminals of different capacities follow:

Terminal Costs for Receiving 100,000 tons of Ammonia per Year

Terminal Capacity	Annual Terminal Cost, \$/ton of Capacity	Size of Shipments, tons[a]	Number of Shipments/Year	Throughput Cost, \$/ton of NH_3
10,000	55.00	7,500	13.3	5.50
20,000	41.50	15,000	6.7	8.30
30,000	32.00	22,500	4.4	9.60

a. Size of shipment is assumed to be 75% of terminal capacity.

Thus, the terminal cost for any given annual throughput decreases as the size of the terminal decreases. However, a smaller terminal capacity requires a larger number of shipments in smaller ships which may increase freight costs, as discussed later. Therefore, determination of the minimum cost of importing ammonia involves a balance between freight costs and terminal costs. In the above illustration it was assumed that the size of shipments was not limited by harbor depth, pier space, etc. If harbor improvement or pier construction is required, the cost of these facilities must also be considered.

Transportation of Ammonia

Ocean Transportation of Ammonia

For overseas or coastal shipment of ammonia, ships are commonly used that are equipped with well-insulated tanks or holds to contain liquid ammonia at slightly above atmospheric pressure and at a corresponding temperature of about -33°C. The ships are equipped with refrigeration facilities which, in principle, are similar to those of a storage facility. The ships are also equipped with pumps of sufficient capacity to discharge the cargo at a rapid rate.

The cost of ocean transport depends on a large number of factors--the cost of the ships or the cost of chartering the ship, distance, ship speed, fuel cost, crew cost, port charges and time in port, number of destination ports, and the supply and demand for shipping space. The last factor is an important one which causes freight costs to fluctuate widely. For the last year or two, available shipping space has exceeded demand and, as a result, freight costs have been low. In contrast, demand exceeded supply in 1974-75, and freight costs were high.

The following tabulation taken from an ISMA report lists ships that are suitable for transport of anhydrous ammonia or other similar liquefied gases at minimum temperatures usually ranging from -34° to -48°C (3).

Liquid Gas Carriers

Capacity, tons	Number of Ships
30,000 to 46,500	9
20,000 to 30,000	4
10,000 to 20,000	18
5,000 to 10,000	28
2,000 to 5,000	33
Less than 2,000	100
Total	192

Overseas shipments of ammonia are usually by chartered ships; the ships may be chartered for a single trip, for multiple trips, or for a time period. Following are some published single-trip freight costs during 1977 and 1978.

Ammonia Freight Costs (Single Trip)[a]

Origin	Destination	Tonnage	Freight, \$/ton
Persian Gulf	North Europe	30,000	23.30
Persian Gulf	North Europe	15,000	35-40
Persian Gulf	Mediterranean Europe	15,000	25-30
U.S. Gulf	Colombia	8,000	22.50
U.S. Gulf	Santos, Brazil	12,000	27
U.S. Gulf	Rio Grande, Brazil	8,000	23
U.S. Gulf	Spain	5,000	25
U.S. Gulf	North Europe	10,000	24
U.S. Gulf	Italy	8,000-9,000	27.50-29.50
Kenai, Alaska	United Kingdom	14,500	38
Australia	Brazil	10,000	40
West Europe	United States	15,000	19.50
Holland	Finland	7,000	18
Soviet Baltic	United States	8,000	31

a. From various issues of Fertilizer International, Nitrogen, and Green Markets.

Information received from a ship brokerage firm on current (September 1978) approximate spot rates for overseas shipment of anhydrous ammonia follows:

Approximate Freight Costs for 15,000-ton Lots of Anhydrous Ammonia[a]

Origin	Destination	Freight, \$/ton
Persian Gulf	Turkey	28-30
	United States	47
	Brazil	44
	India (East Coast)	22
U.S. Gulf Coast	Brazil	28
	United Kingdom	24-25
	Mexico	10-11
Holland	U.S. East Coast	18-19
Russia (Baltic or Black Sea)	United States	35

a. Freight costs for 30,000-ton lots are about 25% lower; for 8,000- to 10,000-ton lots, they are about 15% higher.

When there are definite plans to ship large quantities of anhydrous ammonia, long-term charters may result in lower freight costs. The following freight costs are believed to be typical of costs currently (1978) obtainable through contracts for shipment of large quantities of anhydrous ammonia ("large quantities" does not necessarily imply that the quantity shipped to any specific destination is large).

Freight Costs for Large Volume Shipments (Ship Size Unspecified)

Origin	Destination	Freight, \$/ton
Persian Gulf	Turkey	22.50
	United States	30
	Brazil	30
	India, West Coast	10
	India, East Coast	15
U.S. Gulf Coast	Brazil	17.50
	Mexico	12.50
	Morocco	20
	United Kingdom	22.50
Holland	United States	25
Trinidad	United States	10-15
	United Kingdom	20
United Kingdom	United States	25
	Algeria	22.50
	Spain (north)	15
	Spain (south)	20

As mentioned previously, the freight market is currently depressed because of an excess of shipping facilities, but overseas shipments of ammonia are increasing and are likely to increase further since several new plants intended mainly for export are expected to start production soon. Exports from Russia are increasing, and plans are reported to increase exports further to 1.5 million tpy from terminals on the Black Sea (Odessa) and Baltic Sea (Ventspils) (4). Mexico expects to have 350,000 tpy of exportable surplus ammonia, and expansions in Trinidad, Libya, and the Persian Gulf will add to the ammonia available for export. If all of these plans mature and markets for the ammonia can be found, shipping space may not be equal to the demand, and freight costs may rise.

It should be emphasized that the total cost of shipping and receiving ammonia includes not only the freight but also the cost of operating loading, receiving, and storage terminals, as discussed previously. Also the total cost may include transport to the terminal. For example, the U.S.S.R. terminals at Ventspils and Odessa are supplied by pipeline from ammonia plants located several hundred kilometers inland.

Shipment of Ammonia by Barge

Barge shipment of anhydrous ammonia is economical for countries or regions that have inland or coastal waterways and is extensively used in Europe and the United States. Self-propelled barges are commonly used in Europe where inland waterways are often narrow or shallow. Their capacities may range from 500 to 3,000 tons. Most of the larger barges are fully refrigerated, and smaller ones are semi-refrigerated. For most of the inland rivers and canals, barges of about 1,000-ton capacities are suitable; larger self-propelled barges may be useful for coastal shipping.

In the United States, towed barges are commonly used, and several barges are lashed together and propelled by a single tugboat. A tow may be formed by 6-12 barges or more depending on the width of the waterway. Barges for transport of anhydrous ammonia usually are fully refrigerated, and their capacities may be in the range of 1,500 to 2,500 tons; smaller ones are used mainly where the depth or width of the waterway is insufficient for larger ones. Most of the barge movement of anhydrous ammonia is up the Mississippi River and through coastal waterways adjacent to the Gulf of Mexico. Several large terminals are located on the river. Figure 3 shows a terminal at Pine Bend, Minnesota, on the upper Mississippi River with an 8-barge tow of anhydrous ammonia arriving at the terminal. Similar terminals are located at various points along the river and its tributaries. A typical terminal may have a storage capacity of 60,000 short tons of ammonia consisting of two 30,000-ton tanks. Since the river is frozen during the winter, the terminals that are served by barge need to be filled by late autumn.

Ammonia from the terminal is transported by truck or rail to retail outlets as described in chapter X, usually within a range of 150 km or less. Figure 4 shows a truck arriving at a terminal for loading. Ammonia from the terminal also may be used to produce solid or liquid compound fertilizers, nitrogen solutions, etc. Some of the larger compound fertilizer manufacturers receive ammonia by barge and have their own terminals.

Published barge freight rates from Donaldsonville, Louisiana (near New Orleans), are (5):

Destination	Estimated Distance, km[a]	Freight Cost	
		$/Short Ton	$/Metric Ton
Peoria, IL	1,135	7.60	8.38
Minneapolis, MN	1,700	6.75	7.44
Omaha, NE	1,517	18.80	20.72
Sioux City, IA	1,600	25.00	27.55

[a] Estimated straight-line distances; river travel distance may be 50% more than the straight-line distance.

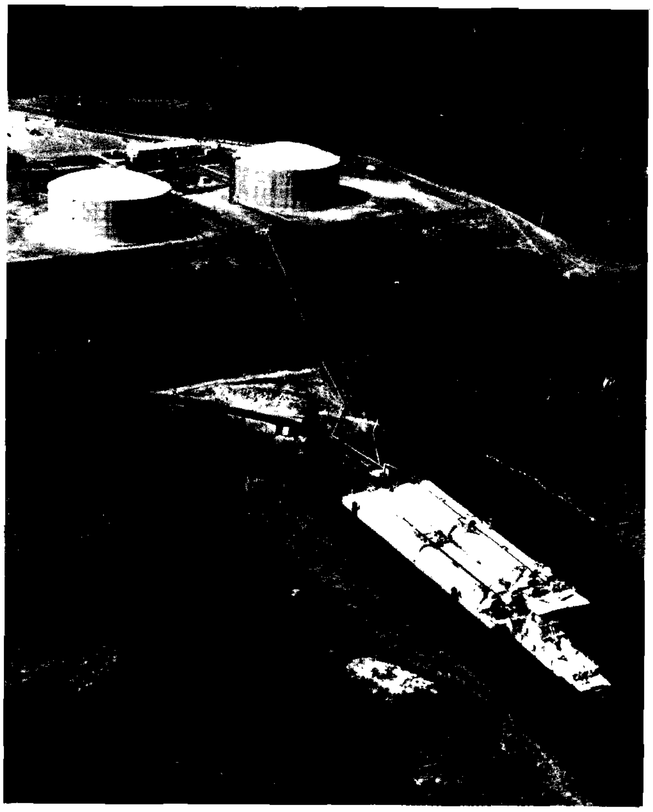

Figure 3. Ammonia Storage Terminal at Pine Bend, Minnesota.

Figure 4. Truck Being Loaded at Ammonia Terminal

The rates reflect differences in difficulty of access more than distance. Peoria is located on the Illinois River which is narrower than the Mississippi, thus fewer barges per tow can be used than to Minneapolis. Since Omaha and Sioux City are located on the Missouri River which is shallow, small barges must be used; other means of transport are more often used to these points.

Although some barges are owned by towing companies, most of them are owned by or are under long-term lease to major ammonia producers or petrochemical companies. Consequently, cost information is scarce, and short-term availability of barge transport cannot be relied upon. However, favorable rates may be available when barges would otherwise be idle. Some shippers may own both barges and tow boats. Others may lease barges and contract for towing, and various other arrangements are possible. A well-planned program is necessary for economical barge transport since the economics depends on full utilization of the equipment. Where waterways are navigable only part of the year as in the northern part of the United States, barge transport may be at a disadvantage unless some use for the barges can be planned in other areas during the winter. The use of barge transport seems to be decreasing; in 1968 there were about 85 barges available for ammonia transport in the United States of which 66 were designated for ammonia only. At present there are about 40; most of them are owned by ammonia-producing companies. In contrast, pipeline shipment has increased.

Transportation of Ammonia by Pipeline

Transportation of anhydrous ammonia by pipeline is economically attractive in some cases. Examples of long distance transport are found in Mexico, U.S.S.R., and the United States. Pipelines may be used to transport ammonia from manufacturing plants to maritime terminals for shipment, to factories that produce finished fertilizers, or to market areas for direct application. A pipeline may serve some combination of these purposes.

Relatively short pipelines, up to 50 km, have been used for 30 years or more for ammonia transportation. For example, in Sterlington, Louisiana, a pipeline 6.4 km long and 7.6 cm in diameter was in use in the 1950s to transport ammonia from an ammonia plant to an ammonium nitrate plant. Likewise, in Portugal a 10-cm diameter pipeline, 17 km long, was in operation in 1960 to connect an ammonia plant with a fertilizer plant. A 50-km pipeline is used to transport ammonia from an ammonia plant in Carling, France, to a urea plant in Besch, Germany; a parallel pipeline supplies carbon dioxide. In Mexico a pipeline which is about 240 km long crosses the country from the Gulf of Mexico to the Pacific. One of the first European pipelines was built in Czechoslovakia between Most and Lovosice.

Pipeline transportation is well developed in the United States where two major pipelines are in operation. Their locations are shown in figure 5.

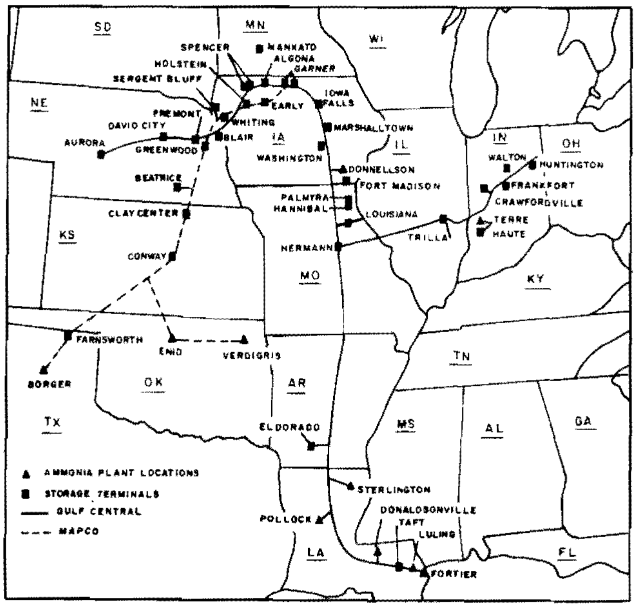

Figure 5. Ammonia Transportation Pipelines within the United States.

The Gulf Central pipeline extends from southern Louisiana northward through Arkansas and Missouri to northern Iowa, then westward into Nebraska, a total distance of about 2,100 km. A branch extends from Missouri through Illinois to northeastern Indiana, a distance of about 650 km. Various sections of the pipeline are 10, 8, and 6 inches in diameter (25, 20, and 15 cm). The cost of the pipeline was reported to be $70 million (completed in 1969). Seven ammonia producers are listed as injection points of which five are in Louisiana, one in Iowa, and one in Indiana. There are 37 terminals at 28 locations including storage facilities at ammonia production plants. The total capacity of storage facilities connected to the pipeline is about 1,500,000 tons with an average of about 40,000 tons per terminal. In addition, the pipeline itself holds about 70,000 tons. Some of the terminals can also be supplied by barge or ship from the Mississippi River. It is possible to transport ammonia from one terminal to another so that ammonia received by barge or ship at some terminals can be transferred to the pipeline for further shipment. Some of the receiving terminals are owned by ammonia producers or companies that purchase the ammonia, and some are owned by the Gulf Central Storage and Terminal Company.

The Mid-America Pipeline System (MAPCO) is supplied by one ammonia producer in Texas and two in Oklahoma. It extends through Kansas and Nebraska to northern Iowa. The line from Borger, Texas, to Garner, Iowa, was originally built in 1969 at a cost reported to be $12 million. Much of the pipeline was laid parallel to MAPCO's other pipelines that carry LPG and refined petroleum products; thus, the expense of acquiring right of way was minimized. The diameter of the pipe is 25 and 20 cm in different sections, and its length is about 1,160 km. The branches connecting the two Oklahoma plants were added later, and still more recently an extension from Garner, Iowa, to Mankato, Minnesota, was added. The total length including all branches is 1,628 km. There are 15 storage terminals connected to the system with a total capacity of about 300,000 tons. The terminal at Garner, Iowa, is served by both the MAPCO and Gulf Central pipeline systems; ammonia received by one pipeline can be transported further by the other. In addition to storage terminals there are various truckloading stations along the pipelines where trucks may be loaded for transportation to retail distributors' storage facilities or to liquid fertilizer manufacturing plants. Also there is at least one station for loading railcars directly from the pipelines, and many of the storage terminals are equipped to load railcars as well as trucks.

The initial capacity of the Gulf Central pipeline was 3,000 tpd, and the MAPCO line's initial capacity was 1,300 tpd. Both capacities have been increased by adding pumping stations; the present capacity probably is at least twice the initial capacity. Lee and Inkofer estimate that the capacity of 25-cm and 20-cm pipelines with pumping stations spaced at 64-km intervals is 3.0 million and 1.7 million tpy, respectively, an average of 8,220 and 4,660 tpd (6). The investment cost was estimated at about $44,000 and $28,000/km for the two sizes using 1969 cost levels when the pipelines were built. The maximum operating pressure of a pipeline depends on its diameter and wall thickness; about 100 kg/cm^2 may be typical. For details of pipeline construction and operation, see reference (6).

Some of the ammonia is used by manufacturers of ammonium nitrate, nitrogen solutions, and solid or liquid compound fertilizers. Some larger manufacturers have their own storage terminal; smaller manufacturers or distributors may contract for space in the storage facilities owned by the pipeline companies, or they may purchase ammonia from terminals owned by ammonia producers. The area served by the two pipeline systems contains several hundred manufacturers of liquid compound fertilizers, thus a substantial portion of the ammonia may be used for this purpose. However, the major use of anhydrous ammonia is for direct application, and most of this is applied in a few weeks in the spring.

During the peak season the pipeline systems are operated at full capacity, and transport may be available only to those companies that have contracted for it in advance. At other times when surplus capacity is available, ammonia may be accepted for transport on short-term contracts, perhaps at a reduced rate.

Specifications for anhydrous ammonia to be shipped by pipeline are:

Temperature: Not less than 35°F (2°C)
more than 85°F (29°C)
NH_3 content: 99.5% minimum by weight
Water content: 0.2% minimum by weight
Oil content: 4 ppm maximum by weight
Inerts: 0.5 cc/g maximum

When ammonia is transported from one refrigerated terminal to another, it must be warmed from -33°C to at least 2°C and then cooled again at the receiving terminal. This is necessary because the pipeline would be susceptible to brittle fracture at temperatures below 2°C, as discussed previously. Many terminals have 100- to 1,000-ton pressure storage capacities for ammonia at above 2°C in addition to 18,000- to 77,000-ton refrigerated storage.

The pipeline systems described above are common carriers and are subject to regulation by the U.S. Government (Interstate Commerce Commission) which requires (among other things) that the rates be published. The rates shown in table 1 are examples of published rates that apply to contracts involving annual shipments of 226,750 mt (250,000 short tons). The rates per ton-km are shown in figure 6. The difference between rates A and B is rather complicated and relates to arrangements for delivery during the peak season. In either case, when the contract is on an annual basis, the ammonia is received at a steady rate throughout the year. During the offpeak season the excess of input over withdrawal is stored in either the shipper's terminals or the pipeline company's terminals until the peak season.

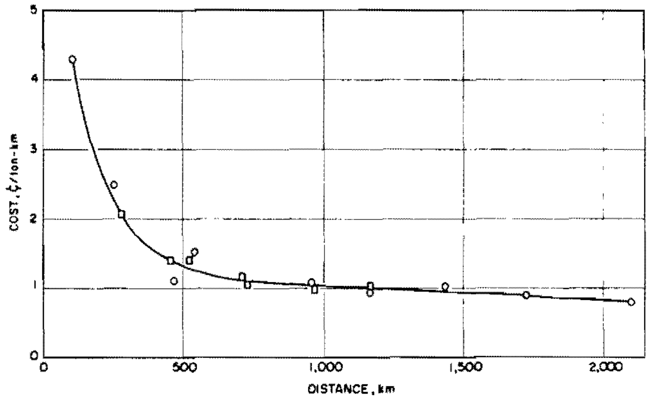

Figure 6. Pipeline Transportation Rates/ton-km.

The rates shown are for transportation only. If the ammonia is loaded directly from the pipeline into trucks, there is a truckloading charge of $1.29/ton if the loading is done by the pipeline company. When the ammonia is stored in the pipeline company's storage terminal facilities, there is an annual charge of $27/ton of storage space plus $2.20/ton of throughput. Thus, if the annual throughput is three times the contracted-for space, the cost is ($27 ÷ 3) + $2.20 or $11.20/ton. Terminal charges for various space:throughput ratios are shown in figure 7. If the storage facilities are owned by the shipper or consignee, he will have a more or less equivalent expense.

In the case of ammonia delivered to a purchaser who uses it at a steady rate (an ammonium nitrate manufacturer, for example), a lower terminal throughput charge is available depending on the use pattern. For example, a manufacturer who uses ammonia at an annual rate of 80,000-90,000 tons and at a weekly rate of 1,520-1,720 tons may contract for 1,700 tons of storage space at $27.00/ton/year plus $1.44/ton of throughput. If the throughput is 85,000 tpy, the total terminal charge amounts to $1.98/ton ($0.54 space charge + $1.44 throughput charge).

Of course, terminal charges are encountered regardless of the method of shipping; in the case of

TABLE 1. COST OF TRANSPORTATION OF AMMONIA BY PIPELINE[a]

Origin	Destination	Rate, $/ton Estimated A	Rate, $/ton Estimated B	Distance, km	Cost/ ton-km, ¢ A	Cost/ ton-km, ¢ B
	-Transported by MAPCO Pipeline-					
Borger, TX	Garner, IA	10.22	11.24	1,160	0.88	0.97
	Blair, NE	8.42	9.31	926	0.90	1.00
	Beatrice, NE	7.63	8.39	726	1.05	1.16
	Conway, AR	6.22	6.83	490	1.27	1.39
Enid, OK	Garner, IA	9.50	10.46	949	1.00	1.10
	Blair, NE	7.60	8.36	715	1.06	1.17
	Beatrice, NE	6.61	7.28	515	1.28	1.41
	Conway, AR	5.22	5.74	280	1.86	2.05
	Transported by Gulf Central Pipeline-					
Donaldsonville, LA	Palmyra, MO	10.41		1,182	0.88	
	Terre Haute, IN	14.22		1,430	0.99	
	Spencer, IA	15.76		1,723	0.91	
	Aurora, NE	16.53		2,100	0.79	
Palmyra, MO	Terre Haute, IN	5.45		471	1.16	
	Spencer, IA	8.21		541	1.52	
	Aurora, NE	9.59		918	1.04	
Terre Haute, IN	Huntington, IN	6.01		245	2.45	
Donnelson, IA	Palmyra, MO	4.57		106	4.31	

a. Selected published rates converted to metric units.

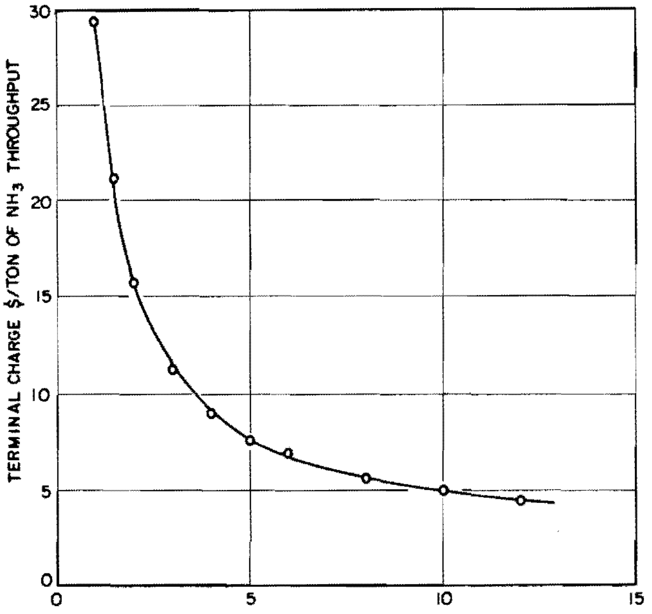

Figure 7. Terminal Charges for Various Space:Throughput Ratios.

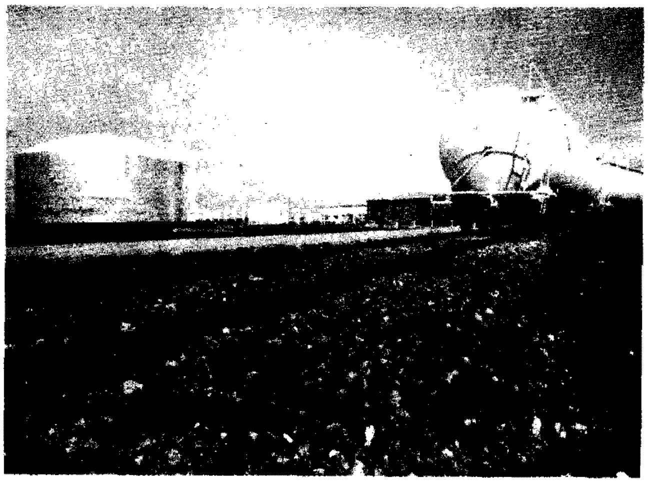

Figure 8. Large Storage Terminal that Receives Ammonia by Rail.

shipment by barge to the northern part of the United States, the throughput ratio is likely to be lower than that for transport by pipeline because the barges can be used only part of the year. Therefore, terminal storage costs are likely to be higher per ton of throughput.

Transportation of Ammonia by Rail

Ammonia is transported by rail in the United States mainly in cars having about 70- to 72-ton capacities, although a few older cars of 25- to 30-ton capacities are still in use and some larger cars (90 tons) are available. In general rail transport is used for shorter distance than pipeline or barge transportation, but this is not always the case since rail transport can be more economical for supplying to some points than a combination of barge or pipeline and rail or truck. One use for rail transport is from pipeline or large terminal to another storage terminal. Figure 8 shows a large storage terminal which receives ammonia by rail. Another use is transport from one ammonia producer to another when one producer has a surplus and the other has a need. A third is transport from a plant or terminal to a retailer or small manufacturer of liquid or solid materials.

For transport by rail (or truck) the ammonia, if taken from refrigerated storage, must be warmed to at least 5°C since abrupt cooling to -33°C causes stresses that may result in cracking of the steel tank. However, there are under development rail cars that are capable of receiving refrigerated ammonia at -33°C and are so well insulated that the temperature rise is only 1°-2°C/day. Such cars would have an obvious advantage for transporting ammonia from one refrigerated terminal to another.

Representative freight costs for transportation of ammonia by rail in cars of 70-ton capacities are shown in table 2. The rates are based on the supposition that the railroad will supply the cars. However, since the railroads have few if any cars suitable for ammonia transportation, the shipper actually supplies the cars and the railroad gives an allowance (reduction in freight cost) to compensate the shipper for the expense incurred in supplying the car. The allowance is based on the distance that the car is

TABLE 2. SELECTED RAIL FREIGHT RATES FOR ANHYDROUS AMMONIA[a]

From Donaldsonville, LA, to:	Distance, km[b]	Single Car Rate,[c] $/ton	Multicar Rate,[d] $/ton
Jackson, MS	339	12.07	-
Little Rock, AR	677	16.92	12.34
Macon, GA	927	19.04	-
Springfield, MO	1,102	23.22	15.83
Peoria, IL	1,361	26.77	20.89
Des Moines, IA	1,643	30.59	24.77
Omaha, NE	1,601	29.65	23.90
From Enid, OK, to:			
Jackson, MS	1,064	21.00	-
Little Rock, AR	653	16.92	12.34
Macon, GA	1,665	27.69	-
Springfield, MO	494	13.98	10.17
Peoria, IL	985	21.38	15.81
Des Moines, IA	763	18.26	13.40
Omaha, NE	665	16.92	12.34

a. Published rates converted to metric units.
b. Shortest distance by rail.
c. Minimum weight per car--70.3 tons.
d. Five cars or more per shipment, subject to annual volume of 36,000 short tons (32,652 mt).

moved by the railroad. The shipper may own the car, or he may lease it on long- or short-term lease. In either case the cost per ton-km of owning or leasing railcars depends on how much use the shipper makes of them. In practice, the cost is likely to exceed the railroad's allowance unless the cars are kept in constant use.

The freight cost depends on the weight of ammonia per car; the cost per ton for a small-car shipment (23-ton) may be twice that of a 70-ton carload. Also, a lower rate applies to multicar shipments, usually 5 or more 70-ton cars per shipment, subject to a guaranteed annual volume which may, for example, be about 33,000 tons (36,000 short tons). An example of rail freight costs, as affected by size of shipment, is tabulated below:

Minimum Weight/ Car, tons	Freight Cost, $/ton for 494-km Distance
Single-car	
22.7	29.97
63.5	20.55
70.3	14.28
Multicar[a]	
70.3	10.17
72.6	10.00

a. Five or more cars per shipment, 32,652 tons annual minimum.

Transportation of Anhydrous Ammonia by Truck

Truck transportation is the most expensive method of moving anhydrous ammonia and hence is used mainly for short distances, usually less than 150 km. However, the use of trucks is growing in the United States because many rail lines are being abandoned leaving a growing number of locations without rail service. The trucks used in the United States consist of a tractor and a detachable trailer (called an "articulated lorry" in the United Kingdom). Each state of the United States has its own regulations governing the total weight of trucks that are permitted to operate on its highways. Therefore, there is some variation in the capacities of ammonia trailers; a common size is 16-18 tons. Figure 4 shows a truck arriving at an ammonia terminal for loading. The trailers may be owned by the company that produces and markets ammonia, or they may be owned by the trucking company. They are used to transport ammonia to retail distribution centers or to small manufacturers of liquid fertilizers. They are also used to transport LPG. In some western states a tractor may be permitted to pull two trailers in tandem. This arrangement reduces the transport cost to the point that it may be competitive with rail transport.

Some examples of truck transport costs are shown in table 3. The first part of the table shows average rates from several trucking firms; the second part shows some specific point-to-point rates. The rates per ton-km, as related to distance, are shown in figure 9. Somewhat lower rates may be available for long-term contracts.

In the United States, about 4.5 million tons of anhydrous ammonia is used for direct application each year. Probably as much as 75%-80% of this amount is

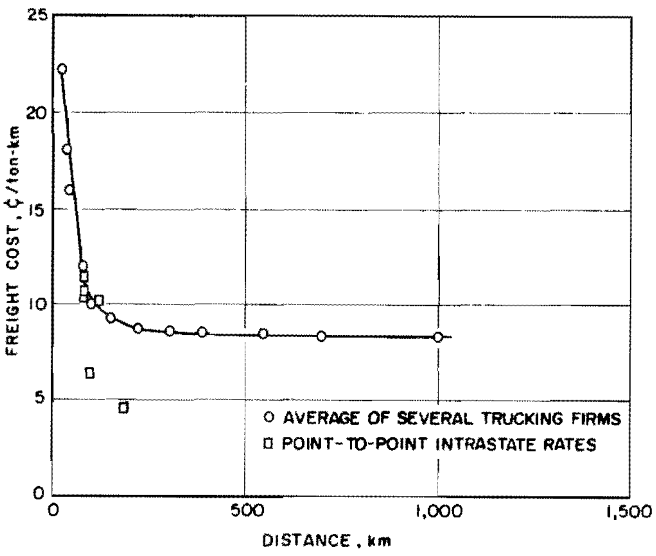

Figure 9. Transportation Rates/ton-km as Related to Distance.

TABLE 3. COST OF TRANSPORTATION OF AMMONIA BY TRUCK (AVERAGE OF RATES FROM SEVERAL TRUCKING COMPANIES)

		Distance, km	$/ton	¢/ton-km
		0 to 32	7.16	22.4 and up
		80	9.50	11.9
		153	14.35	10.7
		225	19.66	8.7
		306	26.18	8.6
		386	32.84	8.5
		467	39.30	8.4
		547	46.44	8.5
		627	52.93	8.4
		708	58.60	8.3
		788	65.40	8.3
		1,000	83.51	8.3
Point-to-Point Rates (Intrastate)				
From	To			
Omaha	Fremont, NE	69	7.23	10.5
Dubuque	Manchester, IA	72	7.82	10.9
Winona	Rochester, MN	72	8.49	11.8
Cincinnati	Circleville, OH	129	13.33	10.3
Lathrop	Fresno, CA	191	9.03	4.7
Lathrop	Sacramento, CA	97	6.17	6.4

used in the spring. In any given area most of it is used within 1 month. This means that most of the ammonia used for direct application must be stored in the market areas--part of it in local retail storage facilities and part in large terminals served by pipelines, barges, rail, or some combination. Since the annual throughput of the storage terminals probably is no more than twice their capacity, terminal storage costs are high. A typical total cost for storage and transport of ammonia produced in Louisiana, Texas, or Oklahoma to a retail center in Iowa might be:

Pipeline transportation from plant to terminal	$10.00
Terminal storage charges	13.70
Truck transport from terminal to retailer	9.50
TOTAL	$33.20

The above total does not include the retailer's storage cost or transport to farms. While this cost may seem high, it should be noted that to supply an equivalent amount of nitrogen as urea (8.0 million tons) or ammonium nitrate (10.9 million tons) probably would be much more expensive. In addition, the cost of converting ammonia to urea or ammonium nitrate would have to be considered.

It should be noted that the hypothetical retailer in Iowa has several alternatives open to him. He may receive direct shipments from the ammonia producer by rail at a cost of about $25. He may receive truck shipments loaded directly from a pipeline. The cost would be about $20.99 ($10 pipeline transport plus $1.29 truckloading charge plus $9.70 truck transport charge). He may receive shipments by rail or truck from a river terminal served by barges. Some of these alternatives may be attractive for filling the retailer's storage facilities during the offpeak season, but during the peak season all transport facilities are overtaxed. When the retailer needs to replenish his supply during the peak season, he may have no other choice than to receive ammonia from whatever terminal storage facility can supply his needs.

Comparison of Various Methods of Ammonia Transportation

Figure 10 shows a comparison of ammonia transportation costs by pipeline, rail, and truck for U.S. conditions. Barge transport is not shown because the cost depends on the character of the waterway more than the distance. However, it is evident that barge transportation is the most economical between points that are located on waterways that permit passage of tows of several large barges. For example, a comparison of costs for roughly equivalent distances follows:

From Southern Louisiana

To	Distance	Method	$/ton
Minneapolis, MN	1,700	barge	7.44
Spencer, IA	1,723	pipeline	15.76
Peoria, IL	1,135	barge	8.38
Palmyra, MO	1,182	pipeline	10.41

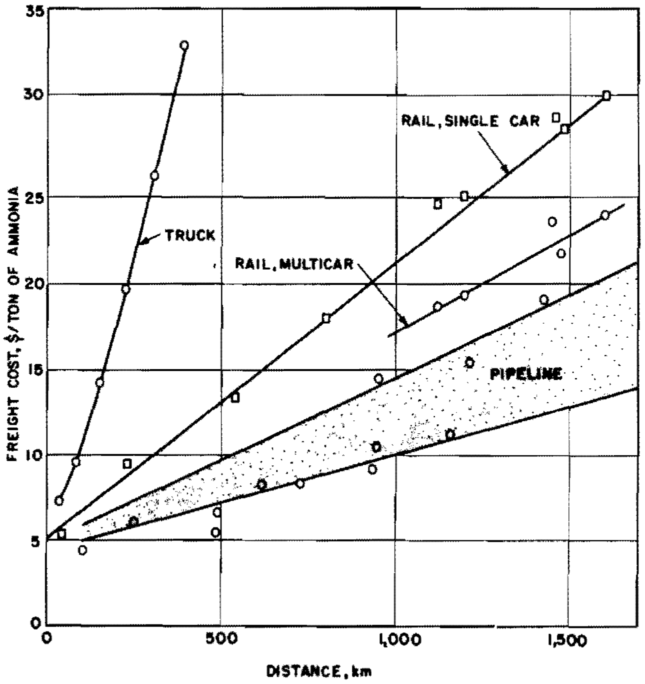

Figure 10. Comparison of Transportation Costs by Pipeline, Rail, and Truck.

Barge transportation is, of course, limited to points on navigable waterways. Another disadvantage is that barge transportation on rivers is likely to be interrupted by ice, floods, and periods of low water. Terminal storage capacity must be increased in relation to throughput to provide for these interruptions. As a result, increased terminal costs may at least partially offset the lower transport cost. The extent of this disadvantage depends strongly on the character of the waterways.

Pipeline transport of ammonia appears to be substantially cheaper than rail while truck transport is the most expensive of all. However, many more points can be reached by truck than by rail, and for most developed countries more points can be reached by rail than by pipeline or waterways. The comparison in figure 10 applies only to the United States and is not necessarily valid for other countries. Also, it relates to transportation costs only and does not include terminal and storage costs.

For the world in general only a few broad observations can be made. Obviously, transportation by ship is the only method available for overseas transport, and it is also the lowest cost method of transport between two points that are accessible to maritime shipping and are a substantial distance apart. Two qualifications should be noted: (1) ocean freight rates are likely to rise substantially and (2) the cost of maritime terminals, harbor improvements, piers, jetties, etc., must be taken into account. For example, if two points are on a tidewater and are also connected by land, it is quite possible that land-based transportation would be more economical in some cases.

For shipment within a country or region, transport by barge or coastal vessels may be economical if there are conveniently located ports or inland waterways and if the volume of shipping is sufficient to justify terminal costs.

Transport by pipeline may be a good choice between points connected by land, e.g., from an ammonia plant to one or more fertilizer plants located in market areas. However, the cost of ammonia pipelines is substantial and varies widely depending on terrain and cost of acquiring right-of-way. The economies of pipeline transport are favored by high volume use and by an even use pattern which minimizes storage terminal costs.

Transport by rail may be the best choice for moderate quantities especially when several scattered fertilizer plants are served by one ammonia plant. Obviously, a suitable rail network must be available and, even so, the cost of suitable rail tank cars is substantial.

Truck transport is relatively expensive but may be the only feasible means in some cases and is much more flexible than other networks.

Finally, there are many cases where some combination of methods of transport must be considered along with storage terminals at transfer points. Obviously, estimates of the cost of alternative combinations can be complicated. When ammonia is not the desired end product, alternatives of producing the end product at the ammonia plant and transporting it to market areas must also be considered. Although shipping ammonia by any method is more expensive than shipping solid nitrogen fertilizers or nonpressure liquids per ton of product, it is often the least expensive per ton of nitrogen because of its high concentration (82% N). However, the estimates of the economics of the entire alternative production, distribution, and marketing system are needed to determine whether systems involving ammonia shipment are economical and, if so, what method of transport is preferable.

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VIII Ammonium Salts, Nitric Acid, and Nitrates

Introduction

As mentioned previously, ammonia is the source of more than 95% of the chemical nitrogen fertilizer currently produced in the world. Ammonia may be used directly as a fertilizer (see chapter X) or converted to ammonium salts, nitrates, or urea. No accurate estimates are available as to the percentage of these various products in world use. In Europe the leading form of nitrogen fertilizer is ammonium nitrate, either as such, in mixtures with calcium carbonate, or in compound fertilizers including nitrophosphates. In Asia urea is the leading form either as such or in compound fertilizers. In North America anhydrous ammonia is the leading form of nitrogen fertilizer. Individual countries within these and other continents may have other preferences.

The purpose of this chapter is to describe the technology of production of ammonium salts for fertilizer use other than ammonium phosphates (which are covered in chapter XIV) and the production of nitric acid and nitrates except potassium nitrate which is covered in chapter XVIII.

Ammonium Sulfate

Ammonium sulfate was once the leading form of nitrogen fertilizer, but it now supplies a relatively small percentage of the world total nitrogen fertilizer because of the more rapid growth in use of urea, ammonium nitrate, and anhydrous ammonia. The actual tonnage of ammonium sulfate capacity has not decreased but has remained fairly steady in recent years at about 6 million tons of nitrogen not including ammonium sulfate formed by the use of sulfuric acid and ammonia in compound fertilizer processes (1). The main advantages of ammonium sulfate are its low hygroscopicity, good physical properties (when properly prepared), chemical stability, and good agronomic effectiveness. It is a good source of sulfur as well as nitrogen. Its reaction in the soil is strongly acid forming (see chapter XXII) which is an advantage on alkaline soils and for some crops such as tea; in some other situations its acid-forming character is a disadvantage. Its main disadvantage is its low analysis (21% N), which increases packaging, storage, and transportation costs. As a result, the delivered cost at the farm level usually is higher per unit of nitrogen than that of urea or ammonium nitrate. However, in some cases, ammonium sulfate may be the most economical source of nitrogen when the transportation distance is short, when it is available as a byproduct at low cost, or when a credit can be taken for its sulfur content.

Ammonium sulfate is available as a byproduct from the steel industry (recovered from coke-oven gas) and from some metallurgical and chemical processes. One large source is a byproduct from production of caprolactam.

Properties of Ammonium Sulfate

Table 1 shows the more important properties of crystalline ammonium sulfate.

TABLE 1. PROPERTIES OF PURE AMMONIUM SULFATE

Color	White	
Molecular weight	132.14	
N content	21.2%	
Density of solid, 20°/4°C	1.769	
Specific gravity of saturated solutions	1.2414 at 20°C 1.2502 at 93°C	
Specific heat of solid	0.345 at 91°C	
Specific heat of saturated solutions	0.67 at 20°C 0.63 at 100°C	
Heat of crystallization	11.6 cal/kg in 42% solution	
Heat of dilution	6.35 cal/kg from 42% to 1.8% solutions	
Melting point	512.2°C	
Thermal stability	Decomposes above 280°C	
pH	5.0	
Loose-bulk density	962 kg/m^3	
Angle of repose	28°	
Stoichiometric requirements, tons per ton of product	NH_3	0.2578
	H_2SO_4	0.7422
Critical relative humidity	At 20°C	81%
	At 30°C	81.1%
Solubility, g/100 g of water		
At 0°C	70.6	
At 100°C	103.8	

Production Methods

Several different methods are used for ammonium sulfate manufacture, in accordance with available raw materials and local conditions.

The principal methods are:

1. Reacting ammonia and sulfuric acid in a saturator-evaporator under vacuum or at atmospheric pressure and recovering the crystals via a centrifuge or filter;
2. Scrubbing town gas or coke-oven gas with sulfuric acid in saturator units of special design and recovering the crystals by centrifuging or filtration;
3. Reacting ammonium carbonate with anhydrite or gypsum derived from natural or byproduct sources, removing the calcium carbonate by filtering, evaporating, and crystallizing ammonium sulfate from the mother liquor prior to centrifuging;
4. Evaporating byproduct liquors containing ammonium sulfate produced from other processes and separating the nearly pure salt by: (a) crystallization and centrifuging or alternatively

(b) recovering by slurry granulation on a moving bed and recycling in a drier-screening system to give granules of the required size range;

5. Directly reacting gaseous ammonia with sulfuric acid in a spray tower to form a dry, amorphous product;
6. Simultaneously producing ammonium sulfate and other ammonium salts in granulated fertilizer processes to produce phosphate, nitrate, and nitrophosphate multinutrient fertilizers containing ammonium sulfate;
7. Using other miscellaneous processes, such as recovering ammonium sulfate from SO_2 in flue gas or in sulfuric acid tail gas (see chapter XII), which are in use or have been proposed.

Crystallization Technology

Except in special cases, such as those described in subparagraphs 4, 5, and 6 above, crystallization is of major importance in ammonium sulfate production, as well as in the manufacture of other salts. Hence, it is appropriate at this stage to review briefly the fundamental process and design features which control crystal formation and influence plant performance (2, 3, 4, 5).

Two major considerations arise in crystallization technology--first, the formation of nuclei in a supersaturated solution and, secondly, the growth of these particles to the product size-range required. In both of these stages, the driving force is the degree of supersaturation in the mother liquor, which, if allowed to rise appreciably, may induce uncontrollable nucleation. Subsequent crystal growth, however, is generally directly proportional to supersaturation and, as a rule, is easier to control than nucleation.

When a solution is supercooled to a point just before fine, solid nuclei appear, it is termed metastable. After initial precipitation, this solution is said to be unstable or labile, and a constant addition of metastable liquor will cause each nucleus to grow into a single crystal. Thus, control of metastable conditions is a major factor in the design and operation of crystallization units; critical items include residence time, agitation, and equipment surface characteristics, as well as the pH, temperature, and soluble and insoluble impurities contained in the liquor. Hence, for continuous, stable operation, an equilibrium has to be established whereby the number of grown crystals removed equals the number of fresh nuclei formed. Under these conditions, uniformly sized crystals should result when a constant feed is supplied, and average crystal size becomes a function of the production rate divided by the nucleation rate.

When the production rate is held constant, as in continuous operation, average crystal size is thus largely controlled by nucleation rate. One gram of typical nuclei may represent 1 billion particles; hence, a continuous crystallizer must provide a way of controlling the number of nuclei and fines produced in this system and also contain provisions for classifying the product in order to minimize subsequent washing, drying, and storage problems. Modern crystallizers are designed to incorporate these features and are also provided with control equipment to ensure virtually automatic operation.

After growth and classification to the required size, ammonium sulfate crystals are removed from the unit by various means, such as a salt catchpot, an airlift, or a helical screw; separated from the mother liquor by a centrifuge; washed with water (and/or ammonia liquor); and dried in a rotary drier prior to screening and storage. In some plants, the production of large, well-washed crystals and the use of high-efficiency centrifuges eliminate the need for a drier. However, when small crystals are produced and particularly when impurities are present, drying, cooling and, perhaps, conditioning with an anticaking agent may be unavoidable. When large, closely sized crystals are desired, the crystals may be screened and the fines redissolved and returned to the crystallizer.

Other methods of crystal recovery and treatment include the use of a top-feed rotary vacuum filter-drier and also the granulation of small crystals by roll compaction equipment. Such machines are especially suitable for the relatively small tonnages of sulfate produced in some coke-oven byproduct units. In a few instances, pugmills or drum-type pelletizers are used to produce granulated sulfate from byproduct caprolactam liquor or other waste streams containing ammonium sulfate in appreciable quantities.

Chemical and Physical Specifications

Fertilizer-grade ammonium sulfate specifications normally indicate a minimum nitrogen content, which is usually not less than 20.5%. Limitations on free acidity and free moisture are also generally demanded; typical figures are 0.02% for free H_2SO_4 and 0.2% for free H_2O. Occasionally, maximum values for certain organic or inorganic impurities may also be specified for byproduct material.

Crystal size-range specifications depend on customer requirements and the type of application. For direct application or bulk blending, large crystals, mainly in the range of 1-3 mm, are preferred although somewhat smaller crystals may be acceptable in some countries for direct application, such as 90% retention on an 0.8-mm screen. To obtain crystals of this size, considerable design and operating skill is usually needed, and in some plants additives are used to promote crystal growth or modify the crystal shape (6). For use in production of compound fertilizers, small crystals are acceptable. There is a trend toward production of small crystals (mainly 0.2-0.8 mm) which are sold as is to producers of granular compound fertilizers or are granulated by roll compaction for direct application or bulk blending. The roll compaction granulation process is described in chapter XVIII.

Production Details

Combined Reaction-Evaporation Methods--Large tonnages of ammonium sulfate are produced from anhydrous ammonia and strong sulfuric acid in continuous saturator-crystallizer units operating either under vacuum or atmospheric pressure. In installations of the vacuum type, the heat of reaction is removed by evaporating water either present in the feed acid or added to the system for temperature-control purposes. This technique is also used for saturators of the atmospheric type; alternative cooling can be achieved in the latter by blowing large volumes of air through the slurry.

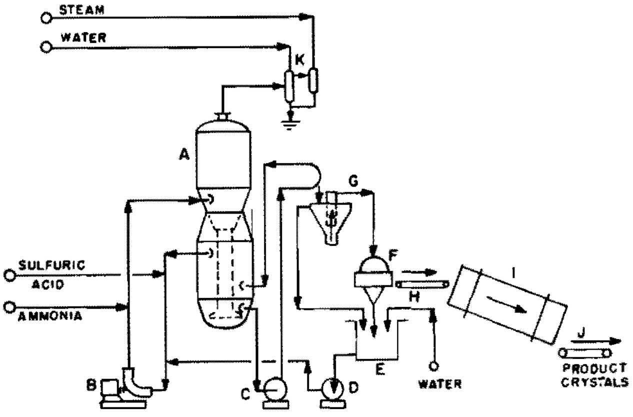
The reaction between gaseous, anhydrous ammonia and sulfuric acid can be shown as follows:

$$2NH_3(g) + H_2SO_4(l) \rightarrow (NH_4)_2SO_4(s) - 67,710 \text{ cal/g-mole}$$

In practice the exothermic heat of the reaction given above is approximately equal to 2,350 kcal/kg of N.

Units of the vacuum type are designed in accordance with the basic principles of crystallization previously reviewed and are usually built in the form of a suspension vessel surmounted by a flash chamber. Ammonia and sulfuric acid are introduced via a slurry recycle line, wherein they react and superheat the recirculating slurry, which is subsequently flashed in the upper chamber at a reduced pressure generally between 55 and 58 cm of mercury. The loss of water in this zone supersaturates the slurry, which recirculates to the lower suspension vessel via an internal pipe and comes into contact with small crystals and nuclei, thereby inducing further crystal growth in terms of size rather than in number. Slurry is recycled by a thermal syphon and/or by an external pump, and as it is brought into contact with newly added reactants, the exothermic heat produced destroys undesirable nuclei and fines. Skilled design of the suspension vessel and the means of slurry withdrawal permits considerable size classification to be attained in the unit, and proper instrumentation ensures long periods of uniform operation.

This type of crystallizer is generally known as the "Krystal" or "Oslo" unit and was developed in Norway by Isaacssen and Jeremiassen (7). Figure 1 illustrates diagrammatically the use of forced circulation in conjunction with this design of crystallizer for ammonium sulfate production. During operation, it is important to control the pH within fairly close limits, e.g., 3.0-3.5, since a lower value yields undesirable, thin crystals. Excessive acidity also promotes an overgrowth of crystals, especially in pipelines, and necessitates frequent redissolving or "killing" with steam. Insufficient acidity, on the other hand, not only produces inferior crystals which are difficult to wash and store but may cause ammonia losses as well. For these reasons, some producers maintain free acidity of 1.0-1.5 g of H_2SO_4/liter of solution.



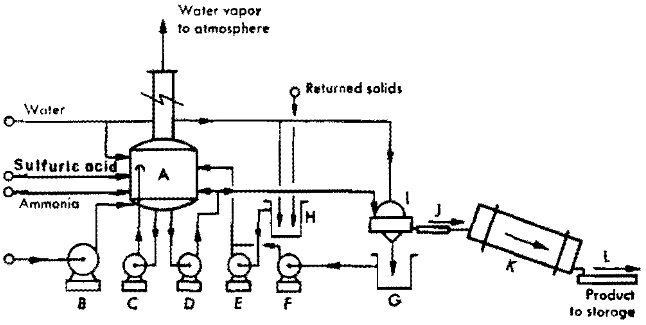
Legend

A "Krystal" type of vacuum evaporator-crystallizer
B Forced-circulation pump
C Slurry-recirculation pump
D Mother-liquor recycle pump
E Mother-liquor tank
F Continuous or batch centrifuge
G Slurry concentrator
H Drier conveyer
I Rotary drier
J Dried-product conveyer
K Vacuum condenser-ejector unit

Figure 1. "Krystal" Type of Unit for Ammonium Sulfate Production.

Another popular type of reduced-pressure crystallizer is the draft tube baffle unit, in which a vigorous upward slurry recirculation is maintained by means of an internal impeller and draft tube (8). Growing crystals are brought to the surface of the flashing slurry, where supersaturation induces maximum crystal growth, and sufficient nuclei are present to minimize scale formation inside the unit.

Atmospheric pressure units are of several types and are preferred by some producers to vacuum crystallizers, especially for small and medium outputs, because of their simplicity and somewhat lower investment costs. Ammonia can be added via a sparger tube or a jet type of mixer. In one proprietary process, a simple absorption column incorporating a few large slotted bubble-hoods is used. Another design employs a single vessel for both reaction and crystallization, and reaction heat is removed by evaporation of water, supplemented in many cases by air blowing, as shown in figure 2. In other designs, separate neutralizing and crystallizing vessels are used to provide easier operation and closer control. An optimum balance between cooling-air energy and crystal yield is usually obtained when crystallization temperatures are controlled in the range of 63°-66°C.



Legend

A Evaporator-crystallizer
B Air blower
C Liquor-recirculation pump
D Slurry-recirculation pump
E Makeup pump
F Mother-liquor pump
G Mother-liquor tank
H Sump tank
I Batch or continuous centrifuge
J Drier conveyer
K Rotary drier
L Product conveyer

Figure 2. Atmospheric-Pressure Process for Ammonium Sulfate Manufacture.

In most cases, crystals are recovered from ammonium sulfate slurry by recycling through the continuous or the automatic batch type of centrifuge, wherein the product is screened and spin-dried, washed with water and weak ammonia, and again spin-dried before being conveyed to the drier. In some plants, continuous top-feed filters are used instead of centrifugals. As previously mentioned, for small outputs, top-feed filter-driers can sometimes be employed with advantage since the product can be separated, washed, and dried in a single machine.

As is well known, ammonium sulfate liquors are quite corrosive, and wetted parts of equipment are usually made of stainless steel or of rubber-lined mild steel. In some earlier plants, vessels constructed in wood and mild steel were employed, and corrosion was minimized by careful pH control. Modifiers intended to improve crystal size and shape include small amounts of trivalent metallic salts. Such corrosion inhibitors as traces of phosphoric acid or arsenic compounds are also added in some cases.

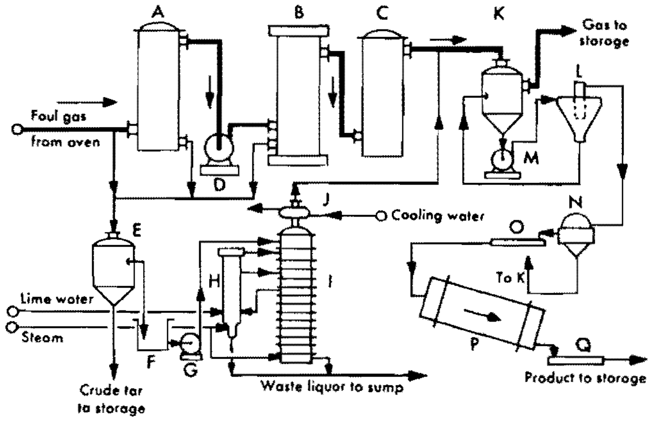
Gasworks Byproduct Methods--Before the availability of synthetic ammonia in the early 1920s, virtually all ammonia was obtained from solid-fuel carbonization plants. Typical bituminous coals used for gas and coke production contain about 1%-2% of nitrogen, and some 15%-20% of this can be recovered as ammonia, amounting to approximately 2.5-3.0 kg of NH_3/ton of coal used. Most of this ammonia is believed to be formed at temperatures in the range of 1000°C, after coking has taken place. Hence, most byproduct ammonia is usually associated with high-temperature carbonization units, e.g., coking plants for iron and steel production, where the amount of ammonium sulfate produced may be equivalent to about 20 kg/ton of steel.

Ammonia is removed from gas for two principal reasons: first, to prevent subsequent corrosion and plugging problems in distribution mains and fittings and, secondly, to produce a useful byproduct at a reasonable profit. However, in more recent years, world ammonium sulfate prices have fluctuated widely, and, from time to time, byproduct material from gasworks and coke ovens has been sold at price levels not much greater than the cost of the sulfuric acid needed as a raw material. As a result, some producers have converted their units to ammonium phosphate production as a more profitable alternative. Other byproducts recovered from gas-washing units, because of necessity or additional financial return, include ammonium thiocyanate, ferrocyanides, pyridines, and tar.

Three principal methods are available for ammonia and/or ammonium salt recovery; they are known as the direct, indirect, and semidirect processes, respectively. In the first method, the entire gas stream is cooled to remove as much tar as possible and is then passed through a saturator of the bubbler type (or, in more recent plants, a scrubber of the spray type), wherein it is washed with sulfuric acid. The ammonium sulfate slurry produced is withdrawn, centrifuged, washed, dried, and sent to storage. Advantages of this type of unit include high recoveries, relatively low investment and operating costs, low steam needs, and small effluent liquor volumes. Nevertheless, in many instances, the product is unavoidably contaminated with tar and pyridines and may be unacceptable unless, perhaps, it is recrystallized prior to sale. In addition, chlorides present in the fuel or water may react to form ammonium chloride and create additional corrosion problems unless linings of rubber or plastic material are used. Furthermore, except in cases where a separate crystallizer is employed, flexibility with regard to size, shape, and purity of product is likely to be very limited since it becomes difficult to maintain an optimum balance between the free acidity needed to suppress impurities and the optimum pH needed to promote good crystal growth.

Earlier problems of direct operation led to the development of the indirect method, whereby the gases are first cooled by contact with recirculating wash liquor, followed in some cases by a further scrubbing with water. Combined liquors are sent to the upper section of an ammonia still of the bubble-cap type, in which contact with steam releases the "free" ammonia present as ammonium carbonate, ammonium sulfide, and other easily dissociated salts. The liquor then passes to an adjoining lime leg, where treatment with lime liquor decomposes the "fixed" ammonium salts, e.g., ammonium chloride. Steam passing upwards from the base of the column strips virtually all of the ammonia gas produced, which is recovered as a crude ammonia solution or is sent to a sulfuric acid washer for ammonium sulfate production. Advantages of this method include the production of a salt substantially free from impurities and also having considerable flexibility, plus an ability to make aqua ammonia and derivatives. However, operating costs are high, and effluent disposal problems may arise. In addition, ammonia losses may be appreciable, owing to incomplete reaction and absorption.

The semidirect process offers a compromise between direct and indirect operation, whereby the gas is first cooled and washed to deposit tar and an aqueous condensate (9). The latter is "sprung" in a relatively small ammonia still, and the released NH_3 is combined with the main gas stream, which is reheated to about 70°C and scrubbed with a solution containing nearly saturated ammonium sulfate and 5%-6% of sulfuric acid at about 50°-70°C, in units either of the spray-absorber type or of the older saturator type incorporating a cracker pipe (or bubbler ring.) Because this process gives ammonia recoveries greater than those attainable by direct operation and also produces a salt largely free from tar, pyridine, and other impurities, it has become the most popular for large installations. Figure 3 shows the basic flow diagram of a semidirect gas scrubber/ammonium sulfate unit, as well as an illustration of an ammonium sulfate saturator.



Legend

A	Primary gas-cooler	J	Dephlegmator
B	Electrostatic tar-precipitator	K	Sulfate saturator-crystallizer
C	Gas reheater	L	Slurry concentrator
D	Main gas-blower	M	Slurry feed-pump
E	Tar separator	N	Batch or continuous centrifuge
F	Crude ammonia liquor storage	O	Drier conveyer
G	Still feed-pump	P	Rotary drier
H	Lime leg	Q	Product conveyer
I	Ammonia still		

Figure 3. Semidirect Process for Ammonium Sulfate Production from Coke-Oven Gas.

Several varieties and modifications of these systems are found throughout the world, principally developed by the Koppers, Otto and Wilputte organizations (10).

Ammonium Carbonate-Gypsum Process--This method, which is also known as the Merseburg Process, was originally developed in Germany and has long been used in Austria, India, Pakistan, and the United Kingdom (11, 12). It is based on combining ammonia and carbon dioxide to produce ammonium carbonate, which is then reacted with gypsum or anhydrite (of natural or byproduct origin) to yield ammonium sulfate and calcium carbonate, as follows:

$$NH_3 + H_2O \rightarrow NH_4OH - 8{,}320 \text{ cal/g-mole}$$

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O - 22{,}080 \text{ cal/g-mole}$$

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O - 3{,}900 \text{ cal/g-mole}$$

Under certain circumstances, this process has several advantages, for example, countries without indigenous sulfur supplies but having natural or byproduct sources of gypsum (or anhydrite) can produce ammonium sulfate without purchasing sulfur from abroad (13). In addition, the byproduct calcium carbonate can be used for cement production or other purposes, such as for agricultural lime or in calcium ammonium nitrate manufacture. One disadvantage is the large amount of energy (steam) required to recover solid ammonium sulfate from the relatively dilute solution.

In one Indian plant (Sindri), ammonia gas is absorbed in water and carbonated at a pressure of about 2.1 kg/cm² (or 30 psig) in two series-connected aluminum towers since this pressure allows a higher cooling-water temperature to be employed than if atmospheric pressure were used. Carbon dioxide is introduced at the base of the primary tower, which is packed with 5-cm (2-in) stoneware rings wetted with a solution of ammonium hydroxide and recycling ammonium carbonate. Final absorption is undertaken in the secondary tower, and reaction heat is removed by recirculating liquor through water-cooled heat exchangers in closed circuit with each tower. The preferred liquor strength corresponds to approximately 170 g of ammonia and 225 g of carbon dioxide per liter. Stainless steel is used for the wetted parts of pumps, and liquor piping is made of aluminum.

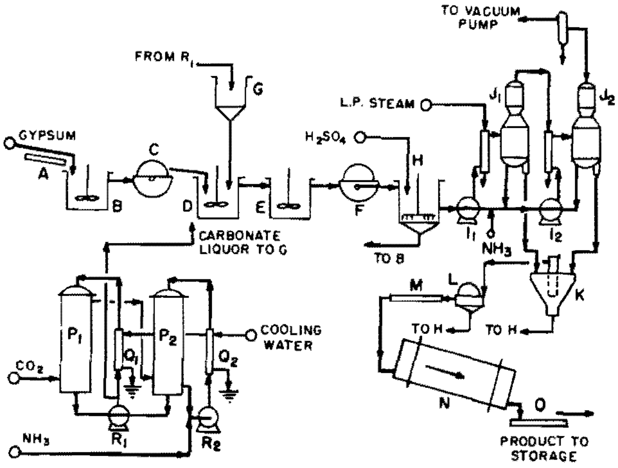
In a more recent Indian plant (Fertilizers and Chemicals Ltd., Travancore), jet absorbers are used to prepare both the ammonia solution and the ammonium carbonate liquor in conjunction with a carbonating tower. Cooling is undertaken by recycling liquor through water-cooled heat exchangers, and the heat of reaction thereby vaporizes the liquid anhydrous ammonia used in the process. When the desired strength has been reached, the solution is sent to storage and subsequent reaction. The relation between liquor strength, moisture in the gypsum, and the resulting ammonium sulfate liquor concentration has been reported by George and Gopinath (14).

When natural gypsum or anhydrite is used, it is crushed and ground before reaction. In one case, the preferred final size is about 90% through 120-mesh although, under certain circumstances, there are indications that a coarser grade is permissible. When using byproduct gypsum of phosphoric acid-plant origin, it may be preferable to remove impurities by repulping the filter cake in an agitated vessel (or, alternatively, by scalping in liquid cyclones) prior to washing and dewatering to the maximum extent on a drum or disc filter before reacting with ammonium carbonate. Some methods of purifying byproduct gypsum will be described in chapter XIII.

Reaction can be undertaken either in a series of wooden vessels or mild-steel tanks fitted with steam coils and agitators, and the reaction train is usually designed to give a total retention time of 4-6 hours. The slurry produced is filtered and the calcium carbonate cake washed and dewatered on continuous vacuum machines of the traveling-belt type, or alternatively, on a two-stage drum-filter installation provided with intermediate repulping. (In some earlier plants, plate-and-frame filter presses were installed for this purpose.) Final clarification by pressure filtration or settling is sometimes employed to ensure maximum purity of product, followed by neutralization with sulfuric acid and heating to about 110°C to remove excess ammonia prior to concentration and crystallization. The evaporator feed-liquor usually contains about 500-520 g of ammonium sulfate and less than 0.1 g of ammonia per liter.

Evaporation is undertaken in continuous multiple-effect evaporator crystallizers, and production can be supplemented, if desired, by adding ammonia and sulfuric acid to the crystallizer recirculating line as previously described. Crystals of the required size range are separated and washed in a centrifuge, dried in a rotary drier at 120°-130°C, and sent to storage. Alternatively, a vertical tray type of drier-cooler can be used since this is said to give reduced crystal breakage and dust formation, compared with the use of a rotary drier and cooler. A diagram of a gypsum-process ammonium sulfate plant is given in figure 4.

Recovery of Byproduct Liquor--Byproduct units have been installed in many countries for producing ammonium sulfate from the waste streams of caprolactam, acrylonitrile, and certain other processes. In such cases, the waste liquor should normally contain at least 35% of ammonium sulfate in solution. Otherwise, recovery may not be justified unless for the purpose of preventing stream pollution. Since recovery often is unprofitable, processes have been developed recently for making caprolactam that produce less byproduct ammonium sulfate or none (15).



Legend

A	Gypsum conveyer
B	Gypsum washing tank
C	Gypsum dewatering filter
D	Primary reactor
E	Secondary reactor
F	Calcium carbonate filter
G	Ammonium carbonate storage tank
H	Sulfate-liquor clarifier
I_1, I_2	Evaporator feed-pumps
J_1, J_2	Vacuum evaporator-crystallizers
K	Slurry concentrator
L	Batch or continuous centrifuge
M	Drier conveyer
N	Rotary drier
O	Product conveyer
P_1, P_2	Ammonium carbonate towers
Q_1, Q_2	Heat exchanger-coolers
R_1, R_2	Carbonate liquor recirculating pumps

Figure 4. Gypsum Process for Ammonium Sulfate Production.

Occasionally, spent sulfuric acid from petroleum refineries, petrochemical plants, and soap factories can be used for ammonium sulfate production if impurities do not cause insurmountable frothing or corrosion problems or render the product unacceptable. If the acid is too badly contaminated, it may be more expedient to burn off the impurities in a specially designed furnace and to produce fresh acid for ammoniation. Another alternative is to ammoniate the contaminated acid and granulate the slurry in a drum or pugmill type of granulating system, similar to those used for producing granular fertilizers.

Spray-Tower Ammoniation--Substantial tonnages of ammonium sulfate have been made for many years in Japan in spray towers from the chamber or contact type of sulfuric acid and anhydrous ammonia. The acid is sprayed into ammonia vapor inside the tower, and the heat of reaction produces a dry, amorphous product, mostly below 300-mesh, which is continuously removed from the base of the tower by a screw conveyer. This form of ammonium sulfate is particularly suitable for use in granular compound fertilizers.

Double- and Mixed-Salt Production--By ammoniating mixtures of sulfuric and nitric acid or by combining their ammonium salts in special ways, it is possible to produce compounds containing both ammoniacal and nitrate nitrogen in the form of true double salts. Three double salts have been identified:

$$(NH_4)_2SO_4 \cdot NH_4NO_3$$

$$(NH_4)_2SO_4 \cdot 2NH_4NO_3$$

$$(NH_4)_2SO_4 \cdot 3NH_4NO_3$$

One German process produces an ammonium sulfate nitrate corresponding approximately to $(NH_4)_2SO_4 \cdot NH_4NO_3$ and containing 62% ammonium sulfate and 38% ammonium nitrate. Total nitrogen content is 26%, about three-quarters being present in ammoniacal form and one-quarter as nitrate nitrogen. It is made by ammoniating the requisite mixture of sulfuric and nitric acids, evaporating to a moisture content of 3%, adding about 1% of ferrous sulfate (to reduce subsequent caking), cooling to 100°C, chilling, and flaking. After further conditioning by spraying with dilute ammonia solution, the double salt is granulated (sometimes with additional ammonium sulfate), dried, cooled, and bagged.

In a simpler process, also of German origin, ammonium nitrate solution is evaporated under vacuum to a 95% concentration, cooled to about 130°C, and reacted with solid ammonium sulfate in a pugmill granulator system having a recycle ratio of 2 or 3:1 of product until a pH of 4.0 is attained, after which the product is dried, cooled, and bagged. Recently, processes for prilling the product have been developed.

For several years, TVA produced an ammonium nitrate-sulfate containing 30% N mainly for use in sulfur-deficient areas. The process involved ammoniation of a mixture of nitric and sulfuric acid followed by pan granulation of the resulting slurry. The product consisted mainly of the double salt $(NH_4)_2SO_4 \cdot 3NH_4NO_3$. Compared with ammonium sulfate, ammonium sulfate nitrate of the usual grade (26% N) contains an additional 5% N. Its storage properties are superior to ammonium nitrate or mixtures of solid ammonium sulfate and ammonium nitrate since free ammonium nitrate is absent. However, the large-scale manufacture of urea, as well as of binary and ternary high-analysis fertilizers in recent years, has diminished the importance of ammonium sulfate nitrate in most countries.

When mixtures of sulfuric acid and phosphoric acid are ammoniated, a variety of mixed and double-salt products can be made. One of the most popular is "ammo-phos," containing 16% N and 20% P_2O_5. After ammoniation, the slurry formed is granulated in a pugmill or drum unit, then dried and screened (and sometimes cooled) to give a water-soluble product containing about two-thirds ammonium sulfate and one-third ammonium phosphate by weight. This material has good storage properties under normal conditions (see chapter XIV).

Granular urea-ammonium sulfate mixtures have been produced by TVA for use in sulfur-deficient areas. The process is similar to the pan granulation of straight urea (chapter IX). One such product contained 40% N and 4% S (16).

Miscellaneous Processes--Numerous processes have been proposed or developed for recovering sulfur from flue gas based on scrubbing with ammonia or injection of ammonia into the flue gas; these processes yield ammonium sulfite, bisulfite, sulfate, or mixtures of these compounds. Ammonium sulfate can be produced as a final product, and some commercial use has been reported in Japan. However, the demand for ammonium sulfate is small in comparison to the potential supply from flue-gas sulfur; therefore, most processes involve disposal of the sulfur as calcium sulfate or sulfite and recycling of the ammonia.

Storage and Handling

Several factors contribute to trouble-free storage of ammonium sulfate and other fertilizers. First, the product should be of uniform crystal size and should contain a low percentage of fines. Secondly, it should be dry and preferably have below 0.1% free moisture. Thirdly, no free acidity should be present on the crystal surfaces. Fourthly, the product should be cooled with dry air under controlled conditions after drying if the ambient temperature and humidity are sufficiently high to cause subsequent moisture condensation after cooling in a bulk storage pile or in sealed bags.

Ammonium Chloride

General Information

Ammonium chloride contains 26% N when pure; the fertilizer-grade product contains 25% N. Global production capacity in 1978 is 365,000 tons of N per year of which two-thirds is located in Japan (17); most of the remaining one-third is in India. Much of the Japanese product is exported; exports during 1974-78 ranged from 400,000-600,000 tpy of product. About three-quarters of the exports were to China; the remainder went to 11 countries, mainly in east Asia. Domestic consumption of ammonium chloride in Japan was 170,000 tons in 1977 which presumably does not include its use in compound fertilizers (18). Ammonium chloride is used in a variety of compound fertilizers (19); examples are:

18-22-0	(ammonium phosphate-chloride)
16-0-20	(ammonium-potassium chloride)
14-14-14	
12-18-14	

Also ammonium chloride is used in other grades of compound fertilizers in combination with urea or ammonium sulfate.

Coarse crystalline or granular forms are preferred for direct application; whereas, fine crystals can be used in compound fertilizers.

Advantages of ammonium chloride are that it has a higher concentration than ammonium sulfate and a somewhat lower cost per unit of N (in Japan). It has some agronomic advantages for rice (20); nitrification is less rapid than with urea or ammonium sulfate and, therefore, N losses are lower and yields are higher.

Although ammonium chloride is best known as a rice fertilizer, it has been successfully tested and used on other crops such as wheat, barley, sugarcane, maize, fiber crops, sorghum, etc., in a variety of climatic conditions. Of particular note, however, is the use of ammonium chloride on palms. The importance of chlorine as an indispensable nutrient for coconut and oil palms was first reported in 1971 by von Uexkull, et al., who noted that chlorine content was closely related to the amount of copra obtained. Further studies by Menoza in 1975 indicated a linear response of coconut to chlorine in terms of copra yield per tree. The highest copra yield was almost 70% above the yields obtained from trees receiving no chlorine (17).

Ammonium chloride contains a very high (66%) chlorine content; hence, it can be regarded as a very suitable fertilizer for coconut where the soil is sufficient in potassium but deficient in nitrogen and chlorine. Where potassium is also deficient in soils, the combined application of ammonium chloride and potassium chloride could be more effective.

Ammonium chloride is as highly acid forming as ammonium sulfate per unit of N which can be a disadvantage. Other disadvantages are its low N content compared with urea or ammonium nitrate and the high chloride content which can be harmful on some crops or soils.

Nevertheless, it is possible that ammonium chloride fertilizer could become a useful outlet for the surplus supplies of chlorine or byproduct hydrochloric acid that arise from time to time in various countries, provided the above-mentioned precautions were observed. Another useful feature of ammonium chloride is that it can be applied to rice with safety in the presence of certain fungi which would reduce ammonium sulfate to toxic sulfides. The industrial uses of ammonium chloride are worldwide, although in relatively small tonnages. The major applications include dry-battery manufacture and use as a flux for soldering and brazing.

Properties of Ammonium Chloride

The properties of ammonium chloride are given in table 2.

TABLE 2. PROPERTIES OF PURE AMMONIUM CHLORIDE

Color	White
Molecular weight	53.50
Density, 20°/4°C	1.526
Nitrogen content	26%
Solubility, g/100 g of water at Temperature (°C)	
0	29.4
20	37.2
40	45.8
60	55.3
80	65.6
100	77.3
115.6 (boiling-point)	87.3
Effect of heat	
Ammonium chloride begins to dissociate at 350°C and sublimes at 520°C	
Critical relative humidity	
At 20°C (68°F)	79.2
At 30°C (86°F)	77.5

Production Methods

Several methods for producing ammonium chloride are used; the order of importance is as follows:

1. The dual-salt process, whereby ammonium chloride and sodium carbonate are produced simultaneously;
2. Direct neutralization of ammonia with hydrochloric acid;
3. Miscellaneous methods.

The Dual-Salt Process--Most ammonium chloride used in India, China, and Japan for fertilizer purposes is produced by the dual-salt process (or in suitably modified Solvay plants) which is described in monograph 4 of the U.N. Fertilizer Industry Series (19). In this method, ammonium chloride is salted out by the addition of solid, washed sodium chloride instead of being decomposed by lime liquor to recover ammonia as in the Solvay ammonia-soda process.

In conventional Solvay plants, an ammoniated solution of about 30% sodium chloride is treated with carbon dioxide in large absorber towers to form ammonium carbonate:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

Additional carbonation produces ammonium bicarbonate:

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$$

The addition of sodium chloride yields sodium bicarbonate and ammonium chloride:

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

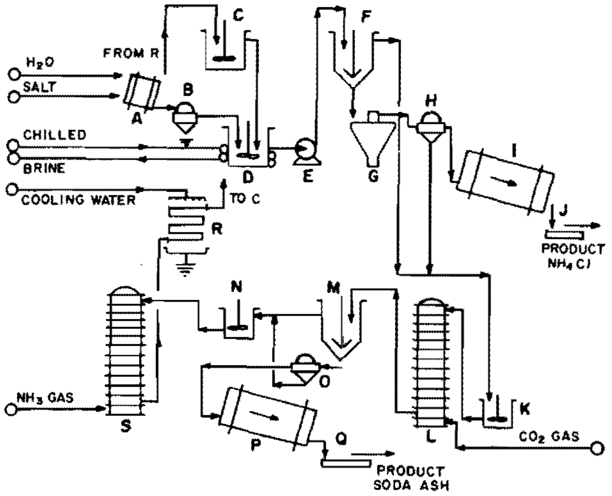
The sodium bicarbonate is separated by centrifuging or filtration and calcined to produce sodium carbonate and CO_2; the latter is recycled to the system. In the Solvay process, reaction reaches equilibrium at about 75% completion, and the mother liquor is reacted with lime liquor to recover ammonia for reuse in the process, i.e.:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The calcium chloride liquor can sometimes be sold but may have to be discarded in the absence of suitable markets.

In the dual-salt process (or the modified Solvay process), the mother liquor remaining after separation of sodium bicarbonate is ammoniated, cooled below 15°C, and salted out by adding washed, solid sodium chloride. The precipitated ammonium chloride is centrifuged, washed, and dried. The fine crystals can be granulated by roll compaction or used in compound fertilizers. More recently, in Japan, a method of producing large ammonium chloride crystals of rice grain shape, 2-3 mm in size, has been developed by undertaking cooling, nucleation, and crystallization of the ammonium chloride under closely controlled conditions in separate vessels of special design.

Slurry from the last crystallizer is centrifuged, washed, and dried to about 0.25% free moisture in a rotary drier at 105°C. After removal of ammonium chloride, the liquor is reammoniated and returned to the carbonating tower to produce further sodium bicarbonate and to commence a new cycle of operations. A basic flow diagram of this process is shown in figure 5.



Legend

A	Salt washer
B	Salt centrifuge
C	Ammoniated-brine tank
D	Salt reactor
E	Slurry pump
F	Ammonium chloride slurry tank
G	Ammonium chloride concentrator
H	Ammonium chloride centrifuge
I	Ammonium chloride drier
J	Ammonium chloride product conveyer
K	Mother-liquor tank
L	Carbonating tower
M	Bicarbonate slurry tank
N	Bicarbonate mother-liquor tank
O	Bicarbonate centrifuge
P	Soda-ash calciner
Q	Soda-ash product conveyer
R	Ammoniated-brine cooler
S	Ammoniation tower

Figure 5. Dual-Salt Process for Ammonium Chloride Production.

The ammonium chloride produced by this method, particularly when granulated or produced in coarse crystal form, is reported to have good physical properties. A typical analysis is given in table 3.

TABLE 3. TYPICAL ANALYSIS OF DUAL-SALT PROCESS AMMONIUM

	%
NH_4Cl (minimum)	95.0
NaCl	1.5
Carbonates as CO_2	0.5
Sulfates as SO_4	0.3
Insoluble material	0.1

The economics of the process must be evaluated in comparison with alternative methods for producing soda ash. This subject is discussed in a UNIDO publication (19). The comparison is most favorable when the process is carried out adjacent to an ammonia plant which serves as a source of CO_2.

As previously mentioned, in a conventional Solvay process, precipitation of sodium bicarbonate is taken to about 75% completion only. The modified Solvay process and the dual process permit the attainment of considerable reductions in sodium chloride requirements, perhaps to 1.25-1.5 tons/ton of soda ash, compared with approximately 2 tons for the orthodox Solvay process. This can represent appreciable savings in foreign exchange to countries compelled to import common salt. Also the dual process avoids the requirement for burned lime and the disposal problem of waste calcium chloride liquor.

In most countries the demand for nitrogen fertilizers greatly exceeds the demand for soda ash; therefore, ammonium chloride from this source is not likely to supply a large percentage of nitrogen fertilizer needs.

The Direct-Neutralization Method--Ammonium chloride of high purity is made in several countries by the direct reaction between anhydrous ammonia vapor and hydrochloric acid gas, according to the reaction

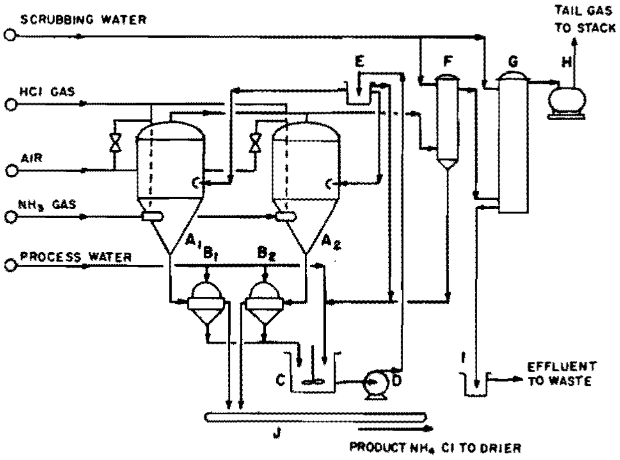
$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) - 42{,}000 \text{ cal/g-mole}$$

In most cases, neutralization is undertaken at reduced pressures of 250-300 mm of mercury in one or more rubber-lined steel vacuum reaction vessels protected with an additional inner lining of inert brick. Concentrated hydrochloric acid gas is passed through an aspirator, wherein it is diluted with air to about 20% concentration and enters the reactor via a vertical sparger tube. According to preference, ammonia gas is introduced either by a second sparger or by tangential nozzles in the base of the reaction vessel. Agitation is provided by the large volume of air entering the reactor with the hydrochloric acid vapor, thus avoiding the need for a mechanical agitator with its additional power requirements and maintenance problems.

Similarly, operation under vacuum not only provides excellent cooling but simultaneously prevents the escape of noxious vapors and eliminates the need for hydrochloric acid-vapor blowers, plus their attendant cost and maintenance charges. A reduced pressure of 250-300 mm of mercury and a corresponding slurry temperature of 75°-80°C represent typical operating conditions.

In most cases, it is usual to maintain a uniform acid feed for the desired output level and to control the ammonia addition to achieve a steady pH of 8.0. The control system should include an audible alarm and provisions for shutting off the acid feed if the pH falls below 7.0; otherwise, those components in the system not protected by rubber or plastic linings (e.g., the centrifuge) would be quickly damaged by corrosion. Slurry is withdrawn from the saturator at about 80% solids concentration, and the ammonium chloride crystals are separated and rinsed in stainless-steel centrifuges. In some cases, drying is also undertaken in the separator by blowing hot air through the crystal bed before discharge. Alternatively, a top-feed filter-drier can be used instead of centrifuges.

Mother liquor from the centrifuges is pumped back to the saturator(s) via a storage tank. Saturator offgases must be well scrubbed before entering the vacuum pump or ejector unit to prevent corrosion and to eliminate air pollution. A two-stage scrubbing system is usually employed and may consist of a direct, barometric scrubber-condenser followed by a wetted, packed tower. Liquor from the scrubber-condenser is returned to the mother-liquor tank and is evaporated in the saturator, thus providing a means of temperature control, as well as of acid recovery. Figure 6 shows the basic flow diagram for a typical direct-neutralization unit.



Legend

A_1, A_2	Neutralizer-crystallizers	F	Primary scrubber
B_1, B_2	Batch or continuous centrifuges	G	Secondary scrubber
C	Mother-liquor tank	H	Vacuum pump
D	Neutralizer feed-pump	I	Seal-pot
E	Splitter feed-box	J	Product conveyer

Figure 6. Direct-Neutralization Process for Ammonium Chloride Production.

As with other processes involving reactions between hydrochloric acid (or chlorides) and ammonia, traces of free chlorine in the acid feed can lead to disastrous explosions caused by the formation of nitrogen trichloride in the saturator. Hence, adequate safety precautions must be installed whereby the HCl gas feed is monitored and the flow shut off when chlorine is detected. This can be accomplished by such means as bypassing a small stream of gas through a photocell-colorimeter unit containing potassium iodide or using a modern continuous gas analyzer of the absorption or chromatographic type.

After separation and drying, the crystalline ammonium chloride is packed as quickly as possible in moisture-proof bags to minimize subsequent storage and application difficulties. Recent trials have shown that such anticaking agents as certain fatty acid derivatives or inert powders, either applied to the crystals after drying or added to the saturator, can be helpful in reducing caking tendencies after manufacture. Granulation by roll compaction would provide a good material for direct application; fine crystals could be used in compound fertilizers.

In accordance with the purity of the feed materials (plus any reworked product) and provided the plant has been properly designed and maintained in good condition, the direct-neutralization method will produce ammonium chloride of high purity. For example, in one Indian plant a product of a quality well in excess of British Pharmacopoea specifications can be achieved.

Byproduct HCl from production of potassium sulfate by the Mannheim process (see chapter XVIII) can be used. Also substantial amounts of byproduct HCl are available from other industries. Production of ammonium chloride could be a convenient way to utilize byproduct HCl which often has a low value and poses a difficult disposal problem.

Miscellaneous Processes--Ammonium chloride can be made from ammonium sulfate and sodium chloride according to the reaction:

$$(NH_4)_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2NH_4Cl$$

In one method, the ammonium sulfate and a 5% excess of common salt are added to an ammonium sulfate solution, followed by heating and stirring for several hours. The resulting slurry is filtered or centrifuged while it is hot and is washed with hot water to separate the solid sodium sulfate from the ammonium chloride liquor. The latter is concentrated, cooled, and crystallized in leadlined pans and the crystals centrifuged, washed with water, and dried. Normally, only ammonium chloride for chemical purposes would be made by this method and in relatively small quantities since the ammonium sulfate used as a raw material could be considered a preferable fertilizer.

Another method is the use of SO_2 or sulfite liquor in conjunction with ammonia and sodium chloride, as shown below:

$$SO_2 + 2NH_3 + H_2O + 2NaCl \rightarrow 2NH_4Cl + Na_2SO_3$$

Ammonia and sulfur dioxide or sulfite liquor are added to a solution of common salt, and an excess of SO_2 equivalent to about 2% bisulfite is initially maintained, which is reduced to about 1% as the reaction reaches equilibrium. As the temperature approaches 60°C, the sodium sulfite precipitates and is centrifuged, washed, and dried. The ammonium chloride mother-liquor is concentrated, crystallized, and centrifuged to yield a product of high purity after washing and drying.

Although the deliberate production of ammonium chloride for fertilizer use is rare in regions other than east Asia, it is a very common constituent of compound fertilizers (granular or liquid) in Europe and North America. It is formed in NPK fertilizers by reaction of ammonium nitrate and/or ammonium sulfate with potassium chloride:

$$NH_4NO_3 + KCl \rightarrow NH_4Cl + KNO_3$$

$$(NH_4)_2SO_4 + 2KCl \rightarrow 2NH_4Cl + K_2SO_4$$

These reactions go substantially to completion in most granulation processes, in nitrophosphate processes, and in liquid compound fertilizer processes. Ando, et al., found that ammonium chloride was one of the most common forms of nitrogen in representative grades of NPK granular fertilizers in the United States (21). Thus, the production and use of compound fertilizers containing ammonium chloride is well established on a worldwide basis even though some people in the industry are not aware of it.

Nitric Acid

Historical Development

Nitric acid has an interesting history and was made in medieval times, if not earlier. About 1100, Geber described a method of preparing aqua fortis by distilling nitre with copper sulfate and alum. In the mid-17th century, Glauber made fuming nitric acid by distilling nitre with strong sulfuric acid. Cavendish, in 1785, established that nitric acid was composed of nitrogen and oxygen by passing electric sparks through a mixture of these gases. Milner of Cambridge obtained nitric acid in 1788 by passing ammonia over heated manganese dioxide and absorbing the vapors in water (22). In 1839, Kuhlman patented a method of nitric oxide formation using platinum to oxidize a mixture of ammonia and air, which has become the basis of virtually all nitric acid manufacture today.

In 1895, Rayleigh demonstrated that nitrogen and oxygen could be removed from air and combined to form oxides of nitrogen by means of an electric arc. This phenomenon was also investigated by Crookes, and a small pilot plant using this principle was operated in Manchester, England, in 1900. However, the yield of nitric oxide by this method was only 1.5%-2.0%, despite huge power requirements. A commercial plant was built by Birkeland and Eyde in Norway in 1902 using 350,000 hp (261,000 kW) from hydro sources and was operated for several years. However, this process gave way to the ammonia-oxidation method using a platinum catalyst, developed by Ostwald and Brauer, and first operated in Germany about 1908 (23). This method also eventually rendered obsolete the nitre process (formerly the major source of nitric acid) whereby sodium nitrate, principally from Chile, was distilled with concentrated sulfuric acid and the vapors simultaneously oxidized and absorbed in water, using stoneware equipment.

The principal use for nitric acid is for fertilizer production, mainly for ammonium nitrate either as such or in compound fertilizers, nitrophosphates, nitrogen solutions, or mixed salts. Smaller fertilizer uses are for calcium and potassium nitrate. Nitric acid also has many industrial uses of which manufacture of explosives is the largest.

Properties of Nitric Acid

Nitric acid is a strong acid and a powerful oxidizing agent. Anhydrous HNO_3 does not normally exist in liquid form. On distilling strong solutions under reduced pressure with concentrated sulfuric acid and ozone, one obtains almost pure nitric acid having a concentration of 99.7% and a specific gravity of 1.52. On freezing a 98% solution, colorless crystals having a melting point of -41.6°C separate. When heated at atmospheric pressure, concentrated nitric acid boils at 78.2°C but begins to decompose and eventually yields a 68% HNO_3 solution with a maximum boiling point of 120.5°C. This corresponds approximately to $2HNO_3 \cdot 3H_2O$ but is not a true hydrate since its composition and concentration are functions of pressure. The more important properties of nitric acid are summarized in table 4.

Two solid hydrates can be prepared--$HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$--having melting points of approximately -38°C and -18.5°C, respectively. Heat of dilution is at a maximum, corresponding to $3HNO_3 \cdot H_2O$, although no true hydrate having this analysis has been found. When dilute solutions of nitric acid are concentrated under atmospheric pressure, a maximum boiling-point solution again corresponding to 68% HNO_3 results. The relation between specific gravity and percentage of nitric acid at 15°C is given in figure 7.

TABLE 4. PROPERTIES OF NITRIC ACID

Molecular weight	63.02
Color	
In liquid state	Transparent to yellow
As gaseous oxides	Transparent to yellow or brown (color darkens on prolonged exposure to light)
Odor	Sweet to pungent
Hazards	
In liquid state	Rapidly attacks flesh and most organic matter
As gaseous oxides	Anesthetic to dangerously toxic
Melting point	-41.6°C
Boiling point of constant boiling point mixture containing 68% HNO_3, at 760 mm Hg	120.5°C
Density of 68% HNO_3, 20°/4°C	1.41
Refractive index at 16.4°C	1.397
Solubility in water	Totally soluble at all concentrations
Acidity	A strong acid, having pronounced oxidizing characteristics. Will passivate some metals, such as iron and aluminum
Entropy	
Liquid at 16°C	37.19 cal/g-mole
Gas at 25°C	63.62 cal/g-mole
Heat of fusion	2,503 cal/g-mole
Heat of vaporization at 20°C	9,426 cal/g-mole
Heat of infinite dilution at 25°C	-7,971 cal/g-mole
Heat capacity at 27°C	26.24 cal/g-mole
Typical impurities in HNO_3 of ammonia origin	Cl_2--less than 5 ppm HNO_2--less than 5 ppm

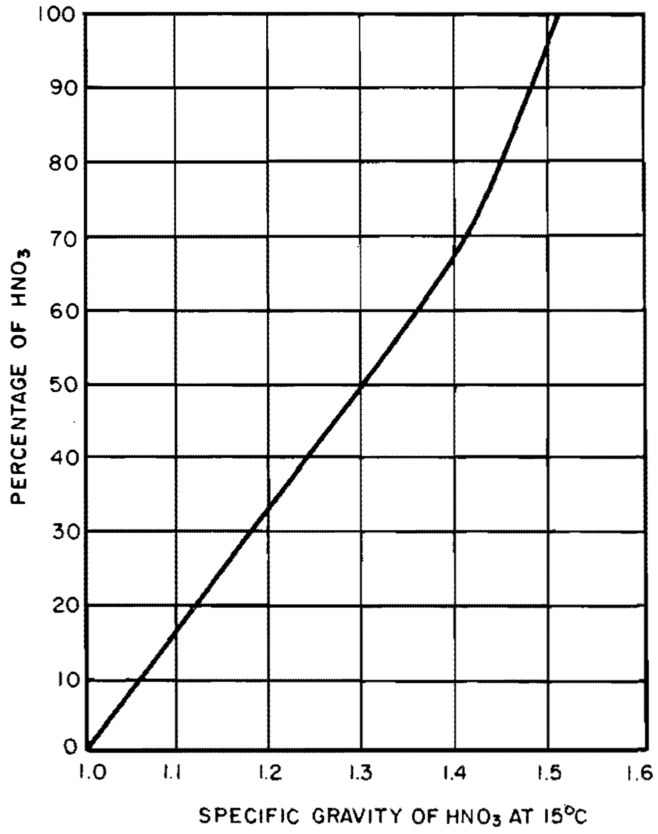


Figure 7. Specific Gravity at 15° C, Nitric Acid Solutions.

Oxides of Nitrogen

The oxides of nitrogen that are of interest in nitric acid production are:

Nitrous oxide	N_2O
Nitric oxide	NO
Nitrogen dioxide	NO_2
Dinitrogen tetraoxide	N_2O_4

Of these, NO and NO_2 are of primary importance. N_2O_4 exists in equilibrium with NO_2 ($2NO_2 \rightleftarrows N_2O_4$) and is not present in significant proportions at temperatures above about 100°C. It acts as a transitory intermediate in low temperature absorption of NO_2 in nitric acid. N_2O is seldom present in significant amounts. A mixture of nitrogen oxides, usually NO and NO_2, is commonly referred to as NO_x, particularly in pollution control parlance.

Chemical and Theoretical Considerations in Production of Nitric Acid from Ammonia

The chemical reactions that occur in the production of nitric acid from ammonia, including both the desired reactions and some undesirable reactions, are listed below together with their heats of reaction:

Chemical Reactions Occurring in Nitric Acid Production and Standard Heats of Reaction

Data from National Bureau of Sciences Technical Note 270-3, Selected Values of Chemical Thermodynamic Properties, January 1962

No.	Reaction	Heat of Reaction[a] Joules/ g mole	Cal/ g mole
1	$\underline{NH_3}(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l)$	-436,918	-104,423
2	$\underline{4NH_3}(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$	-226,523	-54,139
3	$\underline{4NH_3}(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$	-316,832	-75,723
4	$\underline{2NH_3}(g) + 2O_2(g) \rightarrow N_2O(g) + 3H_2O(g)$	-275,780	-65,911
5	$\underline{4NH_3}(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g)$	-451,296	-107,860
6	$\underline{2NO}(g) \rightarrow N_2(g) + O_2(g)$	-90,309	-21,583
7	$\underline{2NO}(g) + O_2(g) \rightarrow 2NO_2(g)$	-57,108	-13,649
8	$\underline{2NO_2}(g) \rightarrow N_2O_4(g)$	-28,617	-6,839
9	$3N_2O_4(g) + 2H_2O(l) \rightarrow \underline{4HNO_3}(aq) + 2NO(g)$	-15,747	-3,764
10	$3NO_2(g) + H_2O(l) \rightarrow \underline{2HNO_3}(aq) + NO(g)$	-58,672	-14,023
11	$4NO(g) + 3O_2(g) + 2H_2O(l) \rightarrow \underline{4HNO_3}(aq)$	-144,334	-34,496
12	$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow \underline{4HNO_3}(aq)$	-87,226	-20,847
13	$2N_2O_4(g) + O_2(g) + 2H_2O(l) \rightarrow \underline{4HNO_3}(aq)$	-58,609	-14,008

a. Heats of reaction per g mole of the underlined compound. All reactions are exothermic.

The overall reaction is strongly exothermic. Of the total heat released more than half is released in the ammonia oxidation step (reaction 2) at a high temperature permitting economical recovery as steam or for other purposes (described later). Also part (about half) of the heat released by reaction 7 can be recovered at a useful temperature level. The remainder of the heat is released at a temperature too low for useful recovery and requires a net consumption of energy for circulation of cooling water, acid, and process gas and, in some processes, for refrigeration.

In the ammonia oxidation step, reaction 2 is the desired reaction, and reactions 3, 4, 5, and 6 are undesirable reactions which must be held to a minimum. The ammonia conversion efficiency, expressed as a percentage of the ammonia that is converted to NO, is mainly a function of the catalyst activity, temperature, pressure, thoroughness of mixing of the incoming air and ammonia, and velocity of gas flow through the catalyst. Conversion efficiencies above 94% can readily be obtained over a wide range of temperatures, 800°-1000°C. Above 1000°C the decomposition of NO (reaction 6) becomes significant, and loss of catalyst by volatilization of platinum and rhodium oxides becomes serious even at somewhat lower temperatures. The following tabulation shows the usual interrelationship of temperature (measured at the catalyst surface), operating pressure, and conversion efficiency (24). The data are typical of good practice and subject to some variation.

Pressure, atm	Temperature, °C	Conversion Efficiency, %
1	790-850	97-98
3.5	870	96-97
8	920	95-96
10.5	940	94-95

The temperature is controlled by preheating the air and ammonia and by the amount of excess air. The percentage of excess air is usually such as to result in 8%-11.5% NH_3 by volume in the ammonia-air mixture. Mixtures containing more than this must be avoided as the explosive limit starts at about 12%, and the stochiometric requirement corresponds to 14.2% NH_3.

Various alloys and metallic oxides have been tried as catalysts, but usual preference is for platinum containing between 2% and 10% Rh. In high-pressure plants (8-11 atm) the usual alloy is 90% Pt and 10% Rh. In medium-pressure plants platinum alloyed with 5%-7% Rh often is used. In the U.S.S.R. a ternary alloy containing 3.5% Rh, 4% Pd, and 92.5% Pt is also used (25). The rhodium improves the mechanical strength of the platinum wire, increases its catalytic activity, and decreases catalyst losses. However, it is more than twice as expensive as platinum.

Many other alloys of the platinum group of elements have been tried. Also, base metal oxide catalysts have been tried experimentally and used commercially in wartime when platinum was unobtainable. Various combinations of oxides of bismuth, cobalt, thorium, cerium, and other metals have shown promise, and studies are continuing (26). However, so far no commercial use of these materials is known at present.

Reaction 1 is the desired overall reaction. The steps in the process are ammonia oxidation (reaction 2), oxidation of NO to NO_2 (reaction 7), and conversion of NO_2 to nitric acid (reaction 12). Reaction 12 is the overall result of a series of steps in which NO_2 or N_2O_4 reacts with water to form nitric acid and NO (reaction 10 or reactions 7, 8, and 9). The NO formed by these reactions must then be reoxidized and reabsorbed forming more nitric acid and NO and this cycle repeated until the amount of NO_x is reduced to a very low level.

An extremely important variable is the rate of gas flowing past the catalyst. Increased flow rates not only increase the weight of ammonia available for oxidation (assuming a constant gas composition) but also probably lead to higher oxygen transport rates on the catalyst surface and quicker removal of the newly formed intermediate products. Furthermore, at low velocities, nitric oxide can diffuse upstream behind the catalyst to form nitrogen dioxide, which will subsequently result in loss of fixed nitrogen (reaction 5). The same reaction can occur if unconverted ammonia passes through the catalyst, which could occur because of poor mixing or holes in the catalyst gauze.

Increased gas velocities, plus the provision of several layers of catalyst, also help to minimize undesirable downstream reactions between unconverted ammonia and nitrogen oxides, as well as the dissociation of nitric oxide into nitrogen and oxygen (reaction 6). Undesirable side reactions are thus minimized, and reaction 2 is favored by providing high gas velocities and a short contact time, which is usually in the region of 0.001 seconds.

Naturally, there is some limiting velocity beyond which undesirable effects occur which may include increased erosion, loss of catalyst, and perhaps incomplete ammonia oxidation. The optimum velocity increases with temperature (26). A common practice is to relate the catalyst weight to the plant capacity for design purposes. The relationship is commonly expressed as the "ammonia loading rate." A recent publication gave usual rates as 246-294 lb of ammonia per troy ounce of catalyst per day (3.6-4.3 kg/g/day) (24). This applies to both high- and low-pressure ammonia oxidation units.

Nitric oxide produced in the ammonia burner must be oxidized to nitrogen dioxide by the excess air present before absorption in water. Some nitric oxide is formed during this absorption and must also be oxidized prior to reabsorption (reaction 7).

This is an unusual, third-order, trimolecular reaction since it has a negative temperature coefficient and is thus assisted by decreased temperatures and increased pressures. Conversion time has been shown to be an inverse function of the square of the pressure. The rate of reaction is a direct function of the cube of the pressure (24). Although this reaction has been studied by several workers in great detail, it is still not fully understood.

The principal absorption reactions of significance in nitric acid manufacture are reactions 7, 8, and 9. The overall reaction between nitrogen dioxide and water is given in reaction 12.

The absorption of nitrogen dioxide in water has been studied extensively, and several principal conclusions can be drawn from the mass of research data available (27). For example, when temperatures are reduced, the gas-phase equilibrium moves toward the formation of additional dinitrogen tetroxide and an increased solubility in HNO_3. As a result, in some cases a reduction of 5°C not only improves the absorption rate but also increases acid concentration by about 2%. In addition, the tendency for nitric acid to decompose is diminished. Hence, the overall absorber operation is greatly improved by lower temperatures.

Absorber performance is also aided by increased pressure not only because of the simultaneous beneficial effect on reaction 7 but also because the absorption rate is increased and the chemical equilibrium moves towards the formation of stronger nitric acid. At pressures of 50 atm and with cooler/absorber residence times as long as 15 seconds, acid concentrations as high as 72% HNO_3 can be obtained although absorption efficiency is low. In commercial operation, however, uneconomic increases in pressure are needed to obtain concentrations above 60% HNO_3, except in absorber units of special design.

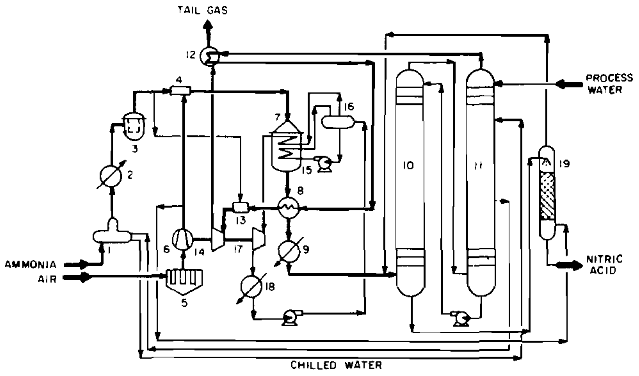
Production Considerations

General Information--Numerous proprietary processes for nitric acid manufacture are now available, but they differ mostly in design details or selected operating conditions and not in fundamental principles. The major features usually found in modern nitric acid plants include:

1. Vaporization, superheating, and filtration of anhydrous ammonia;
2. Preheating, filtration, and compression of process air;
3. Catalytic oxidation of ammonia;
4. Cooling of nitric oxide by heat exchange with various media, e.g., process air, boiler water, tail gas, etc.;
5. Oxidation of nitric oxide to higher oxides;
6. Absorption of nitrogen oxides in water to form nitric acid;
7. Bleaching of acid by additional air or other means;
8. Treatment of tail gas to improve total plant efficiency and to reduce air pollution;
9. Recovery of energy in compressed process gases;
10. Recovery of catalyst for resale.

Commercial processes often are classified according to the pressure used. Monopressure processes use the same pressure throughout; whereas, dual-pressure processes use a lower pressure for the oxidation step than for the absorption step.

The first nitric acid plants used near-atmospheric pressure throughout. However, practically all modern plants use elevated pressures; the following general types are common: (1) monopressure plants using medium pressure (3-5 atm) throughout, (2) monopressure plants using high pressure (8-13 atm) throughout, and (3) dual-pressure plants using medium-pressure combustion and high-pressure absorption. Simplified flow diagrams of each of these types of plants are shown in figures 8, 9, 10, and 11.



MAJOR EQUIPMENT

1 VAPORIZER
2 SUPERHEATER
3 AMMONIA FILTER
4 MIXER
5 AIR FILTER
6 AIR COMPRESSOR
7 CONVERTER
8 TAIL-GAS HEATER
9 COOLER CONDENSER
10 FIRST ABSORBER
11. SECOND ABSORBER
12 TAIL-GAS PREHEATER
13 TAIL-GAS ABATEMENT UNIT
14 TAIL-GAS EXPANSION TURBINE
15 WASTE HEAT BOILER
16 STEAM DRUM
17 CONDENSING STEAM TURBINE
18 STEAM TURBINE CONDENSER
19 BLEACHER

Figure 8. Medium-Pressure Nitric Acid Process (Uhde).

1. VAPORIZER
2. SUPERHEATER
3. FILTER
4. PREHEATER
5. FILTER
6. COMPRESSOR
7. MIXER
8. CONVERTER
9. TAIL-GAS HEATER
10. ECONOMIZER
11. COOLER-CONDENSER
12. WEAK ACID SEPARATOR
13. NITROUS GAS COMPRESSOR
14. TAIL-GAS PREHEATER
15. COOLER-CONDENSER
16. ABSORBER
17. SEPARATOR
18. TAIL-GAS EXPANDER
19. STARTUP TANK
20. STEAM TURBINE
21. CONDENSER
22. BLEACH AIR COOLER
23. BLEACHER

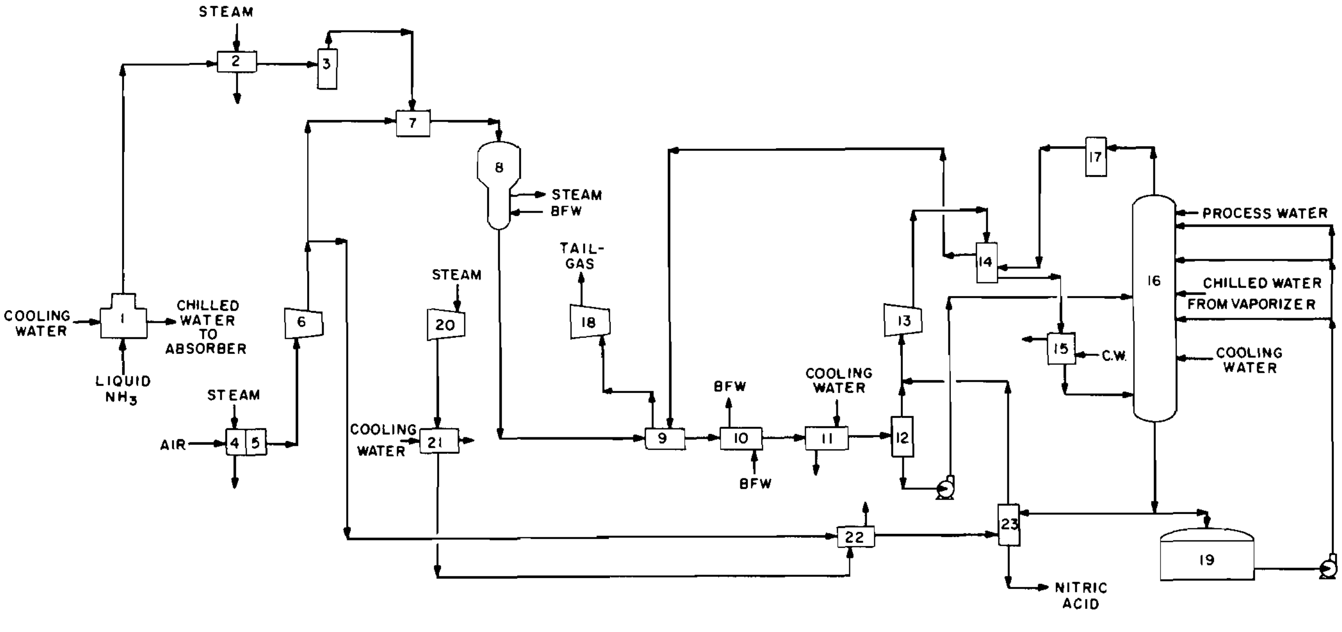


Figure 9. Dual-Pressure Nitric Acid Process (Grande Paroisse).

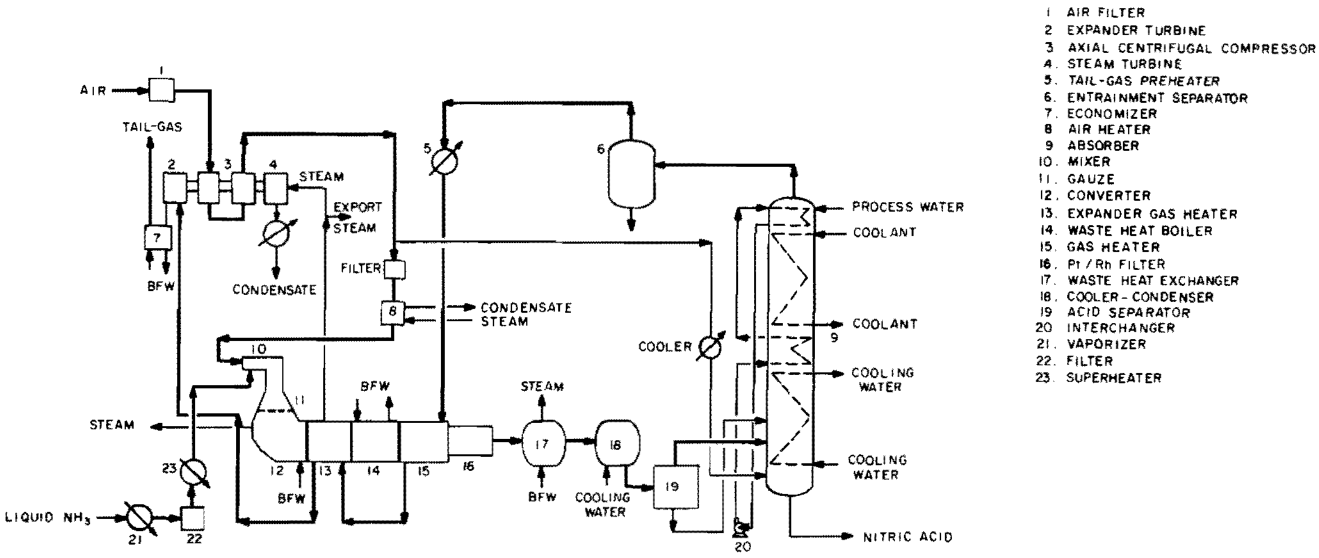


Figure 10. High-Pressure Nitric Acid Process (Weatherly).

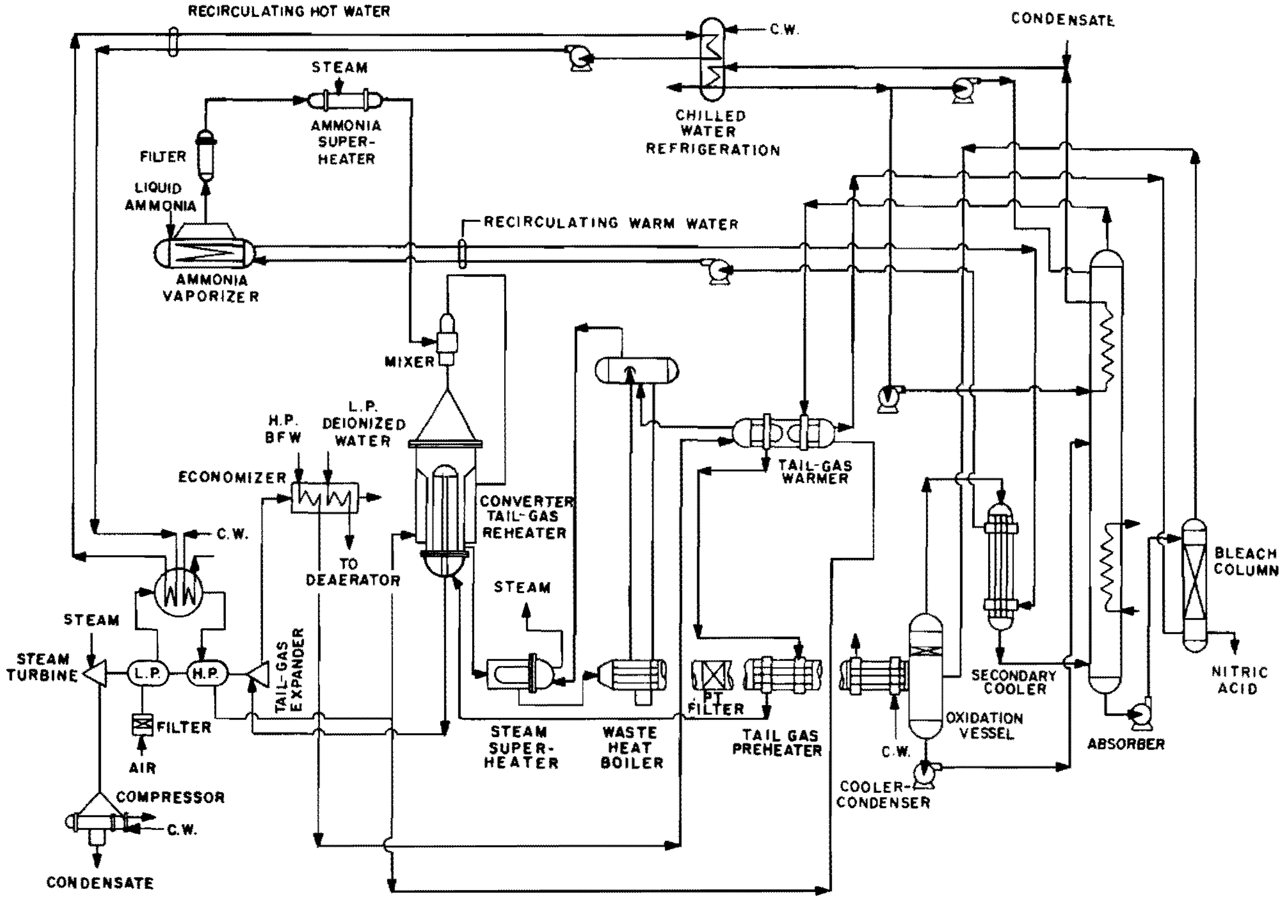


Figure 11. High-Pressure Nitric Acid Process (C&I Girdler).

In commenting on the process diagrams, figures 8-11, it should be noted that each diagram is based on information supplied by a different engineering and construction organization. Each of the organizations offers a range of processes to meet various client needs. For instance, figure 8, identified as an Uhde process is only one of several processes offered by that company. Also several other companies offer nitric acid processes, and there is no intention to imply that processes offered by the four companies mentioned by name are necessarily superior to those offered by other companies.

Some features of specific processes, which may not be evident from the flow diagrams, should be pointed out. In the Uhde medium process operating at 5 atm, ammonia is vaporized by the cooling water, thus furnishing chilled water for cooling the second absorption tower. The cooling water is recycled back to the ammonia vaporizer. With this type of plant nitric acid concentrations up to 65% may be achieved with overall nitrogen recovery of about 96%, and the NO_x content of the tail gas is about 500 ppm. If this concentration is not low enough to meet pollution control regulations, it can be reduced to below

200 ppm by selective reduction with ammonia (BASF) process, which lowers the nitrogen recovery to 95.3%. In this, as in other processes, the compressors may be driven by electric motors, and the heat of reaction that is recovered by steam may be exported if needed in other plant units. However, the arrangement shown usually is more common; the compressor is driven by steam and by expansion of the preheated tail gas. Uhde also offers a high-pressure process (8-10 atm), a dual pressure process (ammonia oxidation at 5 atm and absorption at 10-14 atm), and a process for making highly concentrated nitric acid (98%-99% HNO_3).

The Grande Paroisse dual-pressure extended absorption process (figure 9) typically operates at a pressure of 4 atm for ammonia oxidation and 10 atm for the absorption step. The absorption is carried out in a single tall tower (40 m high) although, for improving the recovery in an existing plant which has a shorter tower, a second tower may be added. Chilled water from the ammonia vaporizer is used to cool the upper part of the absorption tower. The NO content of the tail gas is 200 ppm or less. The company also offers a medium-pressure process. The usual nitric acid concentration is 60%.

The Weatherly high-pressure process typically operates at about 10 atm pressure for both ammonia oxidation and absorption steps. As in other processes there is some pressure drop as the gas passes through the various process steps so the pressure of the tail gas entering the expander may be about 1.6 atm lower than the pressure at the air compressor discharge. All units are built to operate at pressures up to about 13 atm; therefore, by increasing the air compressor speed, the pressure and throughput can be increased. Also, the arrangement permits the operator to take advantage of the increased compressor output when the atmosphere air is cooler and therefore denser. Thus, the plant can be operated at up to 120% of design capacity.

The various heat exchangers from the ammonia oxidizer to the platinum filter are butted against each other to form a compact train and minimize construction costs. Spool pieces are inserted in the train to increase retention time and thereby increase the percentage of NO oxidized to NO_2 at a temperature high enough for economical recovery of the heat of reaction. As in other processes, cooling water is recirculated through the ammonia vaporizer.

In the extended recovery option illustrated in figure 10, the upper part of the absorption tower is cooled to about 2°C using refrigerated potassium carbonate brine as the coolant. Water is chilled in coils by the cold gas leaving the top of the tower and is circulated through heat exchange coils in a middle section of the tower to precool the ascending gas. Refrigeration of the brine may be done in a low-pressure ammonia vaporizer with the ammonia vapor going to ammonium nitrate production. Alternatively, mechanical refrigeration can be used. With the extended absorption system, the NO_x concentration can be lowered to less than 200 ppm. The company also offers the alternative of reduction of tail gas by combustion with fuel gas. The usual nitric acid concentration is 58%.

The C&I Girdler process (figure 11) is a high-pressure (about 10 atm) process. Refrigerated water is used in the upper part of the absorption tower to reduce the NO_x content of the tail gas to less than 200 ppm. Nitric acid concentrations range from 55% up to 65%. As in other processes higher concentrations are attained at the expense of higher NO content of tail gas unless special provision is made for its reduction by additional cooling, a greater number of plates in the absorber column, or chemical reduction.

Ammonia Preparation--The anhydrous ammonia used must be free from the catalyst poisons mentioned below, and the oil content must be limited to a few parts per million to avoid fouling the vaporizer and catalyst screens. Liquid, anhydrous ammonia produced to the required specifications is vaporized, filtered, and superheated to eliminate any possibility of liquid droplets entering the catalyst chamber and burning holes in the screens. The superheated vapor is thoroughly mixed with process air in various ways, e.g., by venturis, spargers, diffusers, etc., according to the type of process. Some plants also use specially designed ducts, baffles, and even packed columns to ensure complete mixing.

Process-Air Preparation--Process air must also be free from catalyst poisons, dust, and oil. In some plants, ambient air is given a preliminary wash with water in a spray tower or packed column before being compressed, filtered, preheated, and mixed with superheated ammonia vapor for subsequent combustion.

In certain plants employing atmospheric or low-pressure oxidation, the process air can be raised to the required pressure by suitably designed fans. For medium- and high-pressure oxidation, rotary machines of the lobe, vane, centrifugal, or axial-flow design can be used, with an increasing preference for the two last types, since these units can be combined with various turbine drives and expanders in the form of one large single-shaft installation. (In some designs the heat of compression provides sufficient air preheat.)

The ratio of ammonia to air, as well as the flow rate of each component, must be carefully controlled to ensure maximum conversion efficiency, freedom from explosion, and maximum plant output. Hence, reliable instrumentation in this section, as well as in other parts of the plant, is of the utmost importance.

Catalytic Ammonia Oxidation--The customary choice is a platinum-rhodium gauze since this alloy promotes reaction and also meets other operating criteria, such as the severe conditions of service. A rhodium content of 4%-10% is usual. Since higher percentages tend to give slightly greater conversions and longer life, a 10% rhodium content has become standard in many processes.

The need to minimize and control contact time in order to suppress unwanted reactions and to minimize catalyst requirements led to the early adoption of fine screens as a suitable catalyst form. These are usually circular in shape and are stacked in multiple array, as the use of several (5 to 50) screens permits the residence time and contact time to be easily varied in order to obtain the maximum yield of nitric oxide. The use of multiple platinum gauzes in conjunction with preheated air was patented in 1909 by Kaiser in Germany, and these principles are still standard practice today. High-pressure burners are frequently fitted with gauzes having wires 0.076 mm in diameter woven with 1,024 meshes/cm^2. Finer gauzes with wires in the range of 0.051-0.057 mm are preferred by some for installation in low-pressure units. Modern looms are capable of weaving catalyst gauzes up to 4 m wide, which are required for some large plants. Chrome-nickel alloy grids are used to support these fine screens because they have a very low mechanical strength when they are operating in the 900°C range and, simultaneously, are being subjected to appreciable differential pressures caused by the high gas velocities in the burner chamber.

When first installed, a new gauze exhibits a relatively low activity, but after several days of operation under proper conditions, catalytic efficiency rises to a satisfactory level and remains nearly constant during the useful life of the screen, which should be several weeks, or even months, for high- and low-pressure burners, respectively. During operation, the crystalline structure of the platinum alloy is modified by the severity of service, and distortion takes place. Erosion also occurs if vibration is present especially at high temperatures and pressures, which also results in diminished activity. Eventually, the screen wears out and has to be replaced.

As is well known, platinum catalysts for most processes can be poisoned by such elements as As, Bi, P, Pb, S, Si and Sn, and ammonia-oxidation gauzes are no exception. Fortunately, synthetic ammonia is normally of high purity, unless accidentally contaminated. However, since air can be contaminated by dust or many other pollutants, thorough air cleaning is necessary. Location of the air intake in an area relatively free from contaminants will help. If poisoning by impure ammonia or air should arise, deep penetration may occur, leading to the formation of inactive compounds in the wires and, perhaps, to ruination of the catalyst. In other instances, contamination by traces of Cr, Fe, or Ni may temporarily reduce conversion efficiency, but this can often be restored by treatment with hydrochloric acid or certain salts. Frequently, activity can also be assisted by dismantling the catalyst screen assembly from time to time and removing accumulated solids by gently brushing the gauzes, which also helps to reduce the pressure drop across the burner. However, catalyst screens should be handled to the minimum extent because they become brittle during service.

Ammonia burners are classified into low-, medium-, and high-pressure types in accordance with conditions of operation. New plants are usually built with medium- (3-6 atm) or high- (8-12 atm) pressure burners although some plants with low-pressure burners are still in operation. Burners for atmospheric and low-to-medium pressures are often 3-4 m in diameter and perhaps may incorporate up to five or so catalyst screens; whereas, high-pressure burners usually are smaller in diameter--perhaps 1.2-1.5 m and may contain 25-45 gauzes. High-pressure units of this size can produce 250 tons of HNO_3, or even more, per 24-hour day. Larger-size plants are now common; up to 1,100 tpd can be produced with a single burner with either high- or medium-pressure burners although two burners may be preferable for the lower range of medium-pressure processes. Gas velocities are much greater in high-pressure burners, and efficiencies are usually less, e.g., in the 93%-95% range, compared with 96%-97% or so for low- and medium-pressure units.

However, recent designs of some high-pressure burners, in which diameters are increased to reduce gas velocities, are said to approach efficiencies formerly only attainable in low-pressure units. Most low-pressure burners operate in the region of 865°C and high-pressure units at about 940°C. The higher temperatures, pressures, and gas velocities associated with high-pressure burners reflect greater catalyst losses. As a typical guide, Mukherjee, et al., gave the following relative losses before recovery (28).

Ammonia-Burner Pressure	Absorption Pressure	Relative Platinum Losses
Atmospheric	Atmospheric	1
Atmospheric	3.2 x atmospheric	1
3.2 x atmospheric	3.2 x atmospheric	3
8.0 x atmospheric	8.0 x atmospheric	5

It should be noted that the cost of reprocessing used catalyst screens and of recovering and refining platinum and rhodium recovered in filters is appreciable. In a recent paper that compared a dual-pressure process (low-pressure oxidation) with a high-pressure process, the following data were given, showing that total catalyst costs were $1.81/ton of HNO_3 higher for the high-pressure process than for the low pressure (24).

Catalyst Cost per ton of Nitric Acid in Plants Using Low- and High-Pressure Ammonia Oxidation

Pressure (Absolute)	High Pressure (10.1 atm)		Low Pressure (3.4 atm)	
	mg/ton	Cost, $/ton	mg/ton	Cost, $/ton
Net loss of Pt	206	1.52	94	0.70
Net loss of Rh	29	0.48	7	0.10
Recovery, refining, etc.	-	0.81	-	0.20
Total catalyst cost		2.81		1.00

Note: Cost of platinum--$230/troy ounce → $7.40/g.
Cost of rhodium--$511/troy ounce → $16.43/g.
(Since the paper was written the cost of platinum has increased to over $300/oz).

Most plants, particularly those with high-pressure burners, have filters of some sort that recover part of the platinum that is lost from the catalyst. Reported net consumption of platinum catalysts is in the range of 100-200 mg/ton of HNO_3 for medium- and high-pressure units. The downtime for catalyst renewal is relatively greater in high-pressure burners for a given weight of installed catalyst. Nonetheless, in some high-pressure plants, an average screen-life of about 60 days of continuous operation is obtained, and further improvement is likely by more thorough cleaning of the combustion air and ammonia.

Cooling of Reaction Products--Hot gases leaving the burner are cooled in order to increase the formation of nitrogen dioxide and to recover heat for use elsewhere in the plant, thereby contributing to the self-sufficiency of the process. In most medium- and high-pressure plants, different sequences are used; the gases may pass in turn through a waste-heat boiler, a tail gas heater, a cooler-condenser, a compressor (in dual-pressure plants), and a second cooler-condenser. In some cases the gases also may pass through a steam superheater and a combustion-air preheater. A platinum-recovery filter usually precedes the cooler-condenser. In one process all major heat exchangers are mounted horizontally end-to-end to simplify plant design and to reduce capital costs (see figure 10). In several European processes, some of the heat exchangers are built as an integral part of other equipment, for example, the burner or the waste-heat boilers. Heat recoveries of the order of 82%-85% are attained in some plants; higher figures are limited by dew point and corrosion considerations. In certain cases, about 1.1 tons of steam per ton of 100% HNO_3 can be produced. Most of this is normally used for power purposes within the nitric acid plant, but as much as 0.4 ton may be available for export.

The optimum gas-cooling sequence is closely associated with the number and types of energy recovery units and also the operating temperatures and pressures selected for each stage of the process. Plant capacities, ammonia costs, and capital and operating costs must also be taken into consideration when selecting the best cooling sequence for a specific installation.

Nitric Oxide Oxidation--In atmospheric- and some low-to-medium-pressure processes, one or more separate oxidation-cooling units are often included prior to gas absorption. These are built in the form of vertical towers cooled with external water curtains, shell-and-tube units, and also drum and cascade coolers. Excess air in the gas promotes initial oxidation, and some of the water vapor also present condenses to form weak nitric acid, which is later concentrated in the absorption section. Additional air for oxidation usually is injected at some point in the process, often in the absorption tower. In some plants, the gas is rapidly cooled in specially designed units to condense the water vapor without forming much weak acid, thereby helping to increase final acid concentration. A combined multistage condenser-cyclone separator unit, designed to remove water from the system and capable of yielding an acid concentration of about 63% HNO_3, has been described (29).

Some high-pressure processes seek to maximize the extent of oxidization of NO to NO_2 in the heat recovery train so that the heat generated by this reaction can be recovered at a relatively high temperature level. This can be accomplished by inserting extra chambers in the train to increase retention time, for instance between the waste heat boiler and the tail gas heater. Up to 80% of the NO can be oxidized to NO_2 before it enters the cooler-condenser by this means. In some other high-pressure processes, gas cooling and NO oxidation may be undertaken in a combined oxidation absorption column. However, the additional flexibility provided by a separate oxidation-cooling unit and the ability to minimize the amount of weak acid formed prior to absorption is considered advantageous by many producers.

Nitrogen Dioxide Absorption--At near atmospheric pressures, oxidation and absorption rates are slow, and some earlier atmospheric and low-pressure plants used between five and ten large, packed stoneware towers in which the partially oxidized gases were absorbed in a countercurrent stream of nitric acid of increasing concentration. Maximum strengths attainable were in the range of 42%-52% HNO_3.

In order to reduce capital investment and to obtain increased operating efficiencies, absorption under pressure was developed, using various types of equipment, e.g., cascade coolers, packed columns, spray towers, and columns incorporating bubble plates, sieves, and such special devices as the Kuhlman tray.

Since acid concentrations are favored by low-temperature absorption, several different cooling methods have also been developed, e.g., by external units of the plate, drum, or cascade type; by water curtains outside the tower; and also by cooling coils strategically located inside the absorption column. In some plants using low-pressure ammonia oxidation, vaporization of the ammonia is used to precool the absorber feedwater and cooling water.

Modern pressure-absorption systems permit absorption efficiencies well over 99% to be obtained, together with acid concentrations in the range of 55%-65%. In some processes, concentrations of up to 70% HNO_3 are achieved by using high pressures and cooled water in conjunction with specially designed absorption columns. In some plants, excess air may be injected into either the cooler or absorption column to speed up the oxidation reaction. Process water for absorption systems must be very pure to reduce corrosion effects in the nitric acid plant and also in applications involving subsequent use of the acid. In particular, the chloride content must be very low. Hence, water from condensate sources or ion-exchange purification units is often used.

Acid Bleaching--Acid produced in most absorber units is invariably yellow or brown in color, because of dissolved nitrogen dioxide. This is removed either in a separate small bleaching tower or in an additional, lower section of the main absorber column by means of compressed-air injection.

Tail-Gas Treatment--Except for atmospheric units, exit gas from the absorber is normally preheated and expanded in a turbine to recover an appreciable amount of the energy used for compression purposes. This gas contains mainly nitrogen plus some water vapor, oxygen, and mixed nitric oxides.

In the 1960s typical concentrations of NO_x in the tail gas ranged from 1,500 to 3,000 ppm. In recent years concern about pollution control has led to laws and regulations that reduced permissible levels of NO_2 in tail gas from nitric acid plants (see chapter XXIII). For example, the maximum concentration in the United States is equivalent to 200 ppm of NO_x for new plants or 500 ppm for existing plants. (The level is stated in kg of NO_2 equivalent per ton of HNO_3).

To meet the requirements that authorities in various countries have set up, a variety of methods have been used. Some countries may take the view that the NO_x output of nitric acid plants is only a small percentage of the total, since far greater quantities are discharged to the atmosphere from combustion of fuels in power plants and internal combustion engines. In such cases dispersion by tall stacks and/or dilution of tail gas by air to control ambient levels may be acceptable. However, most countries require reduction of the actual NO_x output below the levels of 10 years ago.

The principal methods employed to control the level of NO in tail gas are (1) extended absorption, (2) catalytic reduction with fuel such as methane or ammonia plant purge gas, (3) selective catalytic reduction with ammonia, (4) adsorption by silica gel or molecular sieves, or (5) scrubbing with alkalies or urea solutions.

There is a growing preference for "extended absorption" as a method of control of NO_x in tail gas. The method consists simply of increasing the efficiency of the absorption system by adding a second absorption tower, by adding more sections to the absorption tower, or in some cases by reducing the temperature in the last absorption stages by cooling coils using chilled water or other coolant. One company uses refrigerated potassium carbonate solution as the coolant. These methods can be used with either new or existing plants; with new plants there is greater flexibility in selecting the economic optimum combination of parameters, including increased pressure. Several organizations, including Friedrick Udhe (Germany), Societe Chimique de Grande Paroisse (France), C&I Girdler (United States), and D. M. Weatherly and Co. (United States), offer nitric acid plant designs with extended absorption which will give tail gas NO_x concentrations below 200 ppm which is low enough to satisfy the present requirements of the United States or any European country. For countries where less stringent regulations are in effect, some savings in capital cost may be possible. The extended absorption method has the obvious advantage that recovery of nitrogen as nitric acid is increased by 1.0%-1.5% (as compared with former practice) which partially offsets the increased cost.

Tail gas reduction by fuel involves reduction of NO_x with natural gas, naphtha, or ammonia purge gas which contains H_2, NH_3, CH_4, and N_2. Illustrative reactions are:

1. $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
2. $4NO + CH_4 \rightarrow 2N_2 + CO_2 + 2H_2O$
3. $4NO_2 + CH_4 \rightarrow 4NO + CO_2 + 2H_2O$
4. $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$
5. $2NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2H_2O$
6. $2NO_2 + 4H_2 \rightarrow N_2 + 4H_2O$
7. $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$

The tail gas contains about 3.5% oxygen which also reacts with the added fuel. When a deficiency of fuel is used such as to reduce the O_2 content of the tail gas from 3.5% to 2.5%, for example, the NO_2 in the tail gas is reduced to NO as in reaction 3 above. This "decolorizes" the tail gas since NO is colorless while NO_2 has a yellow-to-brown color. In some countries decolorization of tail gas is acceptable although it does not lower the total NO_x output.

For complete reduction of NO_x enough fuel gas must be added to consume all of the oxygen in the tail gas. This method generates much heat and requires two or more catalyst beds in a series with intercooling to prevent excessive temperatures. The heat is recovered as steam. This method is likely to generate other pollutants in the tail gas. If the fuel is methane or any other hydrocarbon, appreciable amounts of CO and HCN are formed; with ammonia purge gas, some ammonia may remain in the tail gas.

Selective reduction of NO by ammonia according to reactions 4 and 7 is a method that has been used successfully in several commercial plants in Japan, the United States, and Europe. Commercial processes are offered by Gulf Oil Chemicals, Inc. (United States); Mitsubishi (Japan); and BASF (Germany). Various catalysts are used, and the reaction takes place at temperatures ranging from 250°C to 450°C depending on the catalyst. The reduction unit may be located between the tail gas expander and the stack where the pressure is near atmospheric, or it may be located at some point between the absorption tower and the expander where the gas temperature is in a suitable range. The method is effective in reducing the tail gas NO concentration well below 100 ppm.

Adsorption by silica gel or molecular sieves is possible; the process requires regeneration of the adsorbent and permits return of the NO_x to the process. One disadvantage is that water vapor in the tail gas must be removed for efficient adsorption.

Scrubbing with alkali solution is effective only when the gas contains NO_2:NO mole ratios of 1:1 or more. Using NaOH as an example, the reaction is:

$$2NaOH + NO + NO_2 \rightarrow NaNO_2 + H_2O$$

Utilization of the alkali nitrite may be a problem. Norsk Hydro has developed a scrubbing process in which the scrubbing medium is an aqueous solution of urea and nitric acid (30). The oxides of nitrogen react with water to form nitrous acid.

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

The nitrous acid then reacts with urea and nitric acid according to the reaction:

$$HNO_2 + CO(NH_2)_2 + HNO_3 \rightarrow N_2 + CO_2 + NH_4NO_3 + H_2O$$

The intermediate reactions are believed to involve formation of nitrous acid (HNO_2) which reacts with urea to form HCNO and N_2; the HCNO reacts with HNO_3 and H_2O forming NH_4NO_3 and CO_2. The loss of fixed nitrogen in the process is a disadvantage.

In the Goodpasture process (United States), the tail gas is scrubbed with ammonium nitrate solution with addition of ammonia in the scrubbing unit under controlled temperature and pH conditions. Part of the NO_x may be recovered as ammonium nitrate, and part may be reduced to nitrogen.

Various other scrubbing systems have been proposed or are under development, but, in general, the "extended absorption" method seems to be the most popular.

Energy Recovery--Except in older plants operating at atmospheric pressure throughout and in very small medium- and high-pressure installations, most or all of the energy needed to drive the air compressor can be recovered in the form of steam and hot tail gas. In some instances, a small amount of surplus steam is generated.

This is made possible by the availability of highly efficient machines, which comprise a compressor, steam turbine, and tail-gas expander built in the form of a single, in-line unit. In dual-pressure processes, a compressor for raising the pressure of nitrogen oxides, prior to absorption, is also included. Occasionally, an electric motor is also added to the power unit for startup or emergency purposes, if sufficient steam is not always available. Electrical requirements for pumps and ancillary purposes are usually drawn from the main factory power supply.

Platinum Recovery--Platinum passes into the gas stream in the form of very fine particles, and its loss can represent an increase of several percent in production costs. Therefore, recovery units are installed in many plants, and the fine dust reclaimed is returned with spent gauzes to the precious metal refinery. Several types of recovery units are in use; the more common incorporate filters of glass wool or silica fibers (31). One device uses calcium oxide as a filter medium, and the retained platinum dust is recovered by slurrying with water and dissolving in nitric acid, followed by filtration. Recoveries should be of the order of at least 50% for dry filters and may be as high as 80% for the lime type of unit, according to the permeability of the filter media used and the type of process. Attempts to increase platinum recovery by using finer filter media may result in greater operating costs; hence, an optimum balance between these two factors must be adopted.

Technical and Economic Comparisons

The availability of low-, medium-, and high-pressure techniques for oxidation and absorption offers a variety of alternative combinations by which nitric acid can be manufactured, and this has led to the development of numerous commercial processes differing largely in accordance with the combination selected (32). In general, high-pressure operation permits smaller plant units to be used for a given output and helps to reduce capital cost. High pressures also favor NO_2 absorption. However, high-pressure ammonia oxidation induces greater catalyst losses and also increases power requirements unless additional equipment is installed for power recovery. Because of recent emphasis on pollution control, the ability of high-pressure processes to attain acceptably low NO_x levels in the tail gas has favored their adoption. Therefore, most new plants use either mono-high-pressure or dual-pressure (medium-pressure combustion--high-pressure absorption) processes, although some mono-medium-pressure processes are used.

According to Honti (24) the advantages and disadvantages of the three types of processes can be summarized as follows:

	Mono-Medium Pressure 5/5[a]	Dual-Medium-High Pressure 5/10[a]	Mono-High Pressure 10/10[a]
NH_3 required, kg/ton HNO_3	284	284	288
Pt loss, mg/ton HNO_3	95	95	150
Electricity required, kWh/ton HNO_3	22	22	8
Steam credit, kg/ton HNO_3	600	300	400
Relative capital cost	120	110	100
NO_x in tail gas, ppm[b]	400	less than 200	less than 200

a. Pressure in atmospheres in combustion and absorption, respectively.
b. Typical values for extended absorption from various sources.

The above values are intended to be illustrative only; actual values may vary widely depending on plant design and operating conditions. However, the tabulation illustrates the point that the high-pressure processes generally will have the lowest capital cost and highest operating cost because of higher platinum losses, less efficient NH_3 conversion, and lower steam recovery. The medium-pressure process will have the highest capital cost and lowest operating cost (assuming the NO_x content of the tail gas is acceptable). The dual-pressure process represents a compromise. The choice may be influenced by local conditions.

A more recent paper compared a dual-pressure process (COFAZ) operating at 3 and 10 atm with a single, high-pressure process (C&I Girdler) operating at 10 atm, both on a scale of 900 tpd and both with absorption efficiency sufficient to ensure tail gas NO_x content of less than 200 ppm (24). Under U.S.

conditions the capital costs were 13% higher for the dual-pressure process ($13.8 versus $12.2 million); under French conditions the cost differential was about 10%. Process requirements cover:

	Requirements per ton of HNO_3	
	Dual Pressure	High Pressure
NH_3, kg	282.1	286.6
Catalyst loss, mg	101	235
Electricity, kWh	4.7	7.5
Steam export, kg	341	456

The cost of production, with ammonia at $121/ton, was estimated to be $1.34/ton of HNO_3 lower for the dual-pressure process ($34.28 versus $35.84), not including capital charges. The authors concluded that, under the conditions assumed in the estimate, the saving in operating cost was not sufficient to justify the higher capital cost for U.S. conditions. However, changes in the cost of catalysts or in the value of steam could lead to a different conclusion. It was noted that the value of export steam would depend on what use could be made of it at the plant location.

Materials of Construction

The strongly oxidizing properties of nitric acid produce a passivating effect on certain metals, e.g., iron, steel, and aluminum, via the formation of complex oxides and nitride films. Hence, these metals can be employed for the construction of certain equipment items and storage vessels when used in conjunction with acids containing 55%-65% HNO_3 under mildly agitated or static conditions and not at elevated temperatures. For severe service, silicon-iron and some of the highly corrosion-resistant stainless steels are needed. Type 304 stainless steel is widely used for storage tanks. Dilute HNO_3 solutions, especially if agitated and heated, may also require the use of alloy steels, e.g., for the wetted parts of pumps, impellers, and distillation columns. For equipment used in handling hot, dry gases, mild steel is usually adequate. In some instances, plants built almost entirely of stainless steel are preferred since the saving in maintenance costs and the improved operating performance are said to justify the additional investment costs.

As regards nonmetallic materials, earlier plants used stoneware extensively for equipment construction. Industrial glassware has also been employed. Various fluorocarbon plastics in the form of lined and unlined piping, sheet and coatings, as well as gaskets and seals, are used to an increasing degree in nitric acid plants because of the inertness, flexibility, and convenience even though initial costs may be relatively greater than for steel or some ferrous alloys. Some of the latest proprietary fluorocarbon materials are said to be inert even to hot, fuming nitric acid.

Ammonium Nitrate

Ammonium nitrate is the most popular form of nitrogen fertilizer in most European countries and in some other temperate zone countries. It is popular in North America but not the most popular since that place is held by anhydrous ammonia. It is more readily available to crops than urea or ammonium sulfate; most crops take up nitrogen mainly in the nitrate form, thus ammoniacal nitrogen must be converted to nitrate in the soil before it becomes effective. While the nitrification process is rapid in warm soil, it is very slow in cool soil (10°C and below). Also urea is phytotoxic to some crops when placed near the seed while ammonium sulfate is strongly acid forming. For these and other reasons ammonium nitrate is the most popular nitrogen fertilizer in many temperate zone countries including most European countries. It is used as a straight material or in mixtures with calcium carbonate, limestone, or dolomite called calcium ammonium nitrate (CAN) or ammonium nitrate-limestone (ANL) or various trade names and in compound fertilizers including nitrophosphates. It is also a principal ingredient of most nitrogen solutions (chapter X).

The main disadvantages of ammonium nitrate are: (1) it is quite hygroscopic, (2) there is some risk of fire or even explosions unless suitable precautions are taken, (3) it is reported to be less effective for flooded rice than urea or ammoniacal nitrogen fertilizers, and (4) it is more prone to leaching than ammoniacal products.

Increasing quantities of ammonium nitrate are used for blasting purposes in conjunction with fuel oil, and relatively small amounts are consumed by the brewing and chemical industries. The earlier "grained" type of ammonium nitrate, made by rolling the semi-molten salt in an open pan and coating with resins or waxes, has been largely superseded by prilled, granular and crystalline end-products.

Properties of Ammonium Nitrate

The more important properties of ammonium nitrate are given in table 5. The changes in crystal state at 84.2°C and 32.1°C result in sudden expansion, which may cause particle degradation during processing and storage. The change in crystal form at 32.1°C can be particularly troublesome in climates where the ambient temperature often passes through this point; repeated cycling through this temperature can cause disintegration of prills or granules to a powder and lead to caking problems. However, methods of stabilizing the crystal form in the rhombic form IV have been developed and widely used. One

TABLE 5. PROPERTIES OF PURE AMMONIUM NITRATE (CRYSTALLINE FORM IV)

Color	White
Molecular weight	80.04
Nitrogen content	35.0%
Density, 20°/4°C	1.725
Melting point	170.4°C
Solubility, g/100 g of water	
Temperature (°C)	
0	118
20	187
40	297
60	410
80	576
100	843

Crystal states

Temperature (°C)	State	System
169.6	Liquid	-
169.6 to 125.2	Cubic	1
125.2 to 84.2	Tetragonal	2
84.2 to 32.1	Rhombic	3
32.1 to -18	Rhombic	4
Below -18	Tetragonal	5

Critical relative humidities	
20°C	63.3
30°C	59.4

of these methods developed and patented by Mississippi Chemical Corporation (United States) consists of adding a small proportion (about 1%) of a mixture of ammonium sulfate and diammonium phosphate called "Permalene." Magnesium nitrate is also used as a stabilizer in some European countries. Another characteristic of ammonium nitrate is its negative heat of solution: 60 parts of salt will give a reduction in temperature from 13.6°C to -13.6°C when dissolved in 100 parts of water.

Hazards of Ammonium Nitrate

It is well known that ammonium nitrate can be used as an explosive. In fact, several plants were built during World Wars I and II to produce ammonium nitrate for use in bombs and other explosives. For this purpose it was usually mixed with more powerful explosives or detonators. A mixture of ammonium nitrate with about 6% fuel oil is widely used as a blasting agent in mining operations. Fertilizer-grade ammonium nitrate previously (in the 1940s) was conditioned with an organic coating (a mixture of paraffin, rosin, and petrolatum), and some disastrous explosions occurred when shiploads of this material were detonated by fire and confinement. These disasters led to strict regulations governing the manufacture, transport, storage, and use of ammonium nitrate for fertilizer purposes. Some countries forbid the sale of straight ammonium nitrate as fertilizer. In these countries, the mixture of ammonium nitrate with calcium carbonate called CAN is permitted. Formerly CAN contained 20.5% N, corresponding to about 60% ammonium nitrate; at present, the most common grade is 26% N (75% AN).

In other countries (France, U.S.S.R., Romania, the United Kingdom, and the United States, to name a few) straight ammonium nitrate is commonly used as a fertilizer with strict regulations. For instance, the Fertilizer Institute (United States) has published a definition of ammonium nitrate fertilizer which follows:

"Ammonium Nitrate Fertilizer is defined as solid ammonium nitrate containing a minimum of 33.0% nitrogen, having a minimum pH of 4.0 in a 10% aqueous solution, 0.20% maximum carbon, 0.010% maximum elemental sulfur, 0.150% maximum chloride as Cl, or particulated elemental metals sufficient to release 4.60 ml, maximum, of hydrogen from 50.0-g sample and which will pass the detonation propagation test in section 2.0 and the burning test in section 4.0."

The publication contains analytical and test procedures. In the detonation propagation test, ammonium nitrate is packed into a 6-ft (1.83-m) section of 3-in (7.6-cm) diameter iron pipe of specified quality, and a specified explosive charge is placed in the ammonium nitrate in the top of the pipe. When the explosive charge is detonated, the extent, if any, to which the ammonium nitrate is detonated is judged by the length of damaged pipe. Any material that propagates through the length of the pipe and leaves no undamaged pipe is considered unsafe.

The burning test is rather complicated, but in general it is designed to exclude formulations that may catalytically increase the decomposition rate of ammonium nitrate even though the catalytic substance is not excluded by the definition or detected by analytical procedures.

Further regulations cover precautions to be taken in storing, packaging, and transporting ammonium nitrate and in fighting fires where ammonium nitrate is present.

Some compound fertilizers containing ammonium nitrate and chloride, such as potassium chloride, are subject to propagated decomposition or "cigar burning" when ignited. The ignition temperature is about 200°C, but it may be lowered by certain sensitizing agents, such as copper salts. The range of compositions of NPK and NK fertilizers that are subject to decomposition has been studied by Huygen and Perbal (33), TVA (34), and others. As little as 4% KCl (about 1.9% Cl) is sufficient to make some mixtures susceptible to cigar burning. The reaction is inhibited by ammonium phosphate; therefore, many NPK compositions containing ammonium nitrate and potassium chloride are free from this hazard. Figure 12, taken from Perbal (33), shows the area of cigar-burning compositions in the system NH_4NO_3-KCl-$NH_4H_2PO_4$.

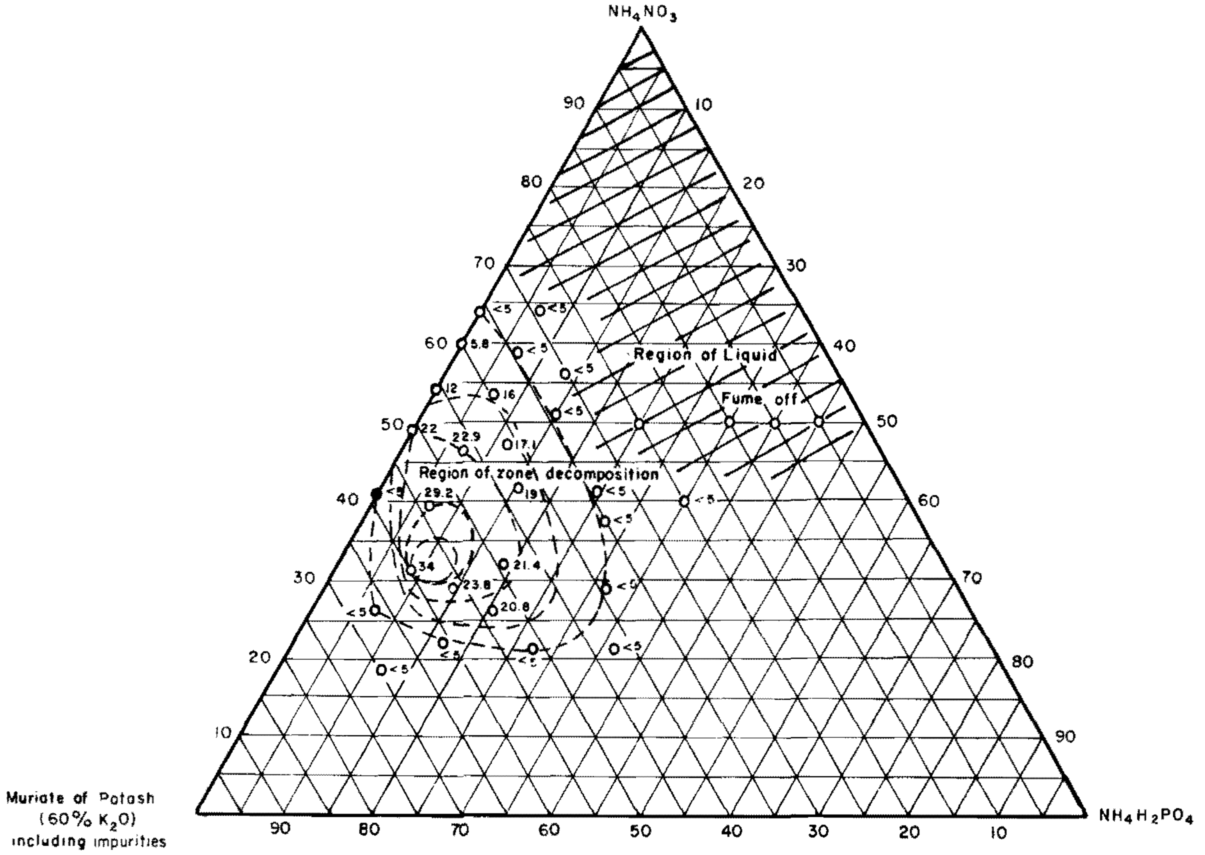
For materials that are susceptible to cigar burning, the reaction may be initiated by such accidental means as a piece of hot metal from a welding operation or an electric light bulb that becomes buried in the fertilizer or by overheating material caked on the flights of a dryer. Once initiated, the decomposition propagates through the mass of material at a rate that usually ranges from 5 to 50 cm/hr. The temperature in the decomposition zone usually is 300°-500°C. The exact nature of the reaction is not entirely clear, but it results in complete destruction of the ammonium nitrate and evolution of some of the chloride. Noxious red, white, yellow, or brown fumes are given off containing NH_4Cl, HCl, Cl_2, NO_2, and other oxides of nitrogen, N_2, and H_2O. The fumes are toxic and have resulted in several fatalities in some incidents.

Since the reaction does not require oxygen, other than that present in ammonium nitrate, the fire cannot be extinguished by smothering. It can only be stopped by flooding with water. If a localized area of decomposition in a bin or pile is discovered early enough, the decomposing material may be removed from the building by a power shovel, for example, and extinguished by water, thereby saving the remainder of the material.

Since compound fertilizers may have a variety of formulations, it is not always possible to predict what composition will be in the cigar-burning class. TVA has developed a simple test; a 50-lb (23-kg) bag of the fertilizer to be tested is heated at one end with a blow torch until decomposition has started as evidenced by copious fumes. If the decomposition stops when the flame is removed, the material is not subject to propagated decomposition. If it continues to decompose the rate of progress of the decomposition zone can be measured by thermocouples inserted in the material at 10-cm intervals.

A more elaborate and precise method is described in a handbook titled Selected Methods of Test for the Thermal Stability of Compound Fertilizers Containing Ammonium Nitrate, which was issued jointly by ISMA and APEA (first printing in 1970). The "zonal decomposition test" is carried out in an apparatus which consists of a trough 15 x 15 x 50 cm constructed of heavy wire mesh.

The trough is filled with the fertilizer to be tested, and a steel plate at one end of the trough is heated to a temperature between 400°C and 800°C, either with gas burners or an electric heating element. Heating is continued until decomposition of the fertilizer adjacent to the heated steel plate is well established or up to 1 hour. Then heating is discontinued and the position of the decomposition front is noted. If propagation of decomposition stops almost as soon as the heat source is turned off, the material does not show self-sustaining decomposition. If the decomposition zone continues through the entire trough, the fertilizer is capable of self-sustaining decomposition. If desired, the rate of progress of the zone may be timed. In some cases decomposition may continue some time after the heat is turned off but stops before it reaches the end of the trough. In this case the handbook suggests that the decomposition should be regarded as self-sustaining if it continues for a distance of 15 cm.



Note: Rates of Movement of Decomposition Zone Are Shown in cm/hr.

Figure 12. Area of Decomposition in the System NH_4NO_3-KCl-$NH_4H_2PO_4$.

The issuing organizations (ISMA and APEA) disclaim responsibility for practical application of the test. However, some countries (mainly Scandinavian) prohibit the sale of fertilizers that are subject to self-sustaining decomposition, and the "trough test" described above is an accepted test method to identify such fertilizers.

The ISMA/APEA handbook also contains test methods for determining explosibility (three methods), homogeneous decomposition at elevated temperatures, self-heating of fertilizers, and oxidizing potential. Various agencies have worked out regulations for transport of potentially dangerous goods by rail, ship or barge, air, and truck.

Ammonium nitrate is generally regarded in most countries as posing no unacceptable hazard when suitable precautions are taken. "Fertilizer grade" ammonium nitrate (see definition above) cannot be exploded by impact. There are no records of explosions due to heat and fire alone. In several cases storage buildings and farm buildings containing ammonium nitrate have burned without explosion. In one case of a warehouse fire, a small amount of ammonium nitrate that had been contaminated by oil drippings from a power shovel exploded, but the rest of the ammonium nitrate did not explode. Some countries may prohibit straight ammonium nitrate from which it is relatively easy to make explosive devices.

The question is often asked "What maximum percentage of ammonium nitrate in fertilizer is nonexplodable?" There is no simple answer to this question; it depends on what materials the ammonium nitrate is mixed with, how much carbonaceous material is present, if any, how much detonator is used, and several other factors. As mentioned previously, pure ammonium nitrate is difficult to detonate, but it can be exploded if it is confined and primed with enough high explosive. Perbal describes tests in which mixtures of ammonium nitrate and various other fertilizer materials were coated with 0.4% fuel oil. The mixtures were then tested for explosibility by two standard test procedures, both involving a standard detonating charge (33). As a result of these and other tests, the Dutch Government authorities have set the following maximum limits of ammonium nitrate in mixtures:

Material Mixed with Ammonium Nitrate	Maximum Allowable % Ammonium Nitrate
Chalk	80
$(NH_4)_2SO_4$	40-45
$(NH_4)_2HPO_4$	65-70
$CaHPO_4$	70
KCl	70
K_2SO_4	70

Perbal concludes that compound fertilizers in general may be regarded as safe from explosion hazard if they contain less than 70% NH_4NO_3 unless there is a high percentage of $(NH_4)_2SO_4$ or other reducible material in the mixture in which case the material should be tested (32).

Production Methods

Several proprietary processes for ammonium nitrate manufacture are available, using various combinations of different neutralization, evaporation, and drying and finishing methods. Solid ammonium nitrate is produced in the form of prills, crystals, and granules, either alone or in combination with other materials. Large tonnages of ammonium nitrate are also made in the form of solutions having concentrations in the range of 80%-90% for use in granular compound fertilizers. The hot solution is shipped to granulation plants in insulated rail or road tankers, especially in the United Kingdom. The solution is also used to prepare nitrogen solutions containing ammonia or urea for use in granulation plants or liquid fertilizer (see chapter X). The major unit operations used in ammonium nitrate manufacture are described below.

Neutralization--When sufficient steam to operate the plant is readily available from byproduct or other low-cost sources, the use of an atmospheric type of neutralizer may be preferable since such units are relatively low in capital costs and simple to operate. Alternatively, most or all of the steam needed to preheat the feeds and to concentrate the ammonium nitrate solution can be generated by neutralizing acids containing more than 50% HNO_3 in a unit of the pressure type. (By using a 64% acid, about 1 ton of steam can be produced for each ton of ammonia neutralized.) In some plants, especially those designed to make a crystalline product, neutralization is performed under vacuum in equipment similar to that used for ammonium sulfate manufacture (35).

In pressure neutralizer processes, the neutralizer usually operates at 4-5 atm and 175°-180°C. Nitric acid is fed to the neutralizer at a usual concentration range of 50%-60%. In some cases it may be preheated with byproduct steam. Ammonia is fed to the neutralizer in gaseous form. If it is available in liquid form, it is vaporized in a heat exchanger by steam or air. If air is used the cooled air may be used to cool the prilled or granulated ammonium nitrate product. The neutralizer may be operated at a low pH (3-4) to avoid ammonia loss, and more ammonia may be added later to adjust the pH to 7. The concentration of the solution from the neutralizer usually is in the range of 80%-87% ammonium nitrate. It is evaporated further by use of steam from the neutralizer to a concentration of 94%-98%. In many plants, a final evaporator-concentrator is used to bring the solution concentration up to 99.5%-99.8%.

In the case of atmospheric pressure neutralization, the temperature in the neutralizer is lower (about 145°C), and the steam generated is at a lower temperature and pressure. The waste steam can be used to vaporize ammonia or to evaporate the ammonium nitrate solution in a vacuum evaporator. Depending on the efficiency of utilization, the heat of reaction, the nitric acid concentration, and other factors, the net steam requirement may range from 0.0 to 0.5 ton/ton of AN; in some cases a small surplus of steam may be available for export.

Finishing Processes

In the past several finishing processes have been used including graining, flaking, granulation, crystallization, and "low-density" prilling. In low-density prilling, the ammonium nitrate solution is fed to the prill tower at about 95% concentration, and the resulting prills are dried and cooled. The prills are somewhat porous and may have an apparent specific gravity of 1.29 compared with 1.65 for high-density prills. Some of these methods are still in use, particularly for AN used as a blasting agent. A porous prill or granule that will absorb oil is preferred for this use.

For fertilizer use, the high-density prilling process, using 99^+% solution concentration, has been used in most new plants that make straight AN. Quite recently, however, there has been a trend toward greater use of granulation processes that also use 99^+% solution. Two granulation processes are in commercial use--a pan granulation process developed by Norsk Hydro (Norway) and a spray-drum granulation ("Spherodizer") process developed in the United States by C&I Girdler, a subsidiary of Bechtel Corp. The advantages of the granulation processes over prilling are: (1) a wider choice of granule size including "forestry grade" (4-10 mm) and (2) less difficult collection of fume and dust to meet new, strict pollution control standards. The granulation processes are also applicable to urea and will be described further in chapter IX. Figure 13 is a process diagram of a high-density prilling process including the neutralization and evaporation step.

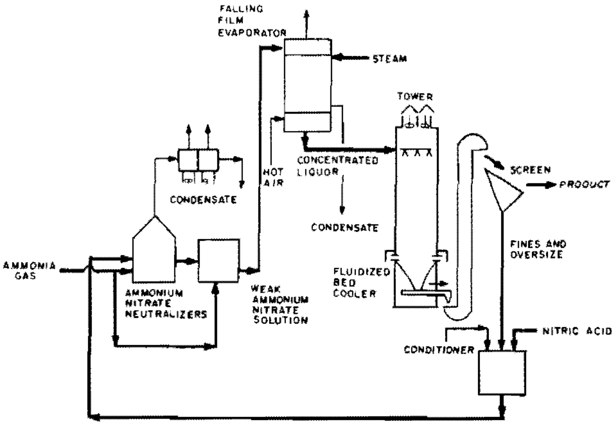


Figure 13. Ammonium Nitrate High-Density Prilling Process (ICI).

When the desired product is CAN, the usual choice is between prilling and granulation. Either rotary drum granulators or pugmills (blungers) are used. The concentrated ammonium nitrate solution is mixed with ground calcitic or dolomitic limestone, chalk, marl, or precipitated calcium carbonate (a byproduct of some nitrophosphate processes, see chapter XV). The mixing should be done quickly to limit ammonia loss by the reaction:

$$2NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + NH_3 + CO_2 + H_2O$$

A soft or chalky limestone is preferred in some granulation processes. Gypsum has been used instead of limestone experimentally with good results.

The usual grade of CAN was about 21% N in the early 1960s; this grade corresponds to 60% AN; the grade has been increased in most countries to 26% N (about 74% AN). As in the case of straight ammonium nitrate, there has been a tendency to use more concentrated AN solution so as to avoid a drying step. However, 98% or even lower concentrations can be used since the heat of crystallization is sufficient to dry the product to an acceptable level. Figure 14 shows a typical CAN process diagram.

The SBA process is widely used in Europe.[1] The SBA granulator is similar to a double-shafted pugmill except that it contains intermeshing helical flights at the feed end where the ammonium nitrate solution is mixed with ground limestone and recycled fines. The remainder of the pugmill is fitted with the usual type of blades. The rate and direction of rotation is such as to obtain a fluidized bed effect, and a flow of air through the granulator sweeps out water vapor. In rotary drum granulators, the production of granular CAN is much like that of compound fertilizers (see chapter XIX). The product is cooled and screened, and fines and crushed oversize are recycled. A fluidized bed cooler is used in some plants. In some plants part of the ground chalk or limestone is reserved for coating the final product to improve its physical properties. In other plants, a clay conditioner may be used.

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1. Société Belge de l'Azote et des Produits Chimique du Marly.

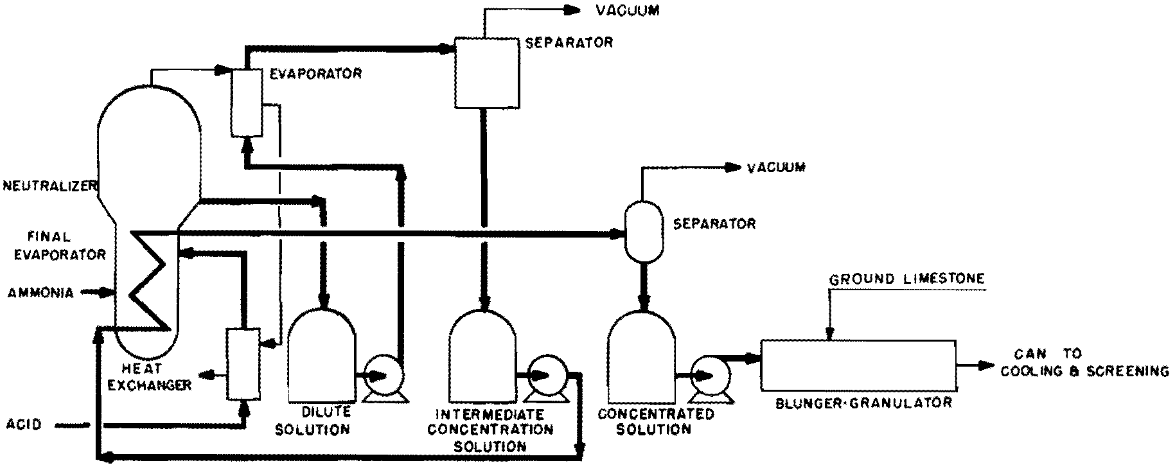

Figure 14. Process Using Pressure Neutralization and Limestone Addition to Make Calcium Ammonium Nitrate (CAN) (Based on SBA Process).

In prilling CAN, the AN solution is premixed with the ground limestone immediately before prilling. A rotating, perforated bucket is the preferred type of drop-forming apparatus. Prill towers for both CAN and AN commonly are 46-56 m high, although shorter ones also are used. For high-density prilling using 99.7% solution, prilling towers that are 15-30 m tall may be used. Cooling may be carried out in a rotary cooler or in a fluidized bed either in the bottom of the prill tower or in a separate unit.

Prilled or granulated AN or CAN materials are often coated with a powdery conditioning agent such as china clay, kieselguhr, or calcined fullers earth, in amounts ranging from 1%-3%. Conditioned ammonium nitrates usually have a guaranteed N content of 33.5%-34.0%. In some climates, coating to prevent caking is not considered necessary, especially with stabilized, high-density prills of very low-moisture content. In this case the guaranteed N content is 34.0%-34.5%. As mentioned previously, stabilizers that prevent change in crystal form at 32°C have been developed and used. These stabilizers include magnesium nitrate (produced by dissolving magnesite in the nitric acid) and "Permalene," a combination of ammonium sulfate and diammonium phosphate.

Ammonium nitrate may be stored in bulk although in most climates controlled-humidity storage buildings are advisable. In most countries the product is distributed in bags which should be "moisture proof"; at least one ply should be impermeable to moisture. Plastic film bags or bags with plastic liners are suitable if properly constructed. In the United States, bulk shipment is common using covered, hopper-bottom rail cars.

Fisons Ltd. (United Kingdom) has developed a unique ammonium nitrate process called the "Nitro-Top" process in which the AN solution (99.7%) is prilled into a fluidized bed of dust. Figure 15 is a simplified diagram of the process. The dust bed is cooled by circulating cooling water through coils and plates in the dust bed to maintain a temperature of about 50°C. The dust may be clay or talc or other material smaller than 50 µm. Some of the dust adheres to the prills as a coating which improves the physical properties. The amount of dust that adheres depends on the material; by using a mixture of montmorillonite clay and talc or other combinations, the desired coating weight of about 3% is obtained. The fluidizing air passes through a cyclone and a bag filter before it is discharged to the atmosphere; the recovered dust is returned to the dust bed. The prills are discharged from the bottom of the tower countercurrent to an airstream that holds back the dust. The product then goes to a final deduster and then to screens where small amounts of offsize material is separated.

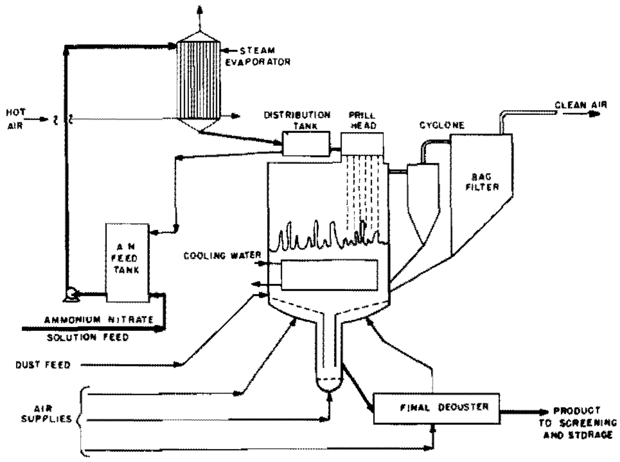

Figure 15. Ammonium Nitrate Dust Prilling Process (Fisons).

- Advantages claimed for the process are:

1. The prill's size is uniform and can be larger than in air prilling, for example, 99% plus 2.4-minus 4.0-mm (mean diameter 2.6 mm). This size is a usual size for granular fertilizer in Europe and, therefore, can be applied by the same machinery without adjustment or used in bulk blends.
2. The prilling tower is only 7 m tall as compared with about 50 m for air prilling.
3. The same equipment combines the function of prilling, cooling, and coating.
4. There are no pollution control problems.

Pollution Control

As in all industrial operations, pollution control requirements for AN and CAN plants have become more stringent in recent years. This has posed a difficult problem for high-density AN prilling because of the large volume of air exhausted from prill towers and because of the very small particle size of the fume in the air. Fuming is much more severe in high-density prilling because the AN melt to be prilled must be at a high temperature (about 180°C) to keep it from freezing. At this temperature there is an appreciable vapor pressure of NH_3 + HNO_3 resulting from dissociation of AN, according to the equation:

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$

The dissociation products recombine in the cooler air to form a blue haze consisting of AN particles of submicron size. Particles of this size are difficult to collect, and they present a highly visible and stable haze or fog. The problem is much less serious with low-density prilling because of lower AN solution temperatures. It is less serious in granulation processes because of much smaller volumes of air in contact with hot solution.

The amount of AN in exhaust gas from the high-density prill tower is likely to be only about 0.1% of total production including both dust and fume. Recovery of this amount is seldom justifiable by economics alone but is often necessary for environmental reasons. A solution to this difficult problem has been developed by the Co-Operative Farm Chemicals Association (CFCA) and is in use at its plants in Lawrence, Kansas, and at least 14 other plants in North America (36). The fume abatement system consists of installing a bell-shaped shroud around the spray head in the upper part of the prill tower to collect fume-laden air from that part of the tower where fume is formed due to contact of the air with hot AN solution or prills in the process of solidification. The air flow through this shroud is only about 25% of the total air flow through the tower; the remaining 75% is practically free of dust and fume and is discharged directly to the atmosphere. The air from the shroud is drawn through a scrubber and Brink high-efficiency mist eliminators. Fume and vapors from the neutralizer and evaporators are treated in the same scrubbing system. The scrubber solution is recirculated to build up its concentration and eventually recycled to the AN solution preparation step. The entire system is reported to cost about \$0.5-\$1.5 million for plants of 250-1,000 short tons/day capacity. The system recovers 3-7 kg of AN/ton of product from all sources (neutralizer, evaporator, and prill tower) which more than offsets the operating cost (excluding capital costs). From a pollution abatement viewpoint the system has met applicable standards; atmospheric emissions less than 0.5 kg/ton of product and opacity of less than 10% have been attained (36).

Sodium Nitrate

General Information

Before the availability of synthetic ammonia and its derivatives, sodium nitrate of natural origin was the major source of nitric acid and chemical nitrogen for fertilizer purposes in many countries. Most of this nitrate originated in Chile, where it is principally found in a large ore body nearly 500 miles long and 10-50 miles wide, on the eastern part of the Chilean coastal range. Nitrate production is still a major industry in Chile and currently (1976) is about 650,000 tons of sodium nitrate annually. Small deposits occur in other areas, e.g., Africa, Australia, Mexico, and Egypt. Substantial amounts of synthetic sodium nitrate were formerly made in Europe and the United States, but production has declined since World War II and now only insignificant amounts are produced from byproduct sources.

Principal Uses

As a fertilizer, sodium nitrate has long been applied as a surface dressing for cotton, tobacco, and some vegetable crops. However, its use as a "straight" nitrogen fertilizer has declined considerably during the last century. For example, in the United Kingdom, some 20,000 tons of N was used in the form of sodium nitrate in 1899; whereas, relatively none is used today. In the United States, current (1977) consumption is about 10,000 tons of N. As with other nitrates, sodium nitrate is prone to leaching in the soil, but it has the advantage of possessing a metallic cation. Unlike ammonia and its derivatives, including urea, sodium nitrate will not promote cation losses in the soil and lead to unsuspected soil acidity.

Industrial applications include meat preservation, heat treatment of metals, and use as a flux in the ceramic and metallurgical industries.

Properties of Sodium Nitrate

The properties of sodium nitrate are given in table 6.

TABLE 6. PROPERTIES OF PURE SODIUM NITRATE

Formula	$NaNO_3$
Guaranteed analysis (typical)	
Nitrogen	16.48%
Sodium	27.05%
Appearance	White crystalline rhombohedra
Molecular weight	85.01
Melting point	308.3°C
Density, 20°/4°C	2.257
Solubility, g/100 g of water	
Temperature (°C)	
0	73
10	96
30	176
100	180
Bulk density	
Pellets	1,202 kg/m^3
Coarse material	1,282 kg/m^3
Fine powder	1,363 kg/m^3
Critical relative humidities	
20°C (68°F)	74.7
30°C (86°F)	73.7

Production Methods

From Natural Deposits--In Chile, the nitrate ore or caliche is widely varying in composition and may range from 80% to virtually zero nitrate content although little high-grade material is available today. A typical analysis of run-of-mine ore might be the following (in percentages):

$NaNO_3$	7-10
NaCl	4-10
Na_2SO_4	10-30
Mg, Ca, K, Br, I_2	2-7
H_2O	1-2
Remainder (Gangue)	41-76

These components are present in the form of complex, mixed sulfates, e.g., darapskite ($NaNO_3 \cdot Na_2SO_4 \cdot H_2O$).

Early production methods were based on hand-picking the higher grade ore containing about 13% sodium nitrate and leaching it in directly heated open pans until saturation was reached. The solution was then piped to settling pans and cooled to produce sodium nitrate crystals, which were drained, dried in the sun, and bagged or shipped in bulk overseas. An improved version of this method known as the

Shanks process, which was first used about 1890 and remained popular for about 50 years, is now virtually obsolete. Most current production is undertaken by the Guggenheim process, which permits ores containing under 10% nitrate to be profitably worked, thus extending the life of the Chilean nitrate industry by several decades.

In the Guggenheim method, caliche is mined by open-pit operations, using draglines and power shovels, and is crushed to about 80% between 3/4 and 3/8 in (1.9-0.95 cm). This product is leached at about 40°C with water in a series of vats, each having a capacity of some 10,000 tons of crushed ore. The underflow from each vat is heated before passing to the next since sodium nitrate has a negative heat of solution. After extraction and washing are complete, the residue is removed from the vats by grabs and is hauled to a waste dump.

Fine material from the crushers is pulped in a separate system, and the gangue is removed by means of Moore filters. The filtrates are combined with liquor from the leach tanks and are chilled in shell-and-tube units to precipitate crystalline sodium nitrate. Initial cooling is effected by heat-exchange with in-process leach liquor and final chilling by ammonia. The sodium nitrate slurry is dewatered and washed in batch centrifuges to yield a crystalline product substantially 48-mesh in size and containing approximately 3.5% of free moisture. When a grained or prill-type product is required, the centrifuged salt is melted at about 400°C in reverberatory furnaces, spray dried in large towers, cooled by heat exchange with mother liquor in shell-and-tube units and screened to yield pellets in the 10- to 20-mesh range containing about 98% sodium nitrate and 0.2%-0.3% free moisture.

Iodine salts which are present in the caliche accumulate in the recycling mother liquor and are reduced to iodine in a separate process; this production amounts to some 2,000 tons annually. In addition, it has been found that salts which are insoluble in recycling leach solutions can be extracted from the caliche by fresh water and recovered by solar evaporation and selective crystallization to yield substantial tonnages of additional sodium nitrate, as well as potassium nitrate, various iodates, borates, and sulfates. These associated salts may be of future significance to the Chilean nitrate industry.

Synthetic Sodium Nitrate--The dependence of the United States and other countries on natural Chilean sodium nitrate during the early part of the 20th century led to the development of several chemical processes for its manufacture. All these methods produce a sodium nitrate solution which is concentrated, crystallized, and centrifuged. In some cases, the dewatered and washed salt is dried in a rotary drier prior to screening, storage, and bagging; alternatively, it may be melted and grained or prilled.

Appreciable quantities of sodium nitrate have also been made in the United States by the salt process developed by the Allied Chemical Corporation. In this method (which is believed not to be currently in operation), nitric acid and sodium chloride are reacted to yield sodium nitrate, chlorine, nitrosyl chloride and water, e.g.:

$$4HNO_3 + 3NaCl \rightarrow 3NaNO_3 + Cl_2 + 2H_2O + NOCl$$

The nitrosyl chloride can be used as an intermediate for other derivatives, or it can be reacted with sodium carbonate to yield additional sodium nitrate, sodium chloride, nitric oxide, and carbon dioxide:

$$3NOCl + 2Na_2CO_3 \rightarrow NaNO_3 + 3NaCl + 2NO + 2CO_2$$

The salts produced can be redigested and the nitric oxide used to make additional sodium nitrate (or nitric acid). Alternatively, the nitrosyl chloride can be oxidized to yield dinitrogen tetroxide and chlorine for further use, e.g.:

$$2NOCl + O_2 \rightarrow N_2O_4 + Cl_2$$

Other methods used to produce sodium nitrate in minor quantities (sometimes as a byproduct) include reacting nitric acid with soda ash or caustic soda and using ion-exchange between calcium nitrate and a sodium zeolite. Several double-decomposition reactions between various nitrates and alkali salts, for example, ammonium nitrate and caustic soda or common salt, have either been proposed or tested on a small scale.

Storage

Sodium nitrate can be stored and shipped in bulk under conditions of low humidity but should be packed in moisture-resistant bags when intended for use in damp or tropical climates. In some countries, it is regarded as a potential fire hazard and may necessitate special labeling, insurance, and other precautions as for ammonium nitrate and potassium nitrate. Such materials as bags or timber, subsequently allowed to dry after impregnation with sodium nitrate, may quickly ignite if exposed to elevated temperatures and should be destroyed or thoroughly washed and fireproofed.

Potassium Nitrate

The production, properties, and use of potassium nitrate will be covered in chapter XVIII (Potash Fertilizers).

Calcium Nitrate

General Information

Although simple methods are available for producing calcium nitrate, its use as a fertilizer is offset by extreme hygroscopicity even in moderately humid climates. It is possible that the more recent availability of impervious plastic bags may increase the popularity of calcium nitrate for agricultural use. As a fertilizer, calcium nitrate has special advantages for use on saline soils since the calcium displaces the sodium that is absorbed by clay in soils. For this reason it may be preferred for use in areas with soil salinity problems, such as parts of Egypt and California. It also has the advantage of being nonacid-forming. Other applications include explosives, pyrotechnics, and inorganic chemical operations.

Properties of Calcium Nitrate

The properties of calcium nitrate are given in table 7.

Production Methods

Most calcium nitrate comes from Europe, where it is produced in two principal ways. In one method a direct reaction between calcium carbonate and nitric acid is employed, and in the other the calcium nitrate formed as a coproduct in some nitrophosphate processes is separated by crystallization and filtration or centrifuging.

Direct Process--In the direct process, crushed limestone is reacted with 50% nitric acid in towers lined with acid-resistant brick, and the residual acid is neutralized with lime. The liquor which contains

TABLE 7. PROPERTIES OF CALCIUM NITRATE

Formula	$Ca(NO_3)_2$
Appearance	White, crystalline
Molecular weight	164.10
Melting point	555.7°C
Density, 20°/4°C	2.36 (anhydride)
Solubility, g/100 g of water	
Temperature (°C)	
0	102
100	364
Approximate analysis (fertilizer grade)	
Nitrogen	15.5%
Calcium	36.0%
Critical relative humidities	
20°C	54.8
30°C	46.5

about 40% $Ca(NO_3)_2$ is clarified in settling tanks and brought to a concentration of 87% in a vacuum evaporator unit. Some 5% of ammonium nitrate is then added as a granulation aid to raise the nitrogen content to 15.5%, prior to spray drying in a prilling tower. The granules or prills are cooled, screened, and packed in moisture-resistant bags.

The above reaction, which is exothermic, is represented by:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O - 15{,}410$$

Nitrophosphate/Calcium Nitrate Production--The production of byproduct calcium nitrate in nitrophosphate processes is discussed in chapter XV.

Nitrophosphate processes can be divided into two categories, namely, those in which calcium nitrate is separated from the nitrophosphate liquor and those wherein calcium nitrate is converted to less hygroscopic compounds, e.g., ammonium nitrate, and no separation is undertaken (10).

Most processes in the first category are variations of the original Norwegian "Odda" method in which 1.0 part of ground phosphate rock is digested with about 1.5 parts of nitric acid at 55°-70°C in a continuous reaction system. The reaction liquor is then chilled by brine in heat exchangers to precipitate calcium nitrate tetrahydrate, which is separated and washed by means of centrifuges or rotary vacuum filters. The crystals are melted at 42°C, clarified, neutralized with ammonia gas, prilled, cooled, and bagged. In some plants, ammonium nitrate is added prior to crystallization to yield the double salt, $5Ca(NO_3)_2 \cdot NH_4NO_3 \cdot 10H_2O$.

A special prilling process has been developed in the Netherlands and used there and in other countries. It consists of prilling the product into an oil bath rather than air. Since the oil contains about 10% paraffin wax which forms a coating on the prills, the rate of moisture absorption is retarded (37). The prills are separated from the oil by settling and centrifuging. They are stored in bulk for a few weeks while the oil remaining on the prills is absorbed into the interior leaving the wax coating on the surface. The usual oil content of the prills is about 1%. The decahydrate salt, $5Ca(NO_3)_2 \cdot NH_4NO_3 \cdot 10H_2O$, will rapidly absorb water when the relative humidity exceeds 50% and will deliquesce; whereas, the anhydrous salt, $Ca(NO_3)_2$, although more hygroscopic, will absorb about 40% of its own weight of water before incipient liquefaction occurs. Both products are promptly packed in moisture-resistant bags to minimize storage and handling problems during shipment.

Storage

Except in very dry climates, calcium nitrate is likely to deliquesce, and storage in moisture-proof bags is usually mandatory. As with other nitrate fertilizer salts, precautions should be taken to avoid impregnation of organic material with calcium nitrate to reduce possible conflagration from a source of heat in the vicinity. For this reason, special storage and shipping regulations may apply in certain countries.

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IX Urea

Introduction

Urea was first identified in 1773 when it was isolated by crystallization from urine. It was first prepared synthetically in 1828 by Wohler from ammonia and cyanuric acid (1):

$$NH_3 + HCNO \rightarrow CO(NH_2)_2$$

This preparation was a milestone in science since urea became the first organic compound prepared by synthesis from inorganic materials. Previously it was believed that organic compounds could be produced only by living organisms. The present method of synthesizing urea from ammonia and carbon dioxide has been known in principle since 1868, but commercial production by this method started in 1922 in Germany, in 1932 in the United States, and in 1935 in England. However, there was some commercial production in Canada (by DuPont) starting in 1920 using calcium cyanamide according to the reaction:

$$CaCN_2 + 3H_2O \rightarrow CO(NH_2)_2 + Ca(OH)_2$$

Use of urea as a fertilizer developed rather slowly at first, partly because early processes were cumbersome and expensive and partly because of some doubt about its agronomic suitability. Urea has been considered a slow-release fertilizer in Europe since it must undergo two transformations in the soil before it becomes available to most crops (1). The first transformation is hydrolysis:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

The second transformation is nitrification in which ammonia is oxidized in the soil by microbiological means first to nitrite and then to nitrate. These reactions proceed rapidly in warm, moist soil, but they are quite slow in cool soils which are characteristic of temperate climates (northern Europe) in the spring season.

Under some circumstances urea can be phytotoxic; and many cases of severe damage to crops have occurred, especially when the urea was placed close to the seeds. These cases were mainly associated with "combine drilling," which is a common practice in some European countries. The practice consists of drilling fertilizer with small grain seed. The phytotoxicity may be caused by locally high concentrations of ammonia during the hydrolysis stage, or it may be caused by accumulation of nitrite during the nitrification stage. A possible third cause is the presence of excessive amounts of biuret as an impurity in urea.

Aside from toxicity, poor agronomic results may be caused by loss of ammonia to the atmosphere when urea is applied on the surface of the soil or as a topdressing to growing crops. This loss is caused by the formation of ammonia by hydrolysis under such conditions that part of it escapes to the atmosphere rather than being adsorbed by the soil. A major use for straight nitrogen fertilizer in the United Kingdom and many European countries is for topdressing cereals and grass. Studies in England and the Netherlands have shown that on the average urea is only 80%-85% as effective as ammonium nitrate for this use.

For the reasons mentioned above, urea has been unpopular in most European countries, and it still finds little use in northern Europe as a straight nitrogen fertilizer. However, recent studies have shown that urea is as effective as ammonium nitrate when incorporated in the soil at or before planting time.

In the United States the general conclusion of agronomists is that urea is as good as any other nitrogen fertilizer if properly used. However, it is not recommended for some uses, such as surface application on grasslands in humid climates or in placements in contact with or near seeds.

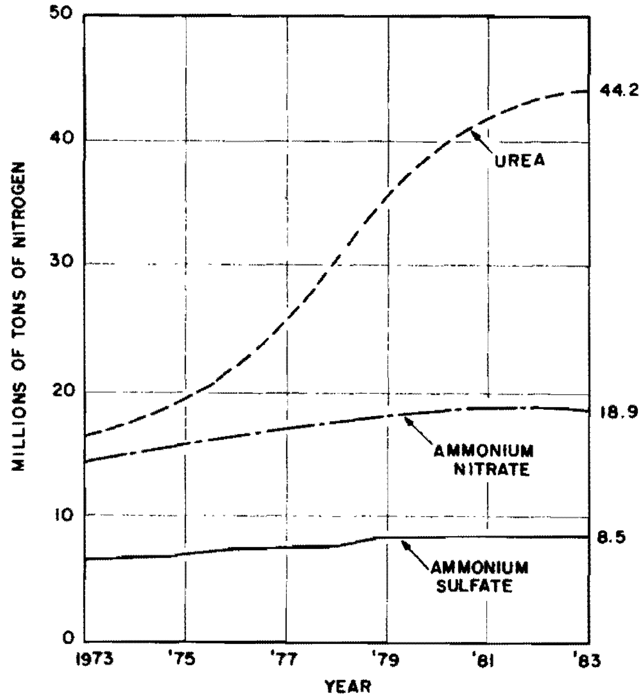
Urea is generally satisfactory for rice and preferable to nitrates for flooded rice since nitrates are reduced to N_2O or N_2 in the anaerobic zone of the rice paddy and hence lost to the atmosphere. Also the rice plant, unlike most other crops, can utilize the ammonium form of nitrogen efficiently. In tropical, subtropical, and warm temperate zones, the hydrolysis and nitrification (in aerobic soil conditions) are rapidly completed; thus, there is no delayed-release effect. For these reasons and because of its high concentration and favorable production cost, it has become the most popular nitrogen fertilizer in Asia and in many countries on other continents. An excellent discussion of the agronomic effects of urea has been presented by Tomlinson who concludes that urea can be used efficiently, but its use requires a higher degree of understanding than is the case with simple inorganic salts (2).

It has been estimated that urea will constitute about 85% of the nitrogen fertilizer capacity in Asia by 1980 (3). On a worldwide basis urea is now the most popular solid nitrogen fertilizer, and its use is growing more rapidly than that of other materials. Figure 1 shows present and planned future trends of world fertilizer capacity of urea, ammonium nitrate, and ammonium sulfate. It is evident that urea capacity is increasing much more rapidly than that of the other two products. However, the capacity figures for ammonium nitrate do not include a substantial amount that is produced directly in compound fertilizers such as ammonium phosphate-nitrates and nitrophosphates. Likewise, a smaller amount of ammonium sulfate is produced directly in compound fertilizers.

Urea is also used as a cattle feed supplement where it may replace a part of the protein requirements. It also has numerous industrial uses, notably for production of plastics.

Properties of Urea

Some properties of urea that are of interest for fertilizer use are:



Source: TVA Unpublished Fertilizer Statistics, May 1978.

Figure 1. World Nitrogen Fertilizer Capacity Trends.

Properties of Pure Urea

Molecular weight	60.06
Nitrogen content, %	46.6
Color	white
Specific gravity	1.335
Melting point, °C	132.7
Solubility in water, parts per 100 parts of water by weight at	
0°C	66.7
20°C	108.0
40°C	167.0
60°C	251.0
80°C	400.0
100°C	733.0
Critical relative humidity at	
20°C	81%
30°C	73%
Specific heat at 20°C	0.320
Heat of solution in water (endothermic), cal/g	-57.8

The relatively low specific gravity, compared with that of other fertilizer materials, must be taken into account in calculating storage space requirements. For instance, storage space requirements per unit of nitrogen are about the same for urea as for ammonium nitrate since the higher analysis of urea is offset by its lower specific gravity. Urea is less hygroscopic than ammonium nitrate but more hygroscopic than ammonium sulfate; it requires protection from humid atmosphere in some climates.

Urea forms addition compounds (adducts) with many compounds; some of those frequently found in fertilizers are calcium sulfate, monocalcium phosphate, and ammonium chloride. In some cases formation of these adducts may lead to severe caking. Urea also reacts with phosphoric acid and nitric acid forming the crystalline compounds, urea phosphate and urea nitrate, respectively. Utilization of these salts as fertilizers or fertilizer intermediates has been proposed, and experimental development is in progress in several countries. However, no commercial use is known at present.

Biuret Formation--Biuret (NH_2-CO-NH-CO-NH_2) is formed during urea synthesis and in the processing of solutions containing urea following the synthesis. Its formation during synthesis is suppressed by excess ammonia. It forms rapidly in urea melts at the usual temperature (about 140°C) used in prilling or granulating urea and at slower rates at lower temperatures in hot solutions. In most processes, biuret formation is limited by minimizing the retention time of the hot solution or melt during the evaporation and prilling or granulation steps.

Urea of very low biuret content (less than 0.25%) can be obtained by vacuum crystallization of urea solution. Less biuret is formed at the lower temperature used in vacuum crystallization, and biuret does not crystallize with the urea. Biuret that accumulates in the mother liquor is disposed of by drawing off a sidestream of the liquor which is returned to the urea synthesis unit where it is reconverted to urea.

Crystalline urea can be dissolved and used for foliar application or melted and prilled or granulated. Some biuret is formed during melting, but prills containing 0.3% or less of biuret can be produced. In the usual evaporation-prilling method, the product commonly contains about 1% biuret. Plant constructors usually will guarantee less than 1% biuret, but with variations in plant operation a range of 0.8% to 2.0% is common.

For most urea fertilizer uses, biuret content up to 2% is of no consequence; it decomposes in the soil and its nitrogen content becomes available to plants (4). However, if urea is placed in contact with the seed or near it, crop damage due to biuret may result. This type of placement can cause damage even with pure urea (or other concentrated fertilizers), but the high-biuret urea (more than 1%) is more toxic than low-biuret urea.

Biuret is toxic to citrus plants and some other crops when applied as a foliar spray. For foliar application on citrus crops, urea containing less than 0.25% biuret is preferred. For other crops sensitivity to biuret in foliar sprays varies widely; solutions made from urea containing 1.5% biuret were considered acceptable for foliar application to maize or soybeans (5).

Biuret is preferred to urea for use in cattle feed as a protein substitute. Processes are under study for recovering biuret from urea production as a profitable byproduct.

Production Processes

All commercial production of urea is from carbon dioxide and ammonia. The carbon dioxide is obtained as a byproduct from ammonia production. The reaction proceeds in two steps: (1) formation of ammonium carbamate and (2) dehydration of ammonium carbamate:

$$2NH_3 + CO_2 \rightleftarrows NH_2CO_2NH_4$$

$$NH_2CO_2NH_4 \rightleftarrows CO(NH_2)_2 + H_2O$$

The first reaction is highly exothermic (37.7 kcal/g-mole) while the second reaction is moderately endothermic (-7.7 kcal/g-mole). The first reaction is slow at atmospheric pressure, but at the elevated pressures used in practice it is practically instantaneous (1). The second reaction does not go to completion; it approaches equilibrium at a rate which depends on temperature and pressure. A summary of the effects of the main variables follows.

Operating Variables

Temperature--Conversion of ammonium carbamate to urea in the absence of excess ammonia increases with temperature to a maximum of about 50% at 170°-190°C when the pressure is sufficiently high to keep the reactants in the liquid state. The rate of reaction increases with temperature; it is slow at 150°C and below (with stoichiometric $NH_3:CO_2$ ratio) and quite rapid at 210°C. A satisfactory approach to equilibrium can be obtained in the temperature range of 180°-200°C in 0.3-1.0 hours or at lower temperatures with excess ammonia. Corrosion difficulties increase with temperature, and a range of 180°-210°C is generally accepted as optimum for most processes.

Pressure--At constant temperature, conversion increases with pressure up to the critical point which is the point at which the vapor phase is substantially eliminated and the reactants are in the liquid state. Further increase in pressure is not beneficial. The critical temperature is a complex function of the temperature and composition of the reactor contents. For example, at 150°C a pressure of about 100 atm might be near optimum for a stoichiometric $NH_3:CO_2$ ratio, but at this temperature the rate of reaction is unacceptably slow. At the preferred temperature of 180°-210°C, pressures of 140-250 atm are commonly used.

Mole Ratio of $NH_3:CO_2$--Excess NH_3 above the stoichiometric mole ratio of 2 favors the rate of the reaction. The percentage of CO_2 converted to urea is increased but, of course, the percentage of NH_3 converted to urea is decreased. Since recycling of excess NH_3 is relatively simple (as compared with CO_2 which remains as carbamate), most processes use 50% or more excess ammonia (a mole ratio of 3:1 or more).

Other Factors--The presence of water decreases conversion; therefore, most processes are designed to minimize the amount of water recycled to the reactor. The presence of small amounts of oxygen (air) decreases corrosion; many processes use this method of minimizing corrosion.

Optimum Conditions--It is generally not economical to maximize the percentage conversion in the reactor since this would require an excessive retention time. The aim therefore is to attain maximum quantity of urea production per unit of time with due regard to the cost of recycling unreacted CO_2 and NH_3 as well as the cost of increased reactor size and corrosion difficulties which increase with temperature. Typical operating conditions are: temperature, 180°-210°C; pressure, 140-250 atm; $NH_3:CO_2$ mole ratio, 3:1-4:1; and retention time, 20-30 minutes.

Once-Through and Partial-Recycle Processes

Most new plants now use total-recycle processes. However, once-through or partial-recycle processes have been popular in some countries and in some cases may still be preferred.

The once-through method is the simplest and least expensive (in both capital investment and operating costs) of the three basic types of processes. A typical unit flowsheet (synthesis section only) is given in figure 2. Liquid ammonia and gaseous carbon dioxide are pumped into the urea reactor at about 200 atm. The reactor temperature is maintained at about 185°C by regulating the amount of excess ammonia; about 100% excess NH_3 is required, and about 35% of the total NH_3 is converted to urea (75% of the CO_2 is converted). The reactor effluent solution contains about 80% urea after carbamate stripping. The unconverted NH_3 and CO_2 are driven off at moderate pressures by steam heating the effluent solution in the carbamate strippers.

While this process is the simplest of the urea processes, it is the least flexible and cannot be operated unless some provision is made to utilize the large amount of off-gas ammonia. It is thus tied to the coproduction of some other material, e.g., ammonium sulfate, ammonium nitrate, nitric acid, or ammonium phosphate, for which the ammonia can be used. One case in which the system can be used is the production of urea-ammonium nitrate solution; the unconverted NH_3 is used to make ammonium nitrate solution which is then mixed with the urea solution. Even in this case, most new plants use a total-recycle process.

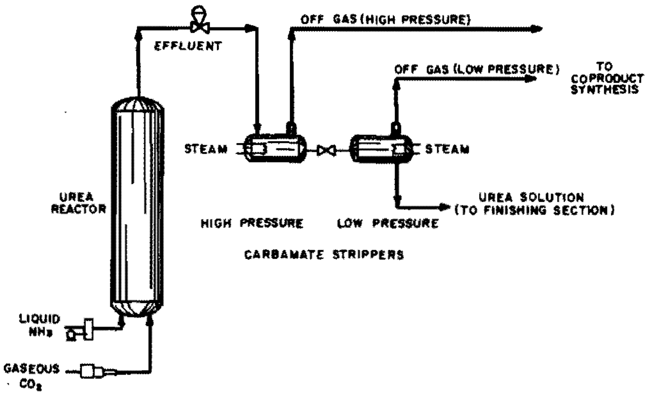


Figure 2. Typical Once-Through Urea Process.

In the partial-recycle process, part of the off-gas ammonia and carbon dioxide from the carbamate strippers is recycled to the urea reactor. Recycling is accomplished by absorbing the stripper gases in a recycle stream of partially stripped urea effluent, in process-steam condensate, or in mother liquor from a crystallization finishing process. In this manner, the amount of NH_3 in off gas is reduced. Any proportion of the unreacted ammonia can be recycled; typically, the amount of ammonia that must be used in some other process is reduced to about 15% of that from a comparable once-through unit.

The Mitsui Toatsu partial-recycle process flowsheet is typical of the first method and is shown in figure 3. Liquid NH_3 and gaseous CO_2 are pumped to the urea reactor at 200 atm. The temperature of the reactor is maintained at about 185°C by proper balance of excess NH_3 and carbamate solution recycle feed. About 100%-110% excess NH_3 is used; about 70% of the NH_3 and 87% of the CO_2 are converted to urea. The remaining 30% of the NH_3 must be used in some other process. The reactor effluent contains about 80% urea.

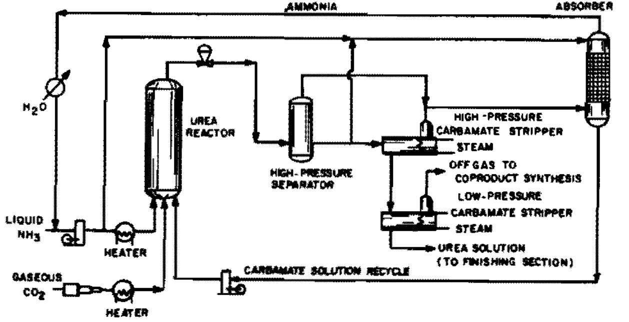


Figure 3. Typical Partial-Recycle Process.

Unreacted NH_3 and CO_2 are separated from the urea solution in the high-pressure separator and in two to three steam-heated carbamate strippers at successively lower pressures. The off gas from the separator and the first-stage stripper is absorbed in the high-pressure absorber by a side stream of partially stripped reactor effluent from the high-pressure separator. Heat evolved in the absorber reaction is removed (to increase absorption capacity) by the addition and expansion of part of the liquid ammonia feed at this point. Pure gaseous ammonia from the top of the absorber is also recycled to the urea reactor after being condensed.

Since the amount of ammonium carbamate which can be absorbed in the absorber solution described above is limited by its solubility in the system H_2O-urea-NH_3, part of the ammonia and carbon dioxide cannot be recycled and must be used in the production of a coproduct nitrogen material. As in the once-through process, the operation of the urea plant still must coincide with that of the coproduct plant.

Other partial-recycle processes differ in detail but accomplish similar results. There is little interest in such processes at present. While the investment cost is somewhat lower than that for total recycle, this advantage apparently does not compensate for the inflexibility arising from the necessity of operating a coproduct plant with mutual interdependency problems.

Total-Recycle Processes

In total-recycle processes, all the unconverted ammonia-carbon dioxide mixture is recycled to the urea reactor (conversion is about 99%), and no nitrogen coproduct is necessary. This is the most flexible of the urea processes because it depends only upon the CO_2 and NH_3 supply from its supporting ammonia plant for operation. However, it is also the most expensive in investment and operating costs. Therefore, if the production of other materials requiring ammonia is planned, an integrated once-through or partial-recycle unit would have lower investment and perhaps lower operating costs. The disadvantages are decreased reliability arising from mutual dependence of two plants, inflexibility in proportions of coproducts, and difficulties in synchronizing the operation of two plants. Because of these difficulties, most manufacturers prefer a total recycle process, even when a second nitrogen product is desired.

The urea reactor effluent contains urea and water resulting from the synthesis reaction; it also contains unconverted carbamate and excess ammonia. These ingredients must be separated to give a urea solution reasonably free from the other materials and to recycle the CO_2 and NH_3 to the synthesis reactor. In order to separate carbamate from urea, it must be decomposed according to the equation:

$$NH_2CO_2NH_4 \rightleftarrows CO_2 + 2NH_3$$

This reaction is the reverse of the first step of the synthesis process and is strongly endothermic (37.7 kcal/g-mole). The decomposition is accomplished by various combinations of supplying heat, lowering pressure, and "stripping" which lowers the partial pressure of one or more ingredients. The NH_3 and CO_2 are removed from the urea solution as gases accompanied by some of the water in vapor form. Naturally the CO_2 and NH_3 will recombine (releasing heat) when the temperature is decreased or the pressure increased. Hence, condensing by cooling and/or compressing a gaseous mixture of CO_2, NH_3, and H_2O produces a carbamate solution.

Total-recycle processes can be classified in five groups according to the recycle principle: (1) hot-gas mixture recycle, (2) separated-gas recycle, (3) slurry-recycle, (4) carbamate-solution recycle, and (5) stripping. The first four groups use carbamate decomposition steps basically similar to those of the once-through and partial-recycle processes; whereas, the last one differs even in this respect.

Hot-gas recycle of mixed CO_2, NH_3, and H_2O has been used in Germany between the two World Wars by I. G. Farbenindustrie at Oppau. The hot gas was compressed in five stages by reciprocating compressors with interstage to an end temperature of 260°-270°C and a pressure of 120-130 atm. It was then cooled to 160°C to condense the gases (with carbamate formation), and the heat was recovered as steam. The process was not very successful; when the plant was destroyed during the last war, it was not rebuilt. The idea was revived by Chemical Construction Company with the proposal that the compression be done with large centrifugal compressors that became available in the 1960s using new materials of construction that can operate at high temperature (400°-540°C) without interstage cooling. The proposed process seems technically sound, but centrifugal compressors of this sort are feasible only in such large sizes that the minimum scale would involve a urea plant of about 1,200-tpd capacity. Since smaller scale development is not feasible, no organization has been willing to risk using the untried process on such a large scale.

The separate-gas recycle method was developed to overcome the difficulties of the mixed hot gas recycle process. The CO_2 and NH_3 can be compressed separately without difficulties caused by carbamate formation. Processes of this type were developed by Inventa (Switzerland) and CPI-Allied (United States). The principle of the processes is that CO_2 in the gas mixture from the decomposers is absorbed selectively in a solvent such as monoethanolamine (MEA). The NH_3 remaining after CO_2 removal is compressed and recycled to the synthesis reactor. The CO_2 is desorbed from the MEA solvent by heating, and it is recycled separately (6).

The process has the advantage that conversion is not reduced by recycling water to the reactor and that the problem of recycling corrosive solution to the reactor is avoided. Offsetting this is the difficulty in recovering heat and cost of MEA makeup. The number of plants using the method is relatively small, and it is not known to be in use in any of the large plants (1,000 tpd and up) built in recent years.

The principle of the slurry-recycle process is that the CO_2-NH_3-H_2O gas mixture goes to a reactor where a light paraffin oil is added. Carbamate is formed in the reactor as a suspension in oil. This suspension containing 35%-40% solids is pumped into the urea synthesis unit together with fresh CO_2 and NH_3. The mixture then goes through the carbamate decomposers, and the oil is separated from the urea solution by decantation for reuse. The process was developed by Pechiney (France) and has been used by that organization.

Carbamate-solution-recycle processes are currently the most popular. There are several proprietary processes (Stamicarbon, Mitsui Toatsu, Montedison, Snamprogetti, etc.) which are offered by their developers and licensees. They differ mainly in engineering details, methods for heat recovery, and means for energy conservation. In general, all solution-recycle processes involve absorbing CO_2 and NH_3 in water and recycling it to the synthesis step as an aqueous carbamate solution. The amount of water must be kept to a minimum, however, because addition of water lowers the percentage of conversion to urea. Also the evaporation of additional water has a negative impact on the economy of the process.

Some years ago there was considerable variation in the design features of the various solution-recycle processes; these differences have gradually disappeared. Today most of the "conventional" processes are much the same. All use similar reactor conditions (temperature about 185°C and pressure about 200 atm), maintain an $NH_3:CO_2$ mole ratio of about 4:1 in the synthesis loop, and get about the same conversion (65%-67%) of CO_2 to urea for each pass through the synthesis reactor. Overall conversion of NH_3 to urea is 99% or more. All reduce the reactor effluent pressure to an intermediate level and then pass the solution through two or three stages of decomposition (by heating) at successively lower pressure levels. In each stage, the evolved gas mixture is condensed (or absorbed in weak solution condensed in a later stage), and the resulting solutions are worked back through the system to the reactor. The excess ammonia (from the excess used in the initial reactor feed) passes through the absorbers, is condensed, and is fed back to the reactor.

Although these major steps are common to the various conventional methods, there is considerable difference in the carbamate solution-recycle systems--in pressure and temperature levels of the decomposition steps, equipment arrangement, and process flow. This phase of the development is still in a state of flux; even for a given company, the flowsheet for a current plant will likely be somewhat different from that of the immediately preceding one. The general design objectives are to:

1. Maximize heat recovery.
2. Minimize amount of carbamate solution recycled (smaller pumps and less power) and amount of water returned to the reactor (better conversion).
3. Minimize power requirement.
4. Maximize ammonia recovery (lower operating cost and less pollution).

Since another major objective, of course, is to minimize investment, the problem becomes the usual one of finding the best balance between utility consumption and maintenance on the one hand and investment on the other.

Several parameters are involved in design of the carbamate-solution-recycle system, and they are so interrelated and interdependent that it is difficult to analyze them separately. Changing one parameter in the direction of improvement almost always changes one or more of the others in an adverse direction, and the extent of the adverse effect can only be determined by somewhat complicated calculations. Hence, it is difficult to evaluate quantitatively the various schemes that have been developed.

One important consideration is the number of decomposition stages. Reducing the number lowers plant investment but increases the amount of water returned to the reactor, makes heat recovery less attractive (decomposer pressures generally lower), and results in higher ammonia loss in gaseous or liquid effluents. The current trend is to three stages as the optimum number. The third stage generally involves both decomposition of carbamate and evaporation of water, with vacuum applied to remove the ammonia down to a very low level as a means of minimizing atmospheric pollution. The flashed gas is passed through a water-cooled condenser, the condensate stripped of ammonia, and the stripped condensate preferably discarded rather than returned to the reactor. Such a procedure gives only traces of ammonia in the gaseous and aqueous effluents.

The point of heat recovery also varies. The main source of heat in the system is carbamate formation in the reactor. In some past designs, recovery or removal of heat directly from the reactor was practiced--by water coils in the reactor or a cooling jacket outside. Today, however, the recycled ammonia and carbamate solution take up the reaction heat and carry it out of the reaction zone.

In the decomposition section, heat must be added in order to get an adequate rate of carbamate decomposition. Much of this is heat released when the evolved gases are recondensed, and it is at this point that heat is usually recovered. The recovery is limited to the first decomposition stage, however, because the gases are at so low a pressure in the later stages that the condensation temperature is too low for economical recovery of the heat.

Thus, the usual source for heat recovery is hot condensed liquor from the first-stage absorber. Practice varies as to the stream used to absorb this heat. In some cases, water is heated and steam is produced; in other published flowsheets a process stream is involved.

Gas release procedure can have an important effect on the amount of water recycled to the reactor. The simplest arrangement--merely releasing pressure, flowing the solution into a vessel, heating it, and allowing the evolved gases to escape--is relatively inefficient because it gives maximum evaporation of water. Two systems have evolved, both of which minimize water evaporation. The first involves a sequence, in each stage, of (1) pressure reduction, (2) gas release, (3) heating, and (4) further gas release. The advantage is that gas which can be evolved by release of pressure alone comes off at lower temperature than in the heated decomposer. The partial-pressure relationships involved are such that this procedure gives less evaporation of water.

In the second system a rectifying column is used as the decomposer; relatively cold incoming solution flows downward in countercurrent flow to the hotter gas evolved in a heated section (or reboiler) at the bottom. Thus, the composition of gas leaving the column approaches equilibrium with the incoming solution, which has a relatively low partial pressure of water because of the reduced temperature.

Both systems are used, but there seems to be a trend toward the rectifying column type. Heaters on the main flow line are preferred by some, however, because of the rapid heat transfer at the high flow rate.

Because of the large number of processes offered and frequent changes in flowsheets, it is not feasible to show flow diagrams for all processes. Figure 4 shows a flow diagram for the Mitsui Toatsu total-recycle process (Process C). No implication is intended that this process is necessarily superior to others.

Stripping processes differ fundamentally from other total-recycle processes in that one of the reactants, CO_2 or NH_3, is used to help decompose the carbamate at relatively high pressure, or even at synthesis pressure. The principle involved is that a flow of inert gas will promote vaporization of a liquid somewhat analogous to the evaporation of water below its boiling point by air flow. In the case of urea solution containing carbamate, either one of the reactants in gaseous form serves as an inert gas to lower the vapor pressure and sweep out gases evolved by decomposition of carbamate.

The Dutch State Mines has developed a stripping process using CO_2 as the stripping agent, starting with a 20-tpd pilot plant in 1964. The process is available through Stamicarbon and numerous licensees and is widely used. It is generally known as the Stamicarbon stripping process. (Stamicarbon also offers other urea processes.)

Kaasenbrood and Chermin have described the process in a recent paper which also explains the complicated thermodynamics and phase equilibria that are involved (7). The stripping operation is best explained with the help of figure 5, which shows the four units comprising the synthesis section. The

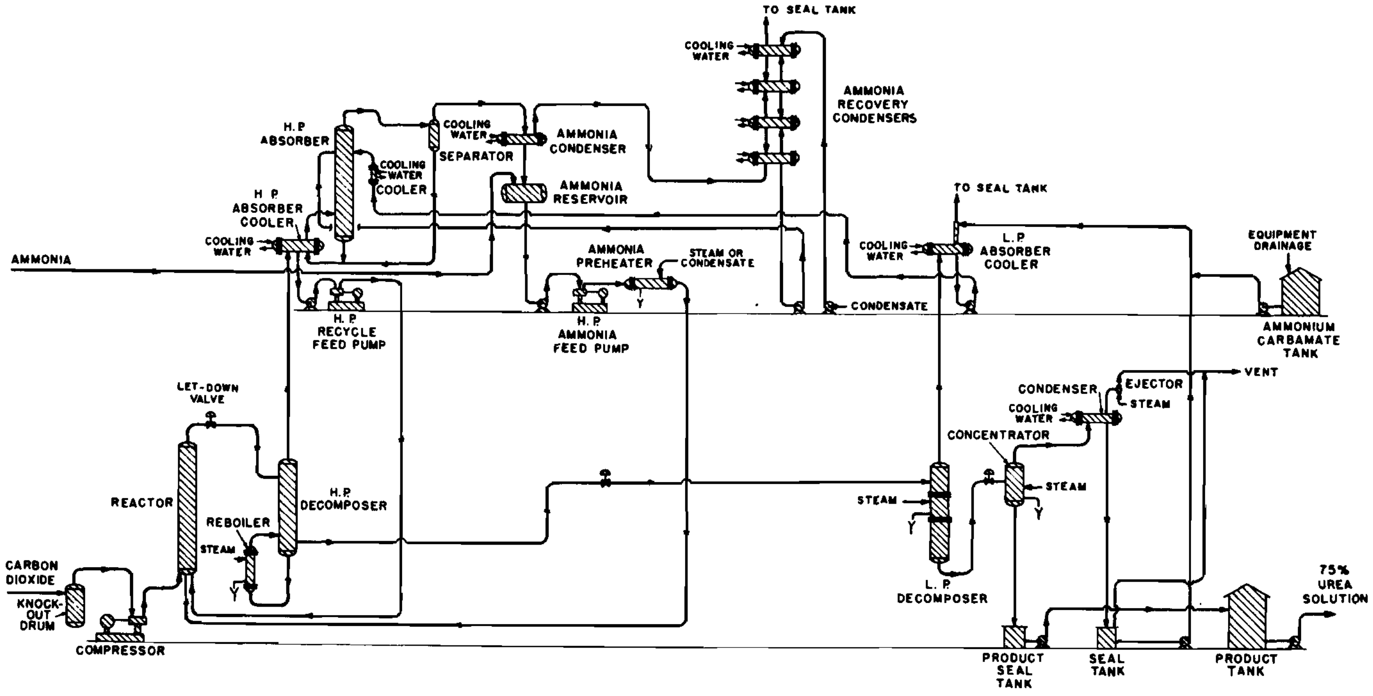


Figure 4. Typical Total-Recycle Urea Process (TVA Plant).

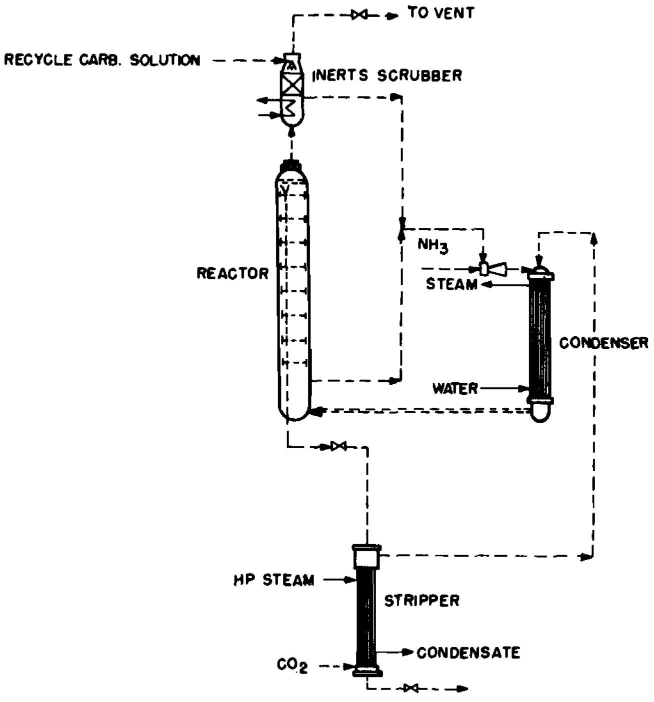


Figure 5. Synthesis Section of Stamicarbon CO_2 Stripping Process.

urea reactor is operated at a pressure of about 140 atm and a temperature of 180°-185°C with an NH_3:CO_2 mole ratio of about 2.8 (40% excess NH_3). The solution from the reactor flows by gravity to the stripper. As in all urea synthesis processes, the solution contains urea, carbamate, excess ammonia, and water. The stripper resembles a falling-film evaporator; it contains parallel tubes externally heated by steam. The steam supplies the heat which is absorbed by decomposition of carbamate; the solution temperature is maintained in the range of 180°-190°C. The solution flows as a film down the interior walls of the tubes. All of the CO_2 required in the process enters the bottom of the stripper and flows upward through the tubes countercurrent to the solution. A small amount of air is added to the CO_2 to inhibit corrosion. The amount of air should be sufficient to give a concentration of at least 5 ppm of oxygen in the synthesis loop. The gas stream leaving the stripper, which contains the CO_2 input plus NH_3 and CO_2 that has been stripped from the solution, flows to the condenser. The stripped solution, which contains urea and water plus a relatively small amount of carbamate, flows to another section of the plant (described later) for further treatment. The gas stream from the stripper enters the top of the condenser together with the NH_3 input for the system. The condenser also receives a stream of recycled carbamate solution and a relatively small sidestream of solution directly from the reactor which provides enough solvent to prevent deposition of solid carbamate. The mixture flows downwardly through the condenser which contains a series of sieve plates to prevent back mixing. The reactor is cooled by water (generating steam at 4-5 atm) which removes the heat released by carbamate formation and condensation.

Condensation is only partially completed in the condenser; the mixture flows to the bottom of the reactor and upwardly through the reactor where carbamate formation is completed and conversion of carbamate to urea takes place. The reactor solution then goes to the stripper; the cycle is completed.

Small amounts of gases accumulate in the top of the urea reactor. The gases consist of air that was added for corrosion control plus H_2 and N_2 dissolved in liquid ammonia and minor impurities in the CO_2. The gases are vented through a high-pressure scrubber where they are washed with carbamate solution to recover most of the NH_3 and CO_2 and then vented to a low-pressure washing column (not shown in figure 5).

The basic flow diagram of the entire process is shown in figure 6. The urea solution leaves the synthesis section through an expansion valve at 160°C; it is first treated at an intermediate pressure (about 2.5 atm) in a rectification column and a heater and a separator to remove most of the remaining carbamate as CO_2 and NH_3. The solution pressure is then reduced to atmospheric pressure for final purification. The NH_3 and CO_2 recovered in these steps are condensed to form a carbamate solution which is recycled to the synthesis section.

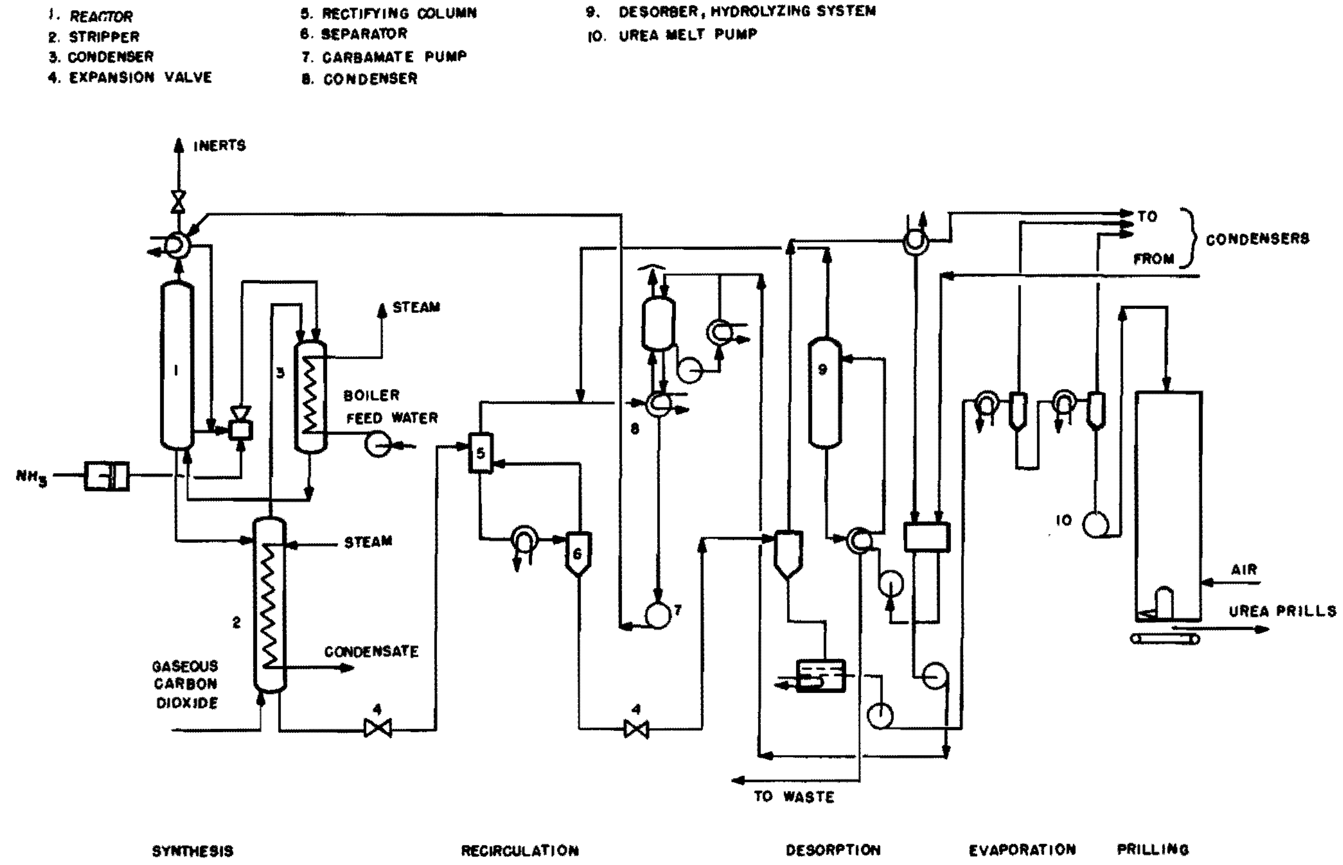


Figure 6. Flow Diagram of Stamicarbon CO_2 Stripping Process.

Most of the equipment is made of low-carbon stainless steel of the 316 or 317 type containing 17%, 12%, and 2% or 17%, 13%, and 4% Cr, Ni, and Mo, respectively. However, corrosion conditions are particularly severe in the stripper, and a 25-22-2 alloy is preferred for this equipment. For some processes, a titanium-lined stainless steel vessel is used for the synthesis step.

The advantages of the stripping process are lower net energy consumption (steam and electricity), somewhat lower investment cost, and reduced maintenance requirements. Energy saving results from doing most of the recycling at synthesis pressure thereby avoiding recompression of reactants. The pumps for recycling hot, concentrated carbamate solution are a major source of maintenance in "conventional" processes, but they are not required in the stripping process.

There are several other stripping processes that have been proposed or used. Some involve stripping at a reduced pressure (such as 75-100 atm) with recompression of the hot gas to full reactor pressure. A major variation is the use of NH_3 instead of CO_2 for stripping as in the Snamprogetti (SNAM) process. The process can be operated with strippers and reactor at the same pressure (130-160 atm) or with stripping at a lower pressure (100-150 atm) and reaction at a higher pressure (200-250 atm). When stripping and reaction are carried out at the same pressure, the reaction pressure must be somewhat lower than in conventional processes which leads to some loss in conversion efficiency in the reactor. On the other hand, if the stripping is carried out at a lower pressure, the stripped gases must be recompressed, thus losing some of the energy-saving advantages of a stripping process.

Integrated Ammonia-Urea Processes--Many new plants produce ammonia solely for the production of urea. It is possible to integrate certain steps of the two processes which, theoretically at least, should result in a saving in both capital and operating costs. Two coincidences make such integration attractive: (1) Since the ranges of pressure commonly used in ammonia and urea syntheses overlap, the same pressure can be used in both processes, and (2) The amount of CO_2 generated by an ammonia plant using natural gas feedstock is approximately equal to that required to convert the ammonia to urea.

Several organizations have studied integrated ammonia-urea processes experimentally. Mitsui Toatsu has operated a pilot plant in Japan for several years (6), and Snamprogetti (SNAM) has developed and tested the process in a small plant (80 tpd of urea) in Sicily (8).

One point at which the ammonia and urea processes can be integrated is by combining the CO_2 removal step of the ammonia process with the carbamate formation step of the urea process. In the SNAM flowsheet this is done by absorbing the CO_2 from the ammonia synthesis gas in a strong ammonia solution in two falling-film heat exchangers in series, one operated at high temperature (130°C) with heat recovery and the other operated at low temperature (40°C). In the Mitsui process the CO_2 is removed from the ammonia synthesis gas by scrubbing with recycled carbamate solution with ammonia addition in a packed tower. In both cases the step is carried out at synthesis pressure (200-250 atm), and the resulting strong carbamate solution is transferred directly to the urea synthesis unit while the scrubbed gas goes to the NH_3 synthesis unit. The potential advantages of this integration are obvious. It replaces a major energy-consuming step in the ammonia synthesis gas purification in which the CO_2 is absorbed in a solvent and then desorbed to liberate CO_2 which must then be recompressed for use in a urea plant.

The other principal point of integration is in the extraction of ammonia from the synthesis loop. In a conventional ammonia plant the gas leaving the ammonia converter, containing about 14% NH_3, is cooled by refrigeration to condense liquid NH_3 and thus separate it from the unreacted N_2 and H_2. In the SNAM integrated process, the NH_3 is absorbed in water in a falling-film absorber producing a solution containing 80% NH_3 and 20% H_2O which goes to the CO_2 absorption step. Liquefaction of ammonia and storage of liquid ammonia are thus avoided. This step also is carried out at high pressure (200 atm or more).

The above descriptions of the integrated ammonia-urea processes are very much simplified. A more complete description of the SNAM process is given by Lagana and Zardi (8) and Lagana (9). The authors claim a 15% saving in capital investment and a 17% saving in raw materials and utilities costs for the integrated process as compared with separate NH_3 and urea plants. However, no large-scale plants have been built and therefore a certain amount of risk is involved in scaling up the process. Snamprogetti sees no basic difficulty in scaling up the process even to 2,000 tpd of urea. On the other hand, the company suggests that small integrated ammonia-urea plants of 150-tpd capacity might prove more economical than large (1,500 tpd) urea plants. Although 10 small plants would cost about 13% more than one large plant, this disadvantage would be more than offset by a saving in marketing costs and in infrastructure requirements (10). The case for decentralized production in small plants has been put forth by others and does not necessarily depend on an integrated ammonia-urea process. However, there would be an obvious advantage in using some standardized design if numerous small plants were built (11).

There are some disadvantages in integrating two processes because of loss of flexibility. Neither the urea plant nor the ammonia plant can operate independently. Even in an ammonia-urea complex that consists of separate ammonia and urea units, there are some problems of interdependency; an interruption of ammonia plant operation forces a shutdown of the urea plant for lack of CO_2. The ammonia plant can continue in operation when the urea plant is shut down as long as ammonia storage is available or when there is some other outlet (use or sale). It is an engineering precept that when two processes (or process steps) are mutually interdependent, the reliability of the combination is the product of the reliability of the individual processes. For example, if a urea plant and an ammonia plant each have a reliability of 90%, the reliability of an integrated plant would be 0.90 x 0.90 = 0.81 or 81%.

When part of the ammonia is to be used for products other than urea or when the ammonia feedstock has a higher C:H ratio than required for urea production, there will be an excess of CO_2 over that required for urea production. The integrated urea-ammonia processes can be modified to meet these conditions but at the expense of losing part of the advantages claimed.

Urea Finishing Processes

The urea synthesis processes described in the previous section produce an aqueous solution containing about 75% urea. The solution can be used directly to prepare nitrogen fertilizer solutions (see chapter X). It can also be used to prepare granular compound fertilizers (in chapter XIX) although further concentration usually is desirable for this purpose.

Methods for production of solid urea include flaking, prilling, granulation, crystallization, and a combination of crystallization followed by melting and prilling or granulation.

Flaking is done by evaporating the solution to a melt (less than 1% H_2O) and solidifying the melt on a cooled metallic surface such as a Sandvik conveyor. The solidified melt is broken up into flakes. This is a convenient means for producing a solid material for shipment when the product is to be used in industrial processes or in solutions. Flaked urea is not used directly for fertilizer. Vacuum crystallization has been described briefly under "Biuret Formation." The crystallization process is similar to that described under "Ammonium Sulfate" (chapter VIII). The crystals are separated from the mother liquor by centrifuging and dried, usually in a rotary fuel-fired dryer. In some countries crystalline urea is bagged and distributed for use as fertilizer, but it is not very satisfactory for this use because of the small size of the crystals which leads to caking. Crystalline urea may also be used for preparing fertilizer solutions for foliar application or for nonfertilizer purposes. For the foliar application a low-biuret content is a specific advantage for crops like citrus fruits that are sensitive to biuret.

Prilling

Until recently nearly all straight urea was prepared for fertilizer use by prilling, and this is still the most widely used process. The prilling process is similar to that described in chapter VIII under "Ammonium Nitrate." The 75% urea solution is evaporated to a melt and prilled using one of two drop-forming devices: (1) a "shower-head" spray consisting of a number of pipes with holes drilled in them or (2) a rotating perforated bucket usually of conical shape. Alternatively, the urea melt may be formed by melting crystalline urea.

The droplets formed by the prilling devices cool and solidify as they fall through an ascending airstream. Urea has a lower melting point than ammonium nitrate or other fertilizer materials that are prilled. Therefore, a longer time is required for solidification for the same size prills, or in a prill tower of given height, the prills may need to be smaller. In practice, urea prills in general are smaller than ammonium nitrate prills and considerably smaller than the usual size of granular fertilizers.

Prilled urea is also weaker than granular urea, both in crushing strength and resistance to abrasion, as shown by the following data from TVA, which also show the effects of particle size and formaldehyde addition (12):

Crushing Strength of Prilled and Granular Urea

Type of Urea	Crushing Strength, kg -7 +8 mesh (-2.74 +2.36 mm)	 -8 +9 mesh (-2.36 +1.98 mm)	 -9 +10 mesh (-1.98 +1.65 mm)	Increase of -16 Mesh in Abrasion Test,[a] %
Products Without Formaldehyde Additive				
Prilled urea	1.20[b]	1.0	0.7	20
Granular urea, spray drum		(No data available)		
Granular urea, TVA pan	1.6	1.2	0.9	2
Products With Formaldehyde Additive (0.3%-0.4% HCOH)				
Prilled urea	1.4[b]	1.0	0.9	10
Granular urea, spray drum	3.3	2.5	2.1	<1
Granular urea, TVA pan	2.4	2.0	1.6	1

a. The resistance to abrasion is determined by measuring the increase in minus 16-mesh (0.99 mm) fraction after the material has been rolled for 5 minutes with steel balls.

b. This fraction is extremely minor (usually less than 5%) in prilled urea; most of the particles are smaller.

In addition to improved strength, granular urea has the advantage of greater flexibility in particle size; any desired size can be made, at least in the range of 1.5 to 15.0 mm. For instance, a size-matching granular DAP or KCl (1.5-3.3 mm or

2.5-4.0 mm) can be produced for bulk blending, or a larger size (6-10 mm) can be produced for aerial forest fertilization or for other special uses, such as deep placement in flooded rice fields. Another advantage of granulation over prilling is the greater ease of control of fume and dust, as mentioned under "Ammonium Nitrate" (chapter VIII).

The advantages of granulation over prilling are sufficiently important that most new urea plants built in the United States and Canada have used granulation, and granulation facilities have been added to some older plants that previously used prilling. Use of urea granulation in some other countries is planned. Present capacity for granular urea is of the order of 2.5 million tpy.

The following description of urea granulation process is taken mainly from an IFDC report (13). Three processes have produced granular urea in commercial-sized units. They are (1) the Spherodizer spray-drum granulation process developed by C&I Girdler, (2) the TVA pan-granulation process, and (3) the Norsk Hydro pan-granulation process. In addition, two more processes that are not known to be in commercial use but have proven feasible on a smaller scale are Fison's rotary-drum process and the spouted-bed granulation process which has been studied by several companies in Japan, Italy, France, and the Netherlands.

TVA Pan Granulation

The inclined pan granulator is now being demonstrated by TVA at 7.7 tph which is the capacity of the TVA urea solution unit. The granulation process and the internal recycle or classifying action in the pan have been described by Young and McCamy (14) and Waggoner, et al. (15). Figure 7 is a sketch of the pan operation. The feed to the process consists of urea melt from an air-swept, rotary-disc, falling-film evaporator. The melt at a concentration of more than 99% and a temperature of 141°C is pumped from the bottom of the evaporator to multiple sprays over the bed of moving solids in the pan granulator. With proper positioning of the hollow-cone spray nozzles which feed the melt and with proper distribution of the recycled undersize on the pan, the melt solidifies in even layers on the undersize in the upper area of the pan. When the particles reach the proper size by layering or "onion-skinning" process, they are discharged by the natural classifying action of the pan before any appreciable amount of oversize is formed. The pan may be rotated in either a clockwise or counterclockwise direction. The particle size and shape are influenced by the rotational speed and slope of the pan. Critical features for best operation of the pan granulator include slope, rotational speed, location of sprays, and the amount, particle size, and temperature of the recycled material.

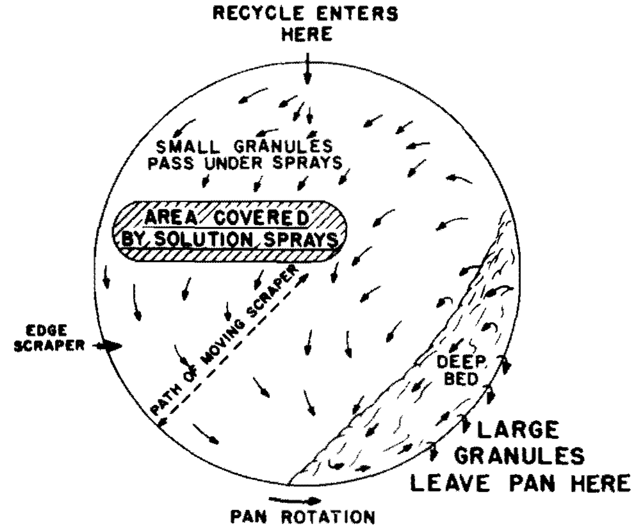


Figure 7. Sketch of Pan Operation.

TVA has made pilot-plant studies of both "high-temperature" and "low-temperature" methods for granulation of urea in the pan granulator. In high-temperature granulation, the bed temperature was kept at only a few degrees below the crystallization temperature of the feed melt (132°C). This was accomplished by regulating the temperature and quantity of recycle. When the recycle temperature was 49°-57°C, a recycle-to-feed ratio of 1.0-1.5 was required. Best granulation was obtained when the bed temperature was maintained at 107°-121°C. In this type of operation the granules are soft while hot and attain a spherical shape by rolling in the pan. An advantage of high-temperature granulation is that the granules are stronger than those made by the low-temperature method. A disadvantage is that an upset in the recycle system can cause the bed in the granulator to melt and interrupt the operation.

Low-temperature granulation is used by TVA in the demonstration-scale unit. Figure 8 is a basic flowsheet for this process. The bed temperature is maintained at 93°-102°C which is substantially lower than the melting temperature of 132°C. Material from the granulator flows to a rotary cooler where the temperature is reduced to approximately 66°C prior to screening. The cooler discharge is screened to separate oversize, onsize, and undersize. The oversize is crushed and returned to the recycle system or dissolved and returned via the scrubber solution system. Undersize is returned to the granulator as recycle. Product from the screens goes to a cooler where the temperature is lowered to 43°C. A drum is provided for coating the product with oil and clay. However, at present (1978) the coating is not used; instead the product is conditioned by adding 0.3%-0.4% formaldehyde to the urea solution before granulation. Use of formaldehyde increases the strength and abrasion resistance of the granules which significantly lowers dust formation. Typical operating data are shown in table 1.

Norsk Hydro Pan Granulation

Norsk Hydro (Norway) has developed a high-temperature process for pan granulation of fertilizers including urea. The process has been named the High Temperature Pan Granulation (HTPG) technique. A description of the process is given by O. Skauli (16). The process employs a pan granulator of conventional design. However, since the process operates at temperatures very close to the crystallization temperature, close control of the pan parameters is necessary. The primary control is the location of the point at which solid recycle is fed to the pan. Norsk Hydro reports that 80% of the material in the pan discharge is onsize (2-4 mm) and that the recycle ratio (solid-to-melt) is about 1. The particles are three times harder than prills of the same size and exhibit good storage and handling properties.

Figure 9 is a simplified flowsheet of the process. Melt and recycled undersize are added to the pan. Onsize material is discharged from the pan to a polishing drum and then to a cooler which can be either a fluid-bed or rotary type. The cooler discharge is screened to separate the oversize, onsize, and undersize fractions. The oversize is crushed and recycled to the pan along with the undersize and dust from the dust-control system. Although this technique has been used to produce granular ammonium nitrate on a commercial scale, urea has been produced only on a pilot scale. However, plans to build commercial-scale units have been announced.

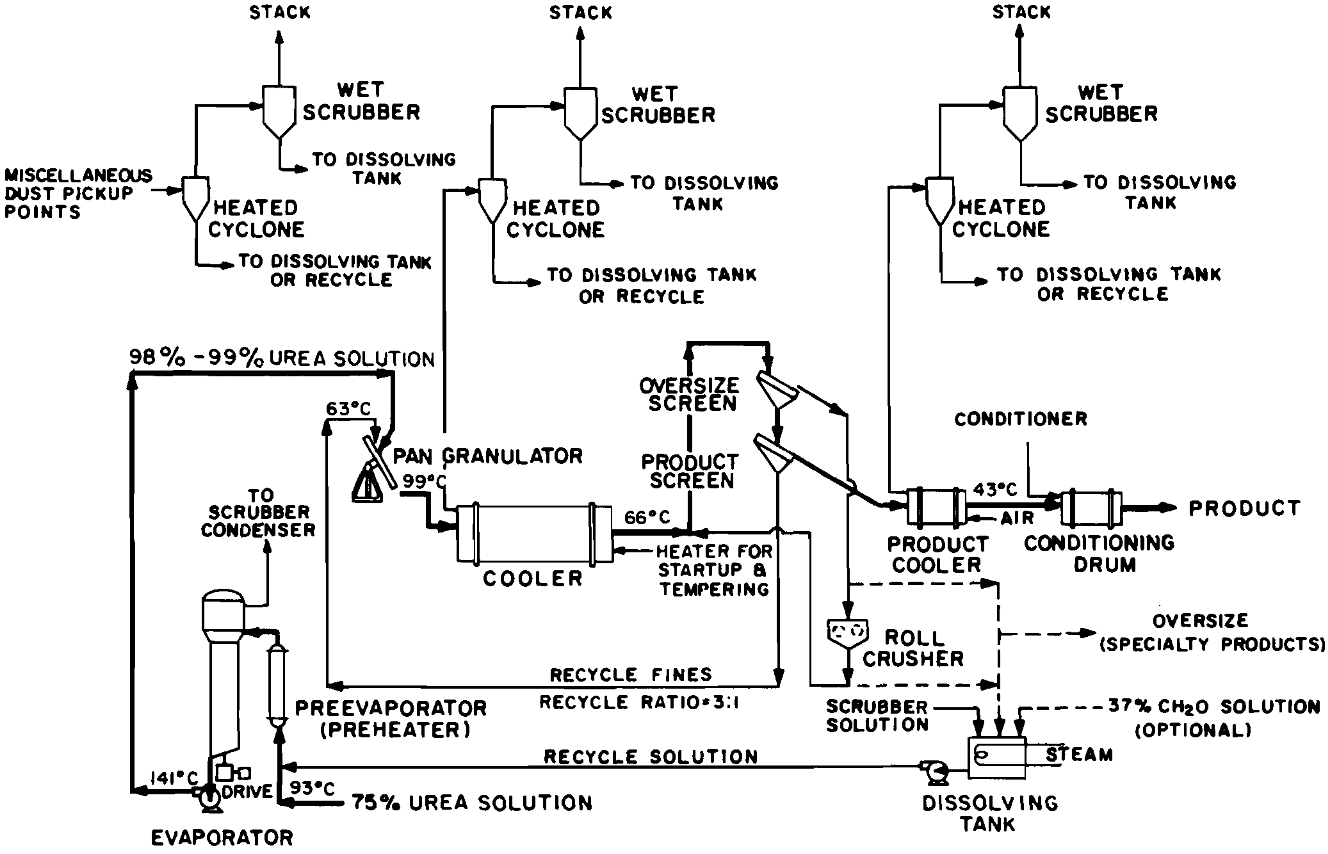


Figure 8. TVA Pan Granulation Process for Urea.

TABLE 1. TYPICAL OPERATING DATA--UREA PAN GRANULATION

Production rate, tph	7.65
Pan granulator	
Speed, rpm	18 to 19
Slope, degrees	60
Number of sprays	10
Urea, 75% solution from plant	
Temperature, °C	93
Concentrated melt to granulator	
Temperature, °C	141
Concentration, %	98.5-99.5
Granulation	
Recycle temperature, °C	60
Recycle ratio, kg/kg of product	2.5 to 3.0
Granulator temperature, °C	93-102
Cooler temperature, °C	43
Product chemical analysis, %	
Total N[a]	45.5
Biuret	1.1
H_2O (Karl Fisher)	0.1 to 0.2
Conditioner, %	
Oil-wax mixture	0.3
Clay	0.7
Screen analysis, % (Tyler screen)	
+6 mesh (+3.3 mm)	0
-6 +10 mesh (-3.3 mm +1.7 mm)	85
-10 +16 mesh (-1.7 mm +0.99 mm)	15
-16 mesh (-0.99 mm)	0

a. In recent operation, the oil-wax plus clay conditioner has been omitted and about 0.35% formaldehyde added; the total N content of the product is 46%.

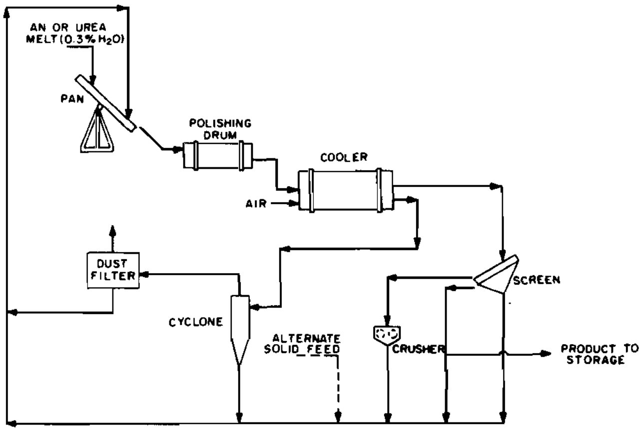


Figure 9. Norsk Hydro Pan Granulation Process for Urea or Ammonium Nitrate.

C&I Girdler Spherodizer Granulation

The Spherodizer, which is a proprietary drum-granulator process, is designed to avoid agglomeration and promote a layering type of granulation. The adaptation of the Spherodizer to a melt granulation process was developed by COMINCO (Canada) which holds the original patents with C&I Girdler as the sole licenser for the process. The process is well proven commercially as evidenced by 5,600 tpd of either newly installed or newly announced capacity in addition to three original plants built in Canada. Four other plants with a total capacity of 4,050 tpd are being engineered at present. Complex fertilizers were first produced in a Spherodizer in 1958, and production of granular urea and ammonium nitrate was introduced in 1965 (17).

A simplified flowsheet is given in figure 10. Molten urea is sprayed inside a rotating drum onto a rolling bed of solid particles. As a result of the rolling action, the particles are coated with thin layers of liquid and gradually build up to hard spherical granules. Cooling air is drawn through the drum countercurrent to the flow of granules. Dust removed by the cooling air is collected in an

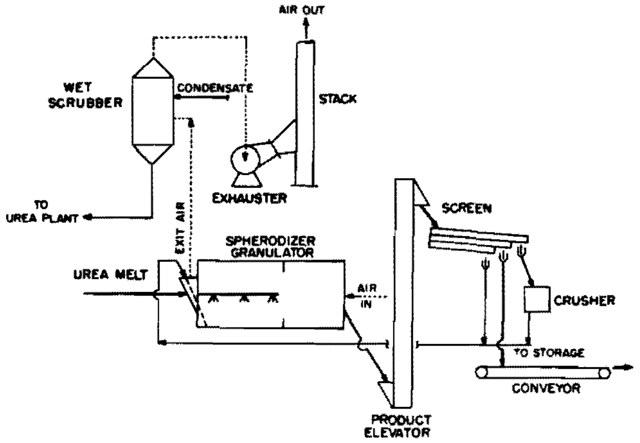


Figure 10. C&I Girdler Urea Spherodizer Process.

impingement-type wet scrubber, and the liquor is recycled to the concentration section of the urea unit. After cooling, the granules flow to a conventional screening section for separation of oversize, onsize, and undersize. The oversize is crushed and returned to recycle along with the undersize. The product size is treated with the conditioner, if desired, and transferred to storage. Typical operating data are shown in table 2 for production of urea by the Spherodizer process at a production rate of 300 tpd and a recycle ratio of 2.

TABLE 2. TYPICAL OPERATING DATA--UREA SPHERODIZER GRANULATION

Melt temperature, °C	138
Melt concentration, %	99.3
Moisture in product, %	0.06
Air inlet temperature, °C	10
Production rate, tpd in 14-foot (4.27 m) diameter drum	300
Recycle ratio (recycle/product)	2
Product temperature, °C	43

Fisons Granular Urea Process

Fisons Ltd. (United Kingdom) has operated a pilot plant to produce granular urea in a rotary-drum granulator. According to a recent paper, urea solution of more than 99% concentration from a conventional evaporation unit is introduced as a spray to the granulator where it contacts a recycled stream of fines; the recycle ratio is 2-3 kg/kg of product (18). Granulation occurs at a high temperature and low-moisture content. After granulation, material flows to a cooler, which may be a rotary-drum or fluidized-bed type where some moisture is removed and the temperature of the material is reduced. In the process no drier is used. After cooling, the material is screened and crushed; oversize and fines are returned to the granulator. Dust from the system is recovered by wet scrubbing and returned to the urea concentration step.

Fisons offers to design and operate plants of up to 1,000-tpd capacity based on the process.

Spouted-Bed Granulation

As mentioned previously, spouted-bed granulation has been studied experimentally in several countries and is said to be in commercial use in Japan for granulating compound fertilizers (chapter XIX). While the method is not known to be in commercial use for granulating urea, the feasibility of urea granulation by this method has been demonstrated in a pilot plant. A recent paper describes the process (19).

Conversion from Prilling to Granulation

Existing plants that are equipped for prilling may be converted to granulation by using the prilled urea as a part of the feed for the granulation unit, replacing part of the recycle. In this case the granulation unit serves to build up the size of the prills to the desired level by layering. This modification has been demonstrated with the Norsk Hydro pan-granulation process and, presumably, could be used with the other granulation process.

Dust and Fume Recovery

A part of the decision to produce granular urea involves not only choice of the process but also choice of the dust recovery method. The TVA process utilizes impingement-type wet scrubbers which were previously installed for another process. The Spherodizer process usually employs wet scrubbing. However, dry collection and a bag filter could be used with either the pan-granulation or the drum-granulation process. Bag filters usually require more maintenance than wet scrubbers, but they do achieve a very low level of particulate matter in the effluent stack gas. A wet-scrubbing system of the type envisioned for a new plant has been included on the flowsheet for the TVA process, figure 8. A separate system is used for each of the coolers and another for the fugitive dust-control system. Each consists of a heated cyclone, wet scrubber, circulation pump, blower, and liquor tank; gas from the three scrubbers is vented to a common stack. Dust from the cyclones is dissolved in the scrubber liquor. The scrubber liquor is collected and fed back to the concentration section. As a variation, the liquor tank and pump could be common to the three systems.

A very important consideration in designing a dust-collection system is flexibility to allow either dissolving the dry collected dust or returning it dry to the granulator. None of the granulation processes operate well if there is a high proportion of dust in the recycle. Therefore, it may be necessary at times to dissolve the dust from the cyclones and bag filters and the crushed oversize and feed it back as a liquor into the concentration section. The concentrator should have this additional capacity designed in at the beginning.

Effect of Finishing Process on Biuret Content

Several investigators have found that biuret is not formed in detectable amounts during the prilling or granulation operation itself, but it is formed during preparation of the melt whether by evaporation of solution or by melting crystalline urea. Also biuret continues to form in the melt so long as it remains in molten form. The practice of recycling recovered urea dust and fume to the evaporation step tends to increase the biuret content. There is probably more recycled material in granulation processes than in prilling. Granular urea produced in U.S. plants averages about 1.5% biuret. No recent data are available on the biuret content of prilled urea in the United States, but a few analyses indicate that a range of 1.0%-1.6% may be typical. In the United States, low-biuret content is not regarded as important, and no special effort is made to control it at a low level. Since there is no known commercial production of granular urea in countries other than the United States, no comparison is available. However, Norsk Hydro has made granular urea containing only 0.56% biuret in a pan-granulation pilot plant. Presumably low-biuret granular urea could be produced by exercising more care in minimizing the retention time in the evaporation step and in melt handling and by recycling recovered scrubber solution and fines to the synthesis step or to a crystallization step rather than to the evaporation step.

As mentioned previously, low-biuret product is produced by vacuum crystallization of urea followed by drying the crystals and then remelting them for prilling or granulation. However, the capital cost of a urea plant using the crystallization step is substantially greater than that of a plant using the evaporation method. In summary, the production of low-biuret granular urea has been demonstrated in a pilot plant but not in a commercial-scale operation, but there is no apparent reason to suppose that granular urea will necessarily contain more biuret than prilled urea.

Comparative Cost of Granulation and Prilling

The relative cost of prilling and various granulation methods depends on the scale of operation. Production of as much as 1,800 tpd is feasible in a single prilling unit; whereas, the spray-drum (Spherodizer) granulation process has been limited to 300-tpd units because of difficulties in fabricating and transporting larger units. (The standard Spherodizer drum for melt granulation of urea is 3.6 m in diameter.) The upper limit of pan granulators is not precisely known, but 600 tpd is known to be feasible for a 4.3-m diameter pan. The upper capacity limit of other types of granulators is speculative although Fisons offers up to 1,000 tpd in a single-drum granulation unit.

The cost of a prill tower increases only moderately with capacity; whereas, with other types of granulators the rate of increase in cost with capacity is generally greater, especially if multiple units are required. The comparison is also complicated by the dust and fume recovery requirements; meeting stringent requirements is more expensive with prilling than with granulation. Thus, for a small (300 tpd) unit, equipment for granulation may be less expensive than for prilling, particularly if good dust control is required. For large units, such as 1,200 tpd, prilling is likely to have a lower capital cost.

Ruskan has compared the economics of prilling, pan granulation, and spray-drum granulation on a scale of about 600 tpd (20). The estimated operating costs, which apply only to the prilling or granulation step, are:

	Estimated Operating Cost, $/ton of Urea[a]	
	Without Capital Costs	With Capital Costs[b]
Spray-drum granulation	5.61	13.85
Pan granulation	3.96	9.55
Prilling with scrubbing	3.50	8.69
Prilling without scrubbing	2.80	6.88

a. Taken from Ruskan, converted to metric tons (20).
b. Capital-related costs include depreciation, return on investment, and interest on working capital.

The investment costs (1976) for the above four cases as read approximately from a graph given by Ruskan for 600-tpd units are (20):

Spray-drum granulation	$4.2 million
Pan granulation	3.0 million
Prilling with scrubbing	2.5 million
Prilling without scrubbing	2.1 million

Waggoner compared pan granulation with prilling (15). At a scale of 400 short tons (363 mt)/day, the capital investment cost was about the same ($2 million), and the production cost, including capital charges, was $1.36/mt higher for granulation. At 900 mt/day the investment costs were $3.9 million for pan granulation versus $3.1 million for prilling; production costs were $2.13/ton higher for pan granulation. The estimates were based on a dry dust collection for pan granulation which was believed to provide adequate pollution control; whereas, for prilling the estimates did not include scrubbing and therefore probably would not meet U.S. pollution control standards.

Both authors concluded that differences in capital and operating costs were a small percentage of the total cost of producing urea, and the advantages of the better physical properties of the pan-granulated product and increased flexibility in choice of particle size would justify the additional cost (if any) of pan granulation. The same general conclusion applies to spray-drum granulation. Although its cost is higher than that of pan granulation, the more widespread experience with the process has led many manufacturers to adopt it.

Conditioning

Prilled or granular urea may be marketed without conditioning treatment in some areas, but it is often treated with a conditioner to improve its physical strength and increase its resistance to caking. The most popular conditioning treatment at present is the addition of formaldehyde to the concentrated solution just before prilling or granulating. The amount added usually is 0.3%-0.4%. The formaldehyde may be added in the form of 37% aqueous solution or as a solution containing 59% formaldehyde, 26% urea, and 15% water. The latter solution is called "UF Concentrate-85." Both solutions are available in tank-car lots in the United States and probably in other countries. The formaldehyde conditioning treatment increases the strength of prills and granules and decreases their caking tendency.

Coating of prills and granules also is used as a conditioning treatment although its use is decreasing because the formaldehyde treatment is generally preferred. Coating materials include powdery materials such as kieselguhr, china clay, talc., etc. A combination of about 1% clay with 0.5% oil has been used; the oil promotes adherence of the clay to the urea prills or granules. Some types of powdery coating materials will adhere without oil. Conditioning treatments and conditioner adherence as related to fertilizers in general are discussed in chapter XXII.

A coating of medium-viscosity oil (without clay) has been developed by the Dutch State Mines for prilled urea to retard moisture absorption. It is intended for treatment of urea that will be marketed in warm humid climates. In such climates, the free-flowing properties of prilled urea can deteriorate very rapidly after the bag is opened and before the urea is used. The treatment is reported to be effective in preventing rapid deterioration.

Process Requirements

The economics of urea production will be discussed in chapter XI. The present section deals with process requirements. Utility requirements claimed or guaranteed by engineering and construction firms vary considerably and are influenced by local requirements, the degree of caution used by the estimator, and process variations. There are numerous tradeoffs; steam requirements can be reduced at the expense of increased electric power consumption or at the expense of higher capital cost for heat recovery equipment. Nitrogen losses can be reduced at the expense of higher capital cost and higher energy requirements. Pollution control requirements may add substantially to capital requirements and energy consumption. For these reasons, it is difficult to make an accurate comparison of the processes, and no such comparison will be attempted.

The following tabulation shows a range of process requirements (per ton of urea) from several sources and a "selected value" which will be used in comparative estimates in chapter XI. These requirements are for total-recycle processes and do not include integrated urea-ammonia processes since experience with such processes is limited.

Item	Range	Selected Value
Ammonia	0.57-0.58 ton	0.575 ton
Carbon dioxide	About 0.76 ton	0.76 ton
Formaldehyde[a]	2-4 kg	3.5 kg
Steam	0.9-1.5 ton	1.2 ton
Electricity	100-160 kWh	125 kWh
Cooling water[b]	55-100 ton	70 ton

a. Other conditioners may be used or, in some cases, conditioner may be omitted.

b. Once-through basis.

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X Production, Properties, and Use of Nitrogen Solutions and Use of Anhydrous Ammonia for Direct Application

Introduction

This chapter will deal with liquid nitrogen fertilizers including nitrogen solutions and anhydrous ammonia. The properties and use of anhydrous ammonia for direct application will be described; its production was discussed in chapter VI. Nitrogen solutions include solutions of ammonia in water (aqua ammonia), solutions containing free ammonia plus ammonium nitrate or urea or both, and solutions of urea or ammonium nitrate or both without free ammonia. Solutions that do not contain free ammonia are called "nonpressure" solutions. Solutions that contain free ammonia will have some vapor pressure of ammonia although the vapor pressure may be below atmospheric ("low-pressure") solutions. The major use for nitrogen solutions is for direct application to the soil as a fertilizer although they are also used to produce compound liquid or solid fertilizers (chapter XIX).

Unfortunately, there are no accurate worldwide data for use of anhydrous ammonia and nitrogen solutions. The tonnage of these materials used is relatively small outside the United States, but in some countries they supply a significant percentage of total N use. Available data from several sources are reported below. The year given in statistical data is the year ended June 30 of the year specified.

Australia--Anhydrous and aqua ammonia supplied about 25% of total N use in 1977 (38% of straight N); consumption of these materials increased by 35% in 1977 over 1976 ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978).

Canada--Anhydrous ammonia was the leading form of nitrogen in 1977, supplying 22% of total N or 35% of straight N. Nitrogen solutions supplied 3.6% of the total N ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978). According to another source, fluid materials supplied 31% of the total N in 1977.

Denmark--Anhydrous ammonia supplied 41% of N consumption in 1976 and 36% in 1977 ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978).

United Kingdom--Nitrogen solutions supplied over 10% of straight N use in 1977 ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978). In 1976 liquids comprised 7.5% of the U.K. fertilizer market and were expanding at the rate of 10%/year. Straight nitrogen solutions accounted for 60% of the total liquids; the remainder was mainly liquid compound fertilizers (*Fertilizer International*, 1978, 106:10).

France--In 1976 nitrogen solutions comprised 10% of total nitrogen market and anhydrous NH_3, 2%. Of straight nitrogen use, nitrogen solutions supplied 15.3% and NH_3, 3.1% ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978).

Mexico--Anhydrous ammonia was the leading form of nitrogen in 1977 (28% of total N). It was expected to increase to 33% in 1978 (estimates prepared by GUANOMEX, September 1977).

Colombia--Liquid fertilizers were estimated to account for between 10% and 20% of all fertilizers in 1975 (Lobo, P. 1975. "Liquid Fertilizer Technology Runs Gamut," *Fertilizer Solutions*, 19:46). Anhydrous NH_3 supplied 10% of total N use in 1977 versus 20% in 1976 ("Fertilizer Consumption Statistics," ISMA Economics Committee, 1978).

In addition, some use of nitrogen solutions or anhydrous ammonia or both is known in many other countries, including Belgium, Brazil, China, India, Japan, Spain, Sweden, and the Netherlands, but quantitative data are lacking.

About 58% of the nitrogen fertilizer used in the United States is applied in liquid form, including the estimated N content of liquid compound fertilizers. Tabulated below are the amounts of N fertilizers used in the United States during the year ended June 30, 1977 (1).

Nitrogen Fertilizers Used in the United States in 1976-77

Material	Thousand Metric Tons of N	% of Total N
Anhydrous ammonia	3,664	38.0
Aqua ammonia	120	1.2
Nitrogen solutions	1,528	15.8
Ammonium nitrate[a]	853	8.8
Urea	775	8.0
Ammonium sulfate	200	2.1
Ammonium phosphates[b]	92	1.0
Other nitrogen materials	107	1.1
Compound fertilizers[c]	2,312	24.0
Total	9,651	100.0

a. Including ammonium nitrate-limestone.
b. Includes 11-48-0, 13-39-0, 16-20-0, 21-53-0, and 27-14-0; other ammonium phosphates are included in compound fertilizers.
c. Includes both solid and liquid compounds.

The advantages of liquid fertilizers in general will be discussed in chapter XIX, "Compound Fertilizers." These advantages also apply to nitrogen solutions for direct application. Some of them also apply to nitrogen solutions for use as intermediates in manufacturing compound fertilizers. In the case of anhydrous ammonia, the main advantage is low cost. The average prices paid by farmers in the United States for various nitrogen fertilizers are tabulated below:

Average Prices Paid by U.S. Farmers for Nitrogen Fertilizers, October 15, 1977

Fertilizer	\$/20-lb Unit of N	\$/kg of N
Ammonium sulfate	5.00	0.55
Ammonium nitrate	4.28	0.47
Urea	3.66	0.40
N solution (30% N)	3.96	0.44
Anhydrous ammonia	2.14	0.24

Source: "The 1978 Fertilizer Situation," U.S. Department of Agriculture, December 1977.

Use of Anhydrous Ammonia

Processes and costs of production of anhydrous ammonia are given in other chapters of this publication. This section will be devoted to the use of anhydrous ammonia for direct application. Some of the physical characteristics of liquid anhydrous ammonia are tabulated below.

Physical Characteristics of Anhydrous Ammonia

Characteristics	Value
Boiling point[a]	-33.4°C (-28°F)
Freezing point[a]	-77.7°C (-108°F)
Latent heat of vaporization[a]	327.4 kcal/kg (589 Btu/lb)
Solubility in water at 25°C[a]	0.456 g/g H_2O
Vapor pressure kg/cm^2 (psig)[b]	
-18°C (0°F)	1.10 (15.7)
0°C (32°F)	3.35 (47.0)
38°C (100°F)	13.87 (197.2)
Specific gravity	
-18°C (0°F)	0.6749
0°C (32°F)	0.6385
38°C (100°F)	0.5831
Explosive mixture	16%-25% NH_3 in air

a. At atmospheric pressure.
b. Gauge pressure (psig = pounds per square inch, gauge).

Pure ammonia contains 82.245% N; fertilizer-grade "anhydrous" ammonia contains 82.02% N (minimum), 0.2%-0.5% water, and less than 5 ppm oil. Anhydrous ammonia is the most popular material for direct application in the United States (3.66 million tons of N, 38% of total N). The reason for this popularity is that it is usually the most economical source of nitrogen for the U.S. farmer to purchase. One of the reasons for this low cost is the excellent facilities for transporting and storing liquid ammonia. There are now two ammonia pipeline systems for the transportation of ammonia from the producing areas to the major consuming areas, and there are plans to install additional pipelines for this purpose. There are many large atmospheric ammonia storage tanks in the United States, such as the one shown in figure 1, with capacities ranging from 5,500 to 45,000 tons. These tanks are maintained at atmospheric pressure by using the ammonia as a refrigerant to keep the liquid at -33°C (-28°F). This is done by withdrawing and compressing the ammonia gas from the tank, cooling it with water to liquefy it, and vaporizing the resulting liquid in the tank to keep its contents cool.

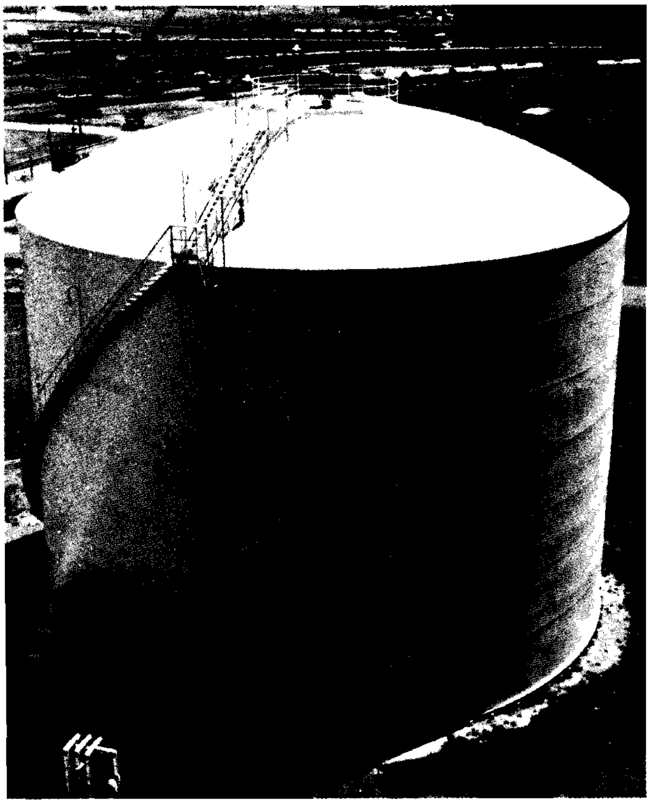
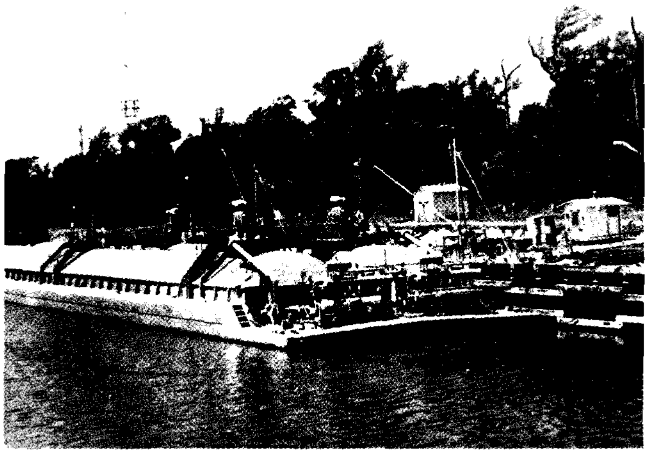


Figure 1. Atmospheric Ammonia Storage Tank.

Similar types of storage tanks are mounted on barges for transportation of the liquid ammonia on the various river systems of the United States.

Figure 2 is a photograph of this type of barge which usually has a capacity to transport about 2,400 tons of ammonia. Each barge is self-sustaining in that it has its own cooling system. Usually, several barges are lashed together as one shipment so that as much as 20,000 tons is transported at one time. There are now large jumbo pressure-type tank cars used for rail transportation of the liquid. These tank cars range in capacity from 24 to 73 tons, and it



Source: Breit & Garcia.

Figure 2. Refrigerated Ammonia Barge.

is a common practice to have "whole train" shipments of ammonia with trains having as many as 100 cars and with all cars shipped directly from the producing area to the consuming area.

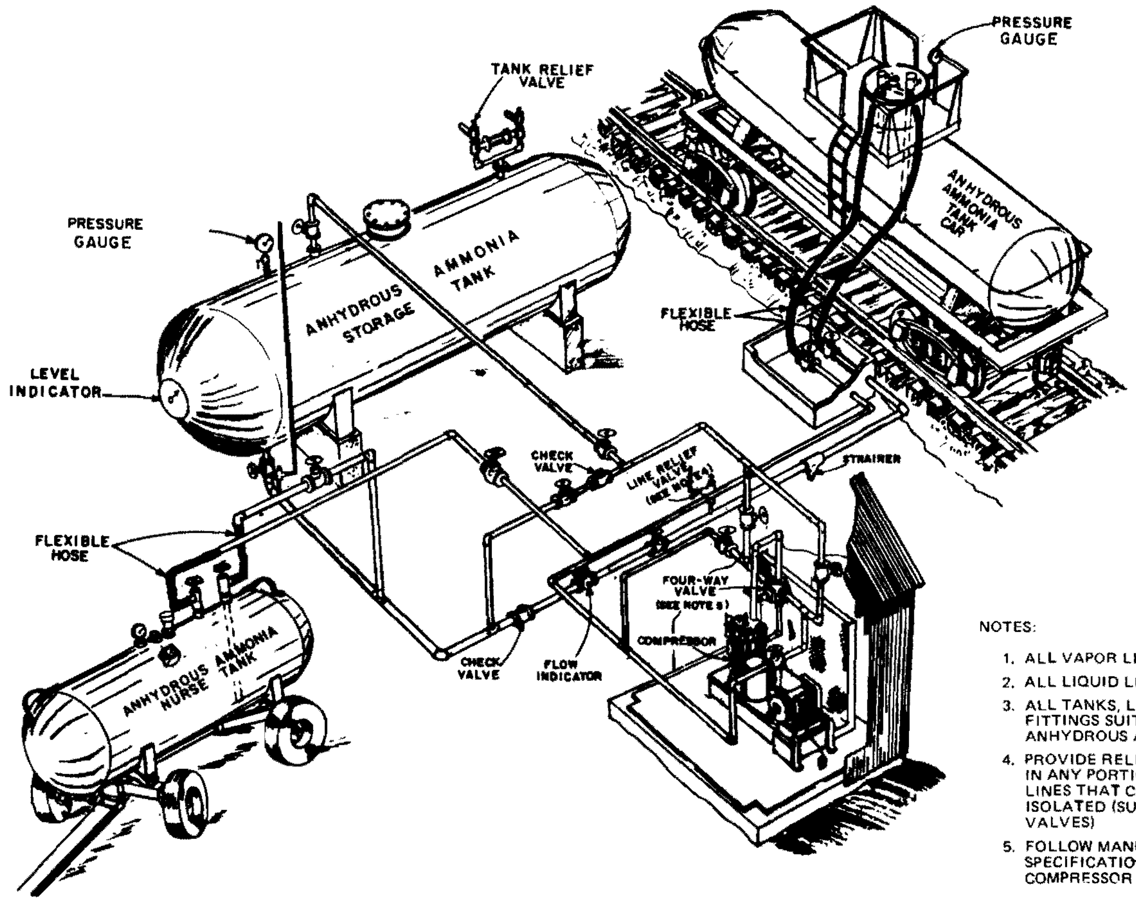
Retail Operations

Usually most of the retail merchants have pressure-type storage tanks that vary in size from 13,000 to 50,000 gal (49,000-189,000 liters). The working pressure in these tanks must not exceed 265 lb/in^2 (18.7 kg/cm^2). It is recommended that all joints be radiographed and the tanks be stress relieved before they are put into operation. The tanks are usually equipped with a liquid-level indicator and have a pressure-type ammonia gauge. Also, they should be equipped with a manway and relief valve. Figure 3 shows a sketch of a typical layout for the pressure-type storage tank at a retail location. Liquid ammonia is transported from the railway tank car to the storage tank by means of an ammonia compressor or a positive displacement pump (usually a gear pump). The ammonia compressor is the most frequently used method of transferring this liquid ammonia (method of figure 3). This transfer is accomplished by removing vapor from the storage tank and pumping it to the railway tank car. Removing vapor from the storage tank causes its contents to cool, compressing the gas causes it to be heated, and the hot gas causes the temperature of the contents of the tank car to increase. These temperature changes cause a pressure differential to form between the railway tank car and the storage tank, thus allowing the liquid ammonia to be easily transferred from the tank car to the storage tank.

Those companies that use a positive displacement pump usually equip it with a bypass and a regulator in the bypass so that the pump will not become vapor locked when liquid is pumped into the nurse tank. These pumps range in size; however, pumps having discharge diameters as large as 7.6 cm (3 in) have been used to transfer ammonia rapidly. Care should be taken to avoid completely filling either the storage tanks or the nurse tanks because of the large variance in specific gravity of liquid ammonia with temperature. Some tanks have been ruptured because they were filled when the ammonia was cool and there was no room for the ammonia to expand as it became warm. For this reason, the storage and applicator tanks usually are never filled to more than 85% of their capacity. At the retail terminal, the farmer's nurse tanks are usually filled by use of the same equipment as that used to transfer the ammonia from the railcars.

Pressure-type nurse tanks (capacity of 1,000-2,000 gal, 3,785-7,570 liters) are often used to transport the ammonia from the retail terminal to the farm. These tanks have the same general specifications as the storage tank. At the farm the ammonia is transferred from the nurse tank to the applicator tank. Figure 4 is a photograph showing a vapor transfer pump moving material from a nurse tank to an applicator. Some farmers fill the applicator by simply bleeding ammonia gas from the applicator tank into the atmosphere; thus, the vapor pressure of the ammonia in the nurse tank causes the liquid ammonia to be transferred to the applicator.

A typical retail merchant may sell other fertilizer materials and other agricultural supplies in addition to anhydrous ammonia; however, usually he supplies the anhydrous ammonia nurse tank and delivers the nurse tank to the farm. Ordinarily the farmer applies the anhydrous ammonia with his own applicator, but he may rent one from the merchant.



NOTES:

1. ALL VAPOR LINES, 2.43 CM
2. ALL LIQUID LINES, 4.93 CM
3. ALL TANKS, LINES, AND FITTINGS SUITABLE FOR ANHYDROUS AMMONIA
4. PROVIDE RELIEF VALVES IN ANY PORTION OF THE LINES THAT CAN BE ISOLATED (SUCH AS BETWEEN VALVES)
5. FOLLOW MANUFACTURER'S SPECIFICATIONS FOR PIPING COMPRESSOR

Figure 3. Pressure Storage for Anhydrous Ammonia.

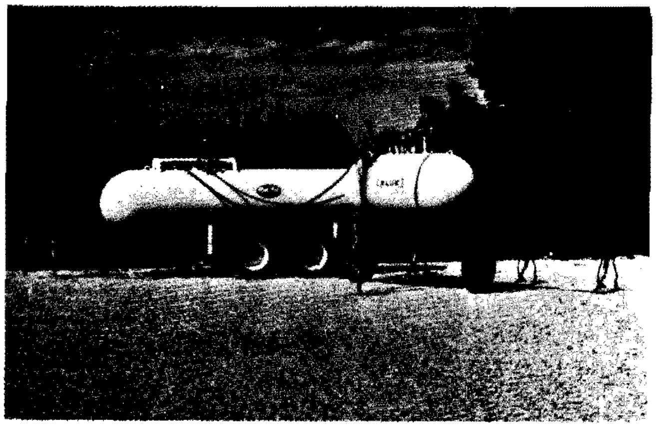


Figure 4. Transfer of Ammonia from Nurse Tank to Farmer's Applicator Using Vapor Transfer Pump.

The cost of a pressure-type storage tank at the retail location ranges from $18,000 for a 45,420-liter (12,000-gal) tank to $30,000 for a 113,600-liter (30,000-gal) tank. Because of regulations, the largest nurse tank usually supplied by the dealer has a capacity of 3,785 liters (1,000 gal) and usually costs about $2,800.

Application of Anhydrous Ammonia

The direct application of ammonia started from rather humble equipment in the early 1940s. One of the first trial applicators is shown in figure 5. As the agronomic effectiveness of anhydrous ammonia was proven, more sophisticated equipment was developed and used.

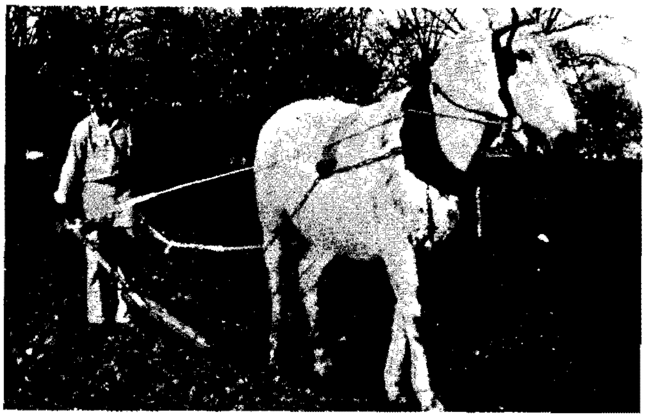


Figure 5. One of First Ammonia Applicators.

Because it is applied as a volatile liquid, anhydrous ammonia must be injected 15-25 cm below the soil surface. This is usually accomplished by an application knife such as those shown in figure 6. Often in sandy loose soil it is applied by an ammonia chisel, also shown in figure 6. Anhydrous ammonia is usually metered by a variable orifice-type meter. The flow rate is set by moving the V-shaped plug into or out of the orifice. A constant differential pressure is maintained at the orifice by the diaphragm. Application rate is controlled by the position of the plug in the orifice and the speed of the applicator (2).

Some farmers like to have their ammonia application rates independent of applicator speed. To do this, the metering device should be actuated by a ground-driven wheel. A piston-type metering pump is the ground-driven ammonia metering device used most frequently. The piston is actuated by a drive chain which is driven by a sprocket attached to a wheel of the applicator. The application rate is changed by altering the length of stroke of the piston. The pump is equipped with a heat exchanger. Ammonia from the pump expands in the heat exchanger which cools the incoming ammonia so that no bubbles form. This ensures that only liquid ammonia is metered.

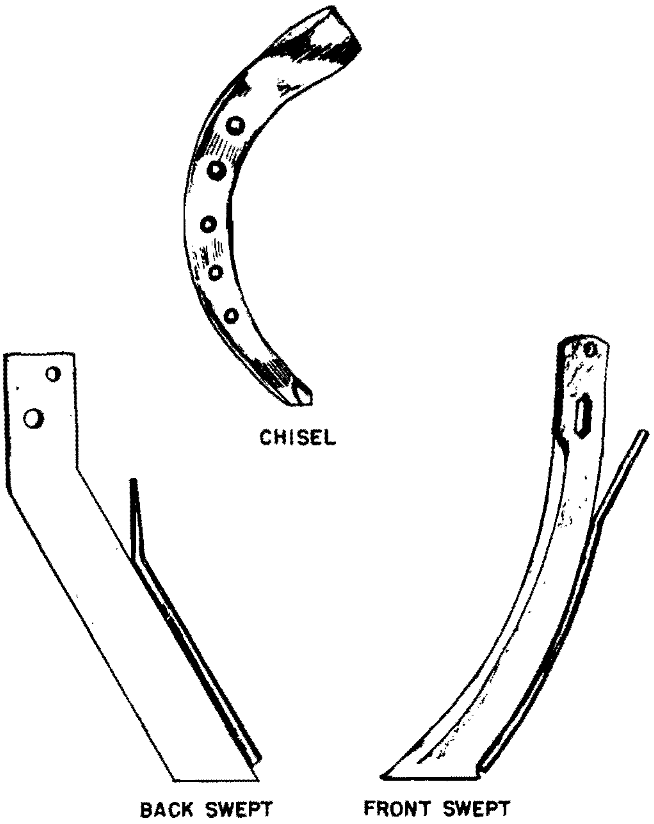


Figure 6. Sketch Showing Ammonia Knives.

Ammonia applicators range in size from the small five-row rigs shown in figure 7 to large rigs which have swath widths up to 20 m and are pulled by crawler-type tractors shown in figure 8 (3).

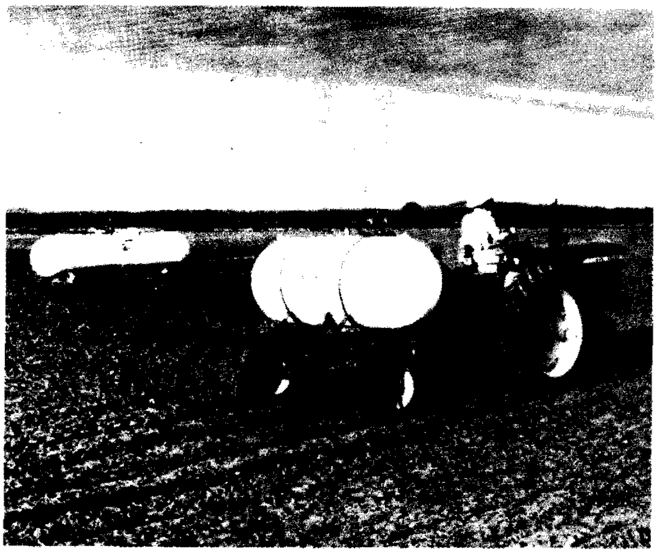


Figure 7. Five-Row Applicator.

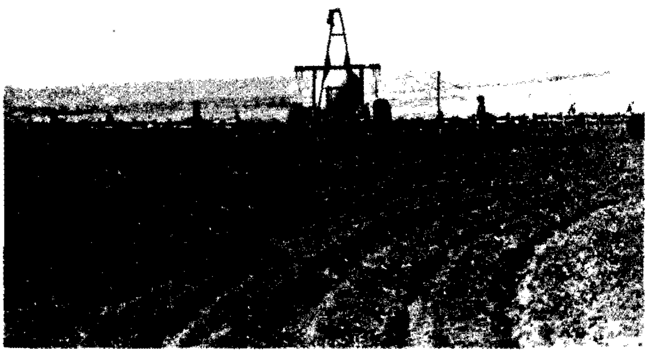


Figure 8. Anhydrous Ammonia Applicator with 20-Meter Swath.

Because of its high vapor pressure, ammonia cannot be surface-applied without losing almost all of the plant food. However, one company has constructed an experimental applicator which shoots ammonia into the ground at 352 kg/cm^2 gauge (5,000 psig). This applicator travels a few inches above the ground and could be used to apply anhydrous ammonia on pastures. The experimental equipment is too heavy, and it needs to be improved so that smaller tractors can be used to move it.

There has been an effort to decrease application costs in the United States, and this has been accomplished by one or more of the following practices. One way is to use larger tractors so that an applicator with wider swath widths can be used. This increases the number of acres that can be treated in a day which results in lower labor and equipment costs per acre of applied nitrogen. Another way to decrease application costs is to use equipment that applies ammonia during other tilling operations. Figure 9 shows a sketch of tilling equipment of this type. This is a concept that has been used for many years in one of the wheat-growing areas where anhydrous ammonia is added during tilling operations which follow the wheat harvest. It is the practice in that area to pass a triangular-shaped plow about 3-4 in (7.6-10.2 cm) beneath the soil. This helps to destroy weed growth, tills the soil, and leaves a protective stubble mulch on the surface to prevent wind and water erosion. Usually about 50-80 lb/acre (56-90 kg/ha) of ammonia can be applied without noticeable losses of ammonia.

Other farmers in the Red River Valley of the United States (Minnesota and North Dakota) add ammonia during plowing operations. The ammonia is added through an open-end pipe directly behind a V-shaped plow which usually passes 10 cm beneath the surface of the soil.

Some companies have tried to keep ammonia in a liquid state long enough for it to be covered with soil during conventional tilling operations, such as disking, etc. By combining tilling and ammonia applications, one pass across the field is eliminated. However, this work is in the initial stages of development, and there is still some disagreement as to the advantages of its use.

Another labor- and equipment-saving practice is to apply anhydrous ammonia along with pesticides or nitrification inhibitors. Recently, it has been shown that inhibitors will decrease the microorganism activity so that the conversion of ammonia nitrogen to nitrate nitrogen will be delayed. Thus, there is less loss of the applied nitrogen due to leaching of nitrate nitrogen from the soil. Therefore, when the inhibitors

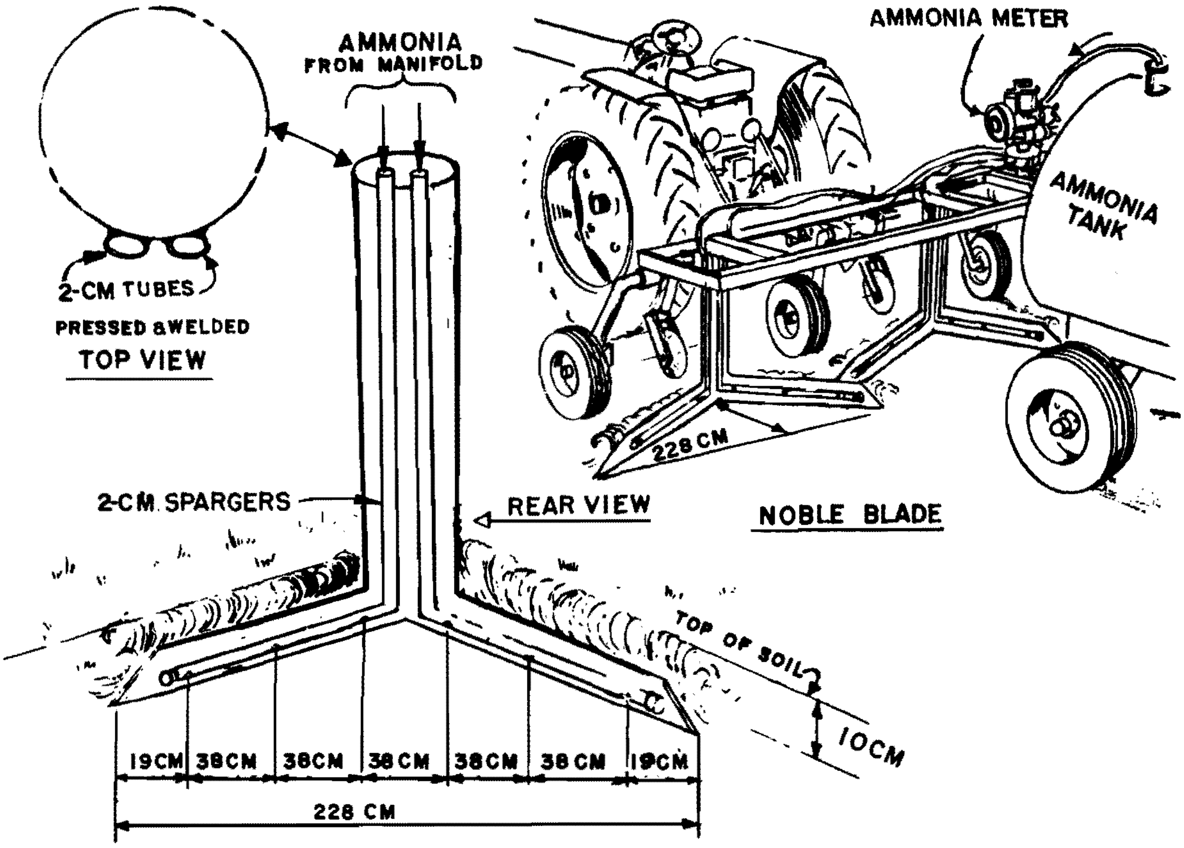


Figure 9. Ammonia Application During Tillage Operation.

are effective there is a more efficient use of the nitrogen. However, to be effective and to save application time, the ammonia and inhibitor must be added at the same time. Figure 10 shows a sketch of equipment used for the dual application of ammonia and pesticides or nitrification inhibitors. The additives are incorporated after the ammonia has been metered, thus avoiding plugging of the meter, corrosion, or contamination of the application tank. When a pesticide and ammonia are applied with this device, only one pass across the field is required.

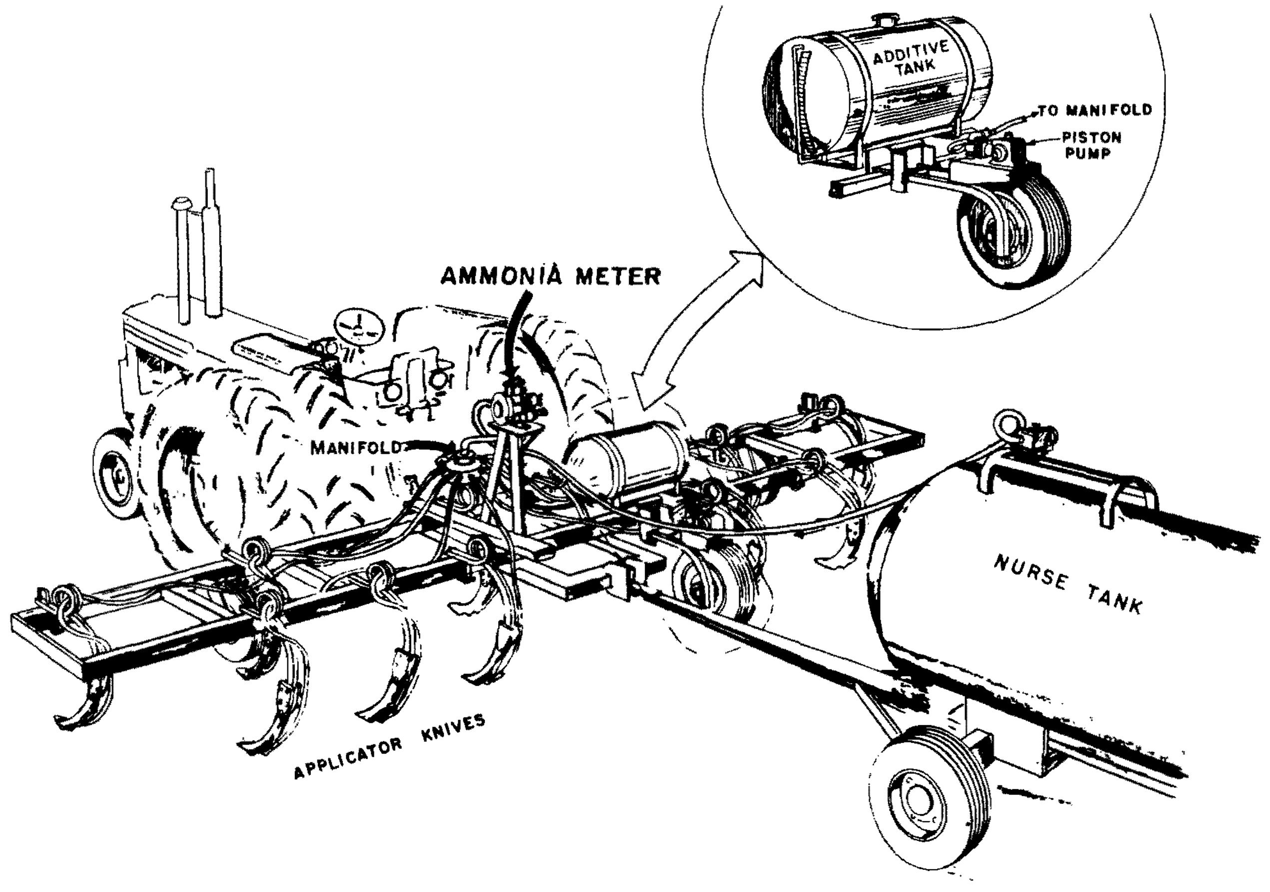


Figure 10. Equipment for Injecting Additives into Ammonia During Application.

The cost of application equipment for anhydrous ammonia has a wide range which is dependent upon the size of the applicator and the auxiliary equipment added to the applicator. Typically, a small four-row anhydrous ammonia applicator with a 757-liter (200-gal) ammonia application tank has an investment cost of $2,300, and a larger eight-row applicator has a cost of $3,400. Usually, a 3,785-liter (1,000-gal) nurse tank is towed behind the large applicator, and its cost is $2,750. However, the larger applicators used to apply ammonia on some of the wheat-growing areas and which have swath widths of 19.8 m (65 ft) and about 40 knives have a cost of about $16,500. In most instances the cost of the ammonia applicator is small when compared with the cost of the tractor used to pull it.

Safety in Handling Ammonia

There are some hazards involved in handling anhydrous ammonia as with any pressure-type solution. The dealer and farmer should be aware of the vapor pressure characteristics of ammonia so that tank ruptures can be avoided. The vapor pressure of anhydrous ammonia versus temperature is shown in figure 11. These data show that at liquid temperatures of 21°C (70°F)--normal summer temperature for most consuming regions--the vapor gauge pressure is about 8 kg/cm^2 (114 psig). At the higher summer temperatures, such as 38°C (100°F), this pressure can be as high as 13.9 kg/cm^2 (197 psig). The pressure tanks normally used at the dealer locations can withstand working pressures in excess of 18.6 kg/cm^2 (256 psig).

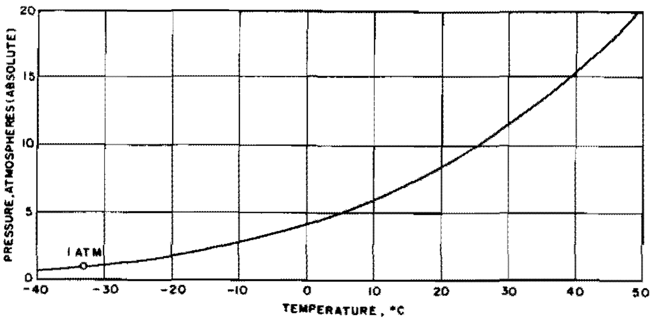


Figure 11. Vapor Pressure of Anhydrous Ammonia Versus Temperature.

Ammonia is a highly reactive alkaline chemical, and it should be handled with caution. Liquid ammonia can cause serious chemical burns. As a gas it is extremely irritating to the eyes and respiratory system. Sufficiently high concentrations can cause death from asphyxiation. From the standpoint of safety it is fortunate that the gas is so irritating because workers will voluntarily leave the danger area before injury occurs. Of course, this is no safeguard against sudden encounter with the liquid or a concentrated accumulation of the gas. A permissible ammonia concentration for repeated exposure for 8 hours has not been universally established; however, federal agencies are now establishing these limitations. Several states have agreed upon a limit of 100 ppm of exposure over an 8-hour period, and at this concentration a slight amount of eye and nasal irritation becomes noticeable. Anhydrous ammonia has a very strong affinity for water, and this is the reason why liquid ammonia can cause severe burns of the skin tissue. It has been generally agreed that no serious or lasting effects have resulted from exposure of ammonia concentrations that do not cause extreme discomfort. Some of the safety precautions for handling ammonia are as follows: (4)

1. Always have ample clean water available.
2. Always stay clear of hose and valve openings.
3. Always wear gloves and goggles when transferring ammonia.
4. Always close valves and disconnect hoses when loading station is unattended.
5. Always be sure pressure is relieved before disconnecting hoses or parts.
6. Never fill a tank to more than 85% of capacity.
7. Never leave transfer operations unattended.
8. Never tamper with relief valves or other safety devices.
9. Never try to "get by"--use only approved ammonia equipment.
10. Never tow a trailer without secure connecting parts and safety chains.

Nonpressure Nitrogen Solutions

The next most popular liquid material for direct application is nonpressure nitrogen solutions. In the United States the consumption of these solutions is increasing at a greater rate than that of anhydrous ammonia. The total amount consumed in the United States during 1976 was about 5.5 million tons (this includes the estimated quantity used for the production of fluid mixtures). The most frequently mentioned reasons for their increased popularity are:

1. Nonpressure nitrogen solutions are easier to handle and to apply than other sources of nitrogen, such as ammonia or solid nitrates.
2. They can be more uniformly applied in the soil than can the solid nitrogen sources.
3. Pesticides can be incorporated with the fluid mixtures and applied at the same time they are applied, thus eliminating the need for one pass across the field.
4. Nonpressure nitrogen solutions can be injected into irrigation systems.
5. They can be transported easily in pipelines, barges, and railcars. The transportation facilities are less expensive than those required for anhydrous ammonia and fewer hazards are involved.
6. Low-cost storage facilities can be used to store the material. Facilities, such as pit-storage, shown in figure 12, are frequently used for storing these solutions, and these facilities have

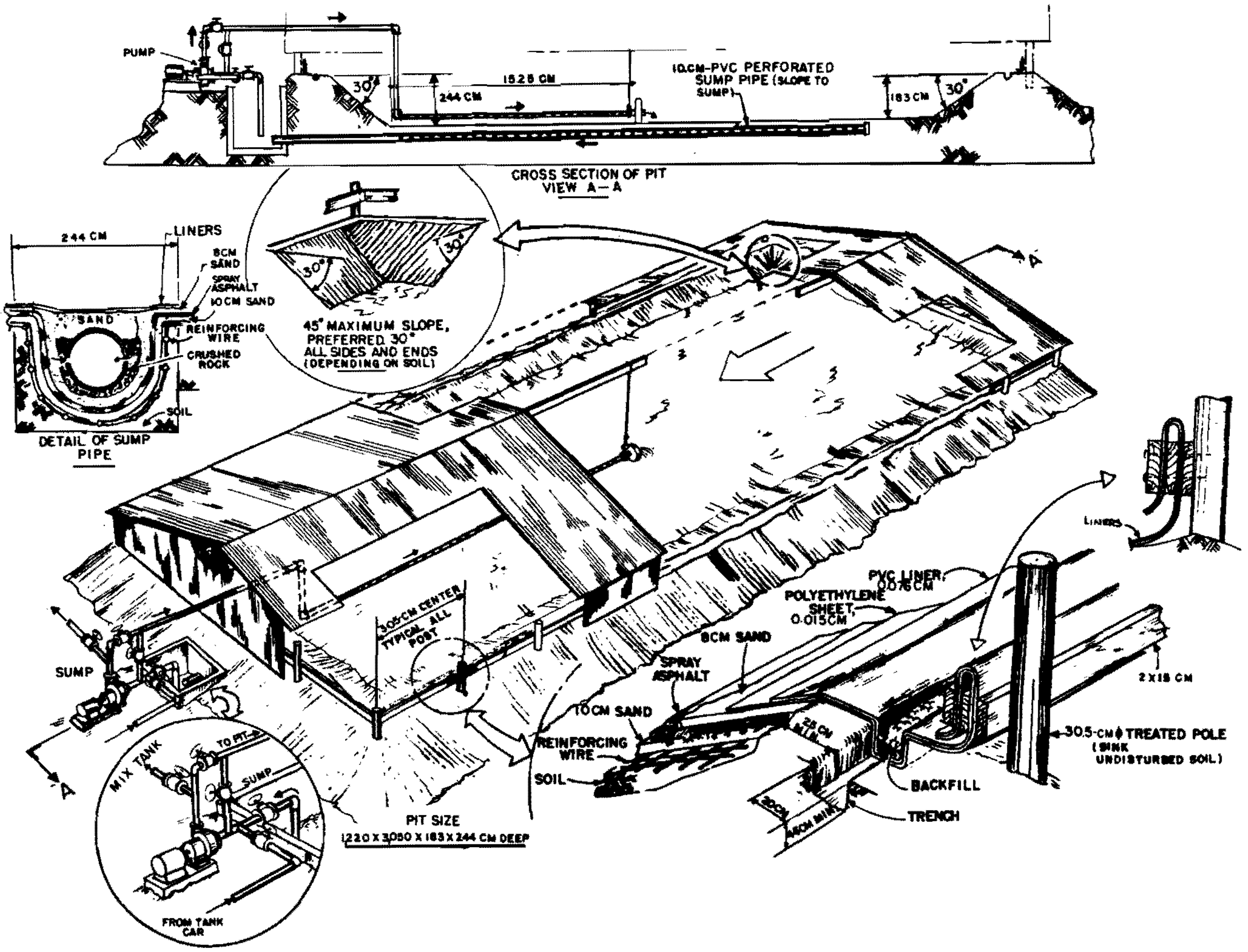


Figure 12. PVC-Lined Earthen Storage Pit.

a lower cost than those for most other nitrogen materials.

7. The solutions are an excellent source of supplemental N for NPK fluid-type mixtures.
8. Cost of production is less than that for most solid sources of nitrogen.
9. They are safer to handle than anhydrous ammonia.

These nitrogen solutions are usually produced from urea and ammonium nitrate solutions plus water. They usually contain a corrosion-inhibiting agent and can be stored and used in mild steel (carbon steel) equipment. Solutions usually sold in the United States have three concentrations: 32%, 30%, and 28% N. Their salt-out temperatures vary directly with their plant nutrient concentration. Figure 13 shows the solubility system of ammonium nitrate, urea, and water; the maximum solubility of the salts in solution is obtained when the urea nitrogen to ammonium nitrate nitrogen ratio is about 1.0. Tabulated are some of the physical and chemical characteristics of the three nonpressure solutions commonly used in the United States:

Physical and Chemical Characteristics of Urea-Ammonium Nitrate Nonpressure Nitrogen Solutions (5)

Grade, % N	28	30	32
Composition by weight			
Ammonium nitrate, %	40.1	42.2	43.3
Urea, %	30.0	32.7	35.4
Water, %	29.9	25.1	20.3
Specific gravity, 15.6°C (60°F)	1.283	1.303	1.32
Salt-out temperature, °C (°F)	-18 (1)	-10 (+14)	-2 (+28)

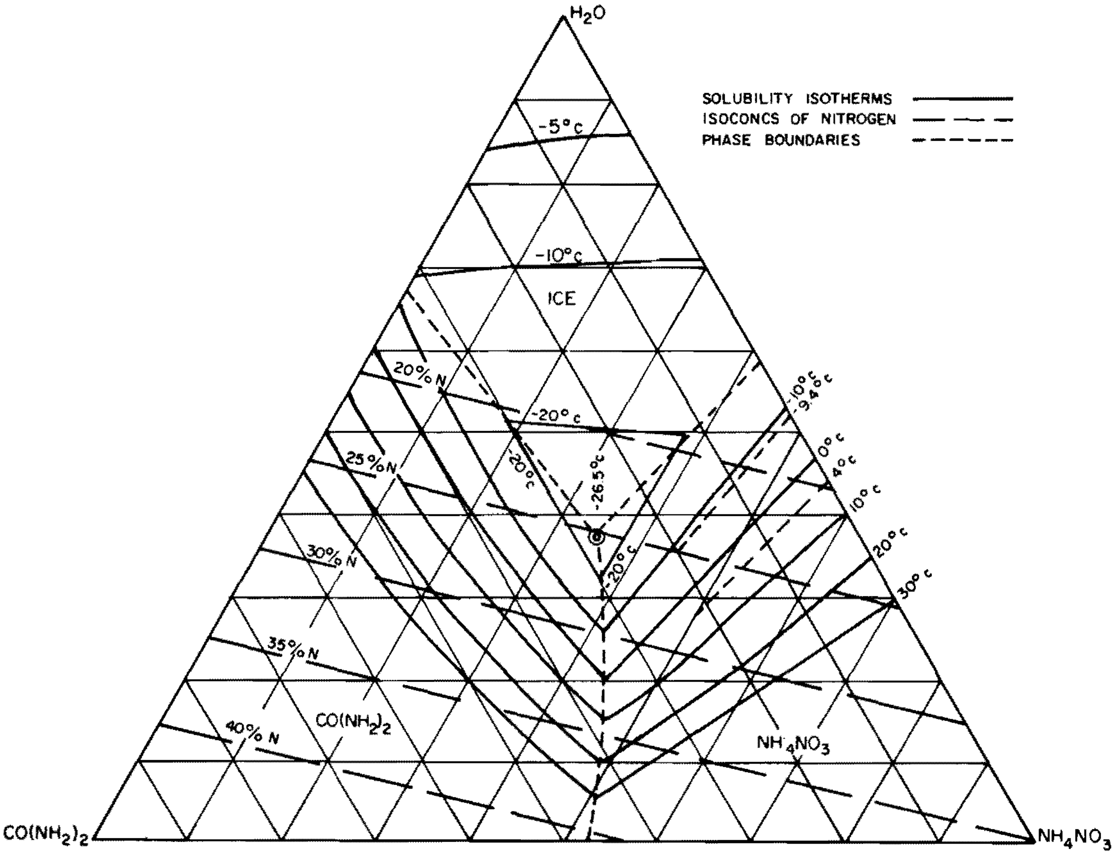


Figure 13. Solubility System of Ammonium Nitrate-Urea-Water.

Solutions of other concentrations may be used; in England a 26% N solution is marketed which has a salt-out temperature of -25°C. In tropical areas more concentrated solutions could be used; for instance, a urea-ammonium nitrate solution containing 35% N would have a salt-out temperature of about 15°C. The inhibiting agent most frequently used for these solutions is anhydrous ammonia, and usually about 5 kg of ammonia per ton of product is added as free ammonia to adjust the pH of the solution to 7.0. Another inhibiting agent which has been found to be effective is ammonium phosphate. Only a small quantity of ammonium phosphate is required to inhibit the solution. Usually about 0.2% P_2O_5 as ammonium phosphate is added. This phosphate material reacts with the mild steel tank to form an iron phosphate film on the tank which is a barrier to further corrosion of the tank. Inhibiting agents which are usually used are tabulated below:

Inhibitor	Concentration
Ammonia	0.5% (pH 7.0-7.5)
10-34-0	0.2% P_2O_5
Ammonium thiocyanate (NH_4CNS)	0.2%
Sodium arsenite (Na_2HAsO_3)	0.1%

Recently several companies in California, Nebraska, and Washington in the United States have started producing a urea solution that contains 18%-19% N. It is produced from prilled or granular urea and hot water (49°C or 120°F). One company that produces aqua ammonia uses the heat generated by conversion of anhydrous ammonia to aqua ammonia to heat the water used to produce the urea solution. The company reports that it can produce an 8-ton batch of solution in a simple mix plant that consists of a batch mix tank with a medium-size recirculating pump (7.6-cm, or 3-in discharge diameter). No agitation other than recirculation is required. About 1 hour of total mix time is required to produce an 8- to 10-ton batch. Field testing of the solution through sprinkler irrigation units shows that it caused substantially less foliage burn than the urea-ammonium nitrate solution which was also added through this type of irrigation unit. Also, small-scale tests show there is substantially less corrosion to mild steel with the urea solution than with urea-ammonium nitrate solution that contains an inhibitor. Most companies report that it is more economical to market urea solution than to market urea-ammonium nitrate solution (28%-32% N) provided the urea is converted to solution at the retail level and sold in a radius of 15 miles of the mix plant. They report the main disadvantage of urea solution is its low analysis.

Other countries, such as India, have produced a limited quantity of urea solution by dissolving prilled urea in water. They report a small solid deposit remains in the solution if the prilled urea contains diatomaceous earth-type parting agent. However, this deposit is a very small quantity of small-size particles which settles to the bottom of the tank and does not cause application problems. When urea conditioned with formaldehyde as a noncaking agent is used, a clear solution with no particles is formed because the methylene urea formed is also water soluble.

Production of Urea-Ammonium Nitrate (UAN) Solutions

Production of ammonium nitrate and urea has been described in previous chapters. Both materials are produced initially in solution form--ammonium nitrate as 75%-85% solution and urea as about 70% solution. Considerable expense and energy (about 1 million kcal/ton of N) are required to convert these solutions to solids; therefore, for production of UAN solution it is preferable to avoid this step. For this reason most of the large-scale production of UAN solutions is located in plants where either ammonium nitrate or urea or (usually) both are produced.

The two types of production processes used are the batch and continuous. Both are uncomplicated, and in each process concentrated urea and ammonium nitrate solutions are measured, mixed, and then cooled. Figure 14 shows a sketch of a batch system in which a batch weigh-and-mix tank is installed on a weigh scale. The solutions are weighed in the mix tank: the inhibitor is weighed separately and added to the mix tank. After mixing, the finished product is cooled. The continuous process is similar, except for the fact that the nitrogen solutions, water, and inhibiting agent are metered and fed continuously to a mixing pipe which is similar to the TVA mixer shown in figure 15. Fluid from the mixing chamber is cooled and pumped to storage.

Most of the larger producers use the continuous system. One such plant is reported to have a capacity of 233,000 tpy, and a second unit of similar capacity is under construction at the same location. Such large plants often are located where transportation by barge or pipeline or both is available. A network of pipelines is available in the United States for transporting petroleum products (gasoline, diesel fuel, etc.), and this network is used alternately for transporting UAN solutions.

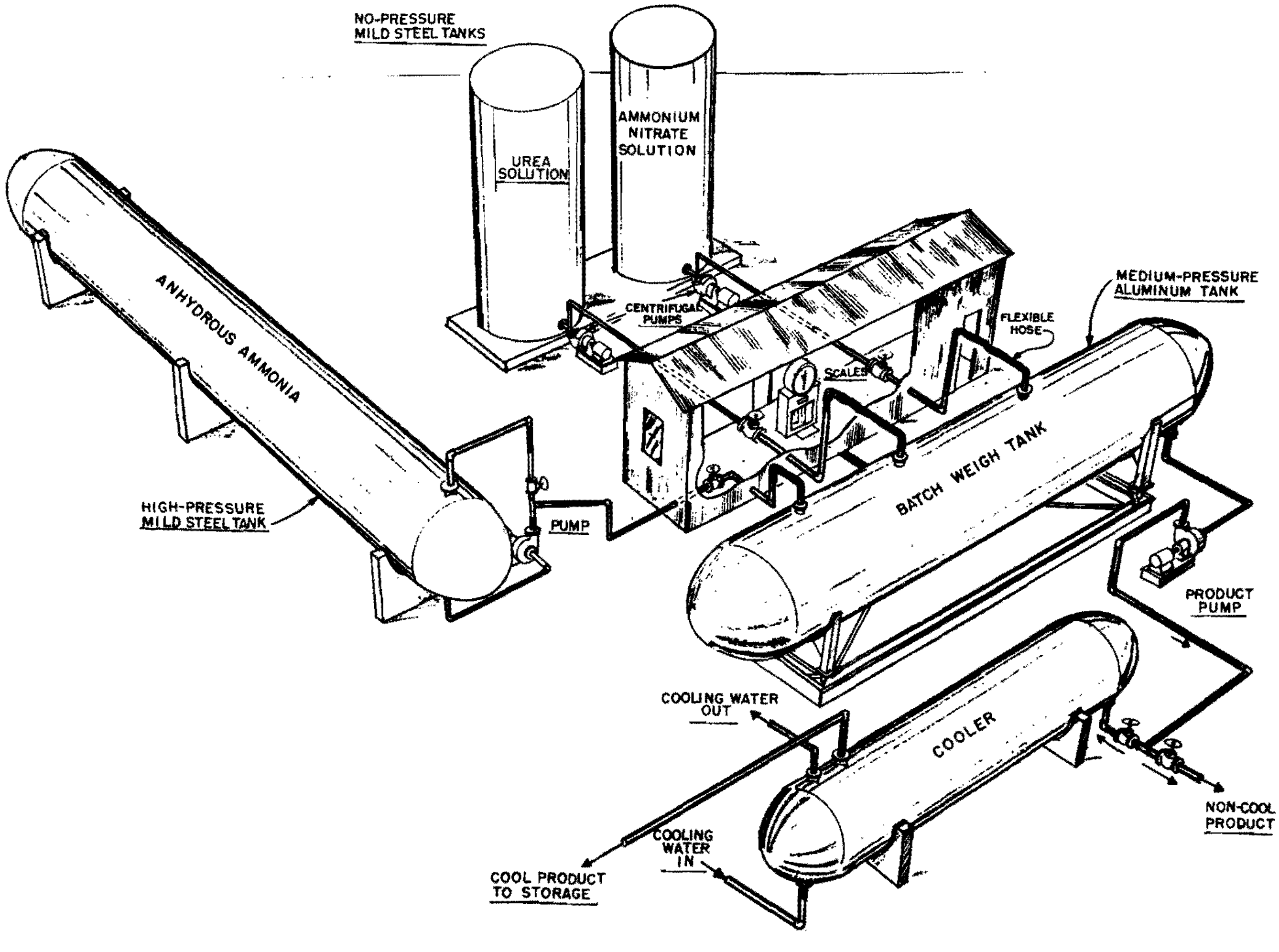


Figure 14. Batch Plant for Nitrogen Solutions.

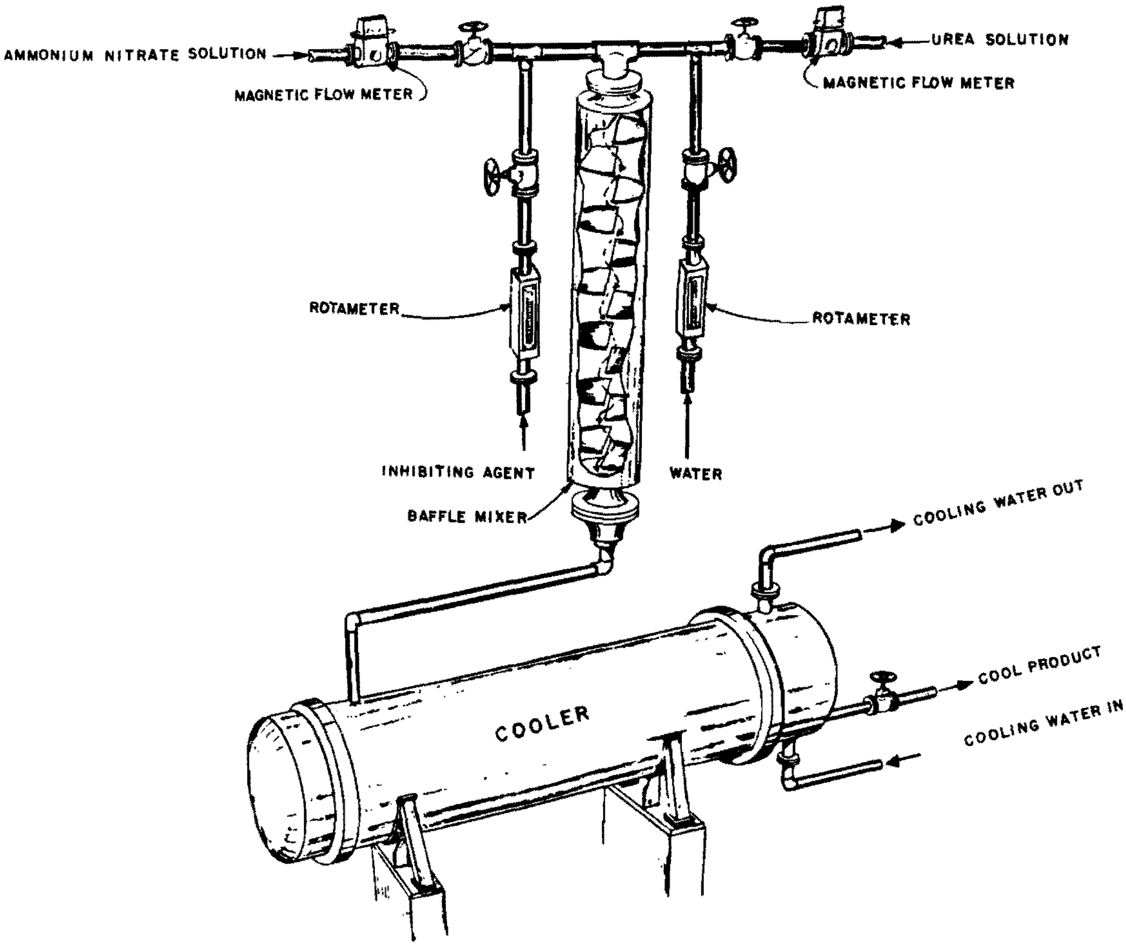


Figure 15. TVA Continuous-Type Urea-Ammonium Nitrate Solution Plant.

Recently there has been some interest in the production of nitrogen solutions from prilled urea and ammonium nitrate. When the solution is produced from these solid materials, it is usually produced in a batch mix tank, and hot water is required to decrease the time required to dissolve the materials. Usually enough heat is supplied so that all of the solid materials will be dissolved at the end of a 30-min mixing time. About 75 kg/ton of saturated steam is required to have a reasonable mixing time. This process is more expensive than the one in which solutions are used; however, sometimes special pricing policies make it advisable to produce a solution from solid materials. Recently one ammonia pipeline company which also has a river terminal close to the pipeline decided it was economical to produce hot ammonium nitrate solution from ammonia at the pipeline and mix it with prilled urea that is received by barge. When this is done, no hot water is required to dissolve the urea, and no cooling is required for the nitrogen solution because the heat supplied by the hot ammonium nitrate solution offsets the negative heat of solution of the urea. This company finds it more economical to produce solutions remote from the ammonia plant because it is more economical to ship anhydrous ammonia and urea (82% and 46% N) than it is to ship solutions (28%-32% N). A similar system is used in a plant in England (6).

Application and Use

Most of the nitrogen solutions are used for direct application; however, a substantial quantity is used to produce fluid mixtures. Most of them are applied by broadcasting using various types of nozzles. Some applicator operators like a fan-type nozzle to apply mixtures of herbicides in nitrogen solutions. They report that they receive a uniform response from the N and a uniform kill of the weeds. Other operators report there is too much drift of the fertilizer when these nozzles are used when the wind is blowing. These latter operators prefer to apply the solution through flooding nozzles. These nozzles emit drops about the same size as the average raindrop. There is little or no drift encountered when they are used. They also give a uniform application across the swath.

The applicator wagons used to broadcast the nitrogen solutions vary in size from the small pull-type that is pulled behind a farmer's tractor (figure 16) to the large self-propelled high-flotation applicator (figure 17). The high-flotation types minimize compaction of the soil during fertilizer application so that the fertilizer can be applied during wet periods. These large applicators are capable of applying an adequate amount of fertilizer solution at a rate of 0.71 ha/min (1.75 acres/min).

Nonpressure nitrogen solutions are added through various types of irrigation systems such as the drip-type, sprinkler, gated pipe, and ditch. This practice has been often referred to as "spoon feeding" of the crop because the solution is added with irrigation water several times during the growing season or continuously in the case of drip irrigation. The apparatus for feeding these solutions to the irrigation unit usually consists of a storage tank and a piston-type metering pump. The rate is varied by changing the length of stroke and the strokes per minute of the pump.

Some of the solutions are mixed with other clear liquids such as 10-34-0, 11-37-0, and potash to produce clear liquid mixtures. Typical grades are 8-8-8,

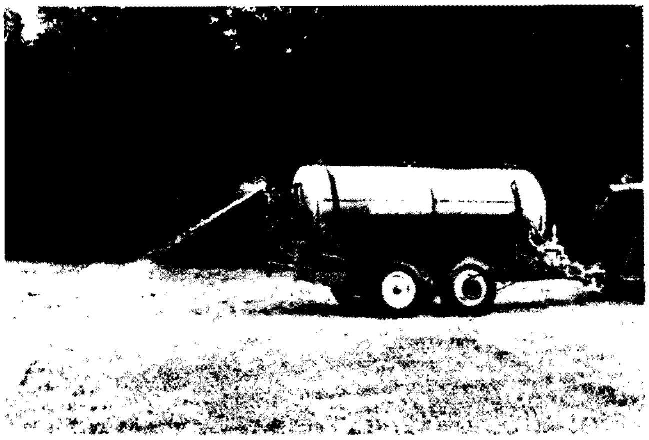


Figure 16. Pull-Type Applicator for Fluid Fertilizers.

21-7-0, and 12-4-4. A typical liquid mix plant for this purpose is shown in figure 18 (cold mix plant). The nitrogen solutions are also used in combination with base suspension materials such as 11-30-0 or 13-38-0 (containing 1.5% gelling clay) and potash to produce mixtures such as 20-10-10, 14-14-14, and 24-8-8. They are also used in combination with phosphoric acid, ammonia, and potash to produce fluids by the hot-mix process.

Aqua Ammonia

Aqua ammonia is not nearly as popular as anhydrous ammonia; however, it is gaining in popularity because it is safer to use than anhydrous ammonia.

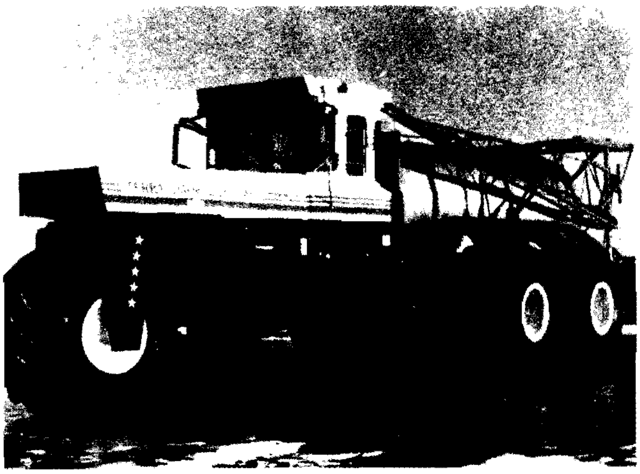


Figure 17. Five-Wheel-High Flotation Applicator.

The most popular aqua ammonia solution contains 20% N, and it exerts no gauge pressure at temperatures below about 36°C (97°F). Therefore, aqua ammonia of this concentration can usually be stored in covered, nonpressure-type storage tanks. These tanks are usually constructed to withstand a pressure of 0.35 kg/cm^2 (5 psig), and they are equipped with pressure and vacuum safety valves. These valves are set to open at 1.051 and 0.991 atm absolute pressure.

Aqua ammonia is usually produced in distribution centers near the market in a continuous-type plant similar to the one shown in figure 19 (7). Anhydrous ammonia, water, and recycled cooled aqua ammonia are mixed in a simple pipe-type mixing chamber. Enough

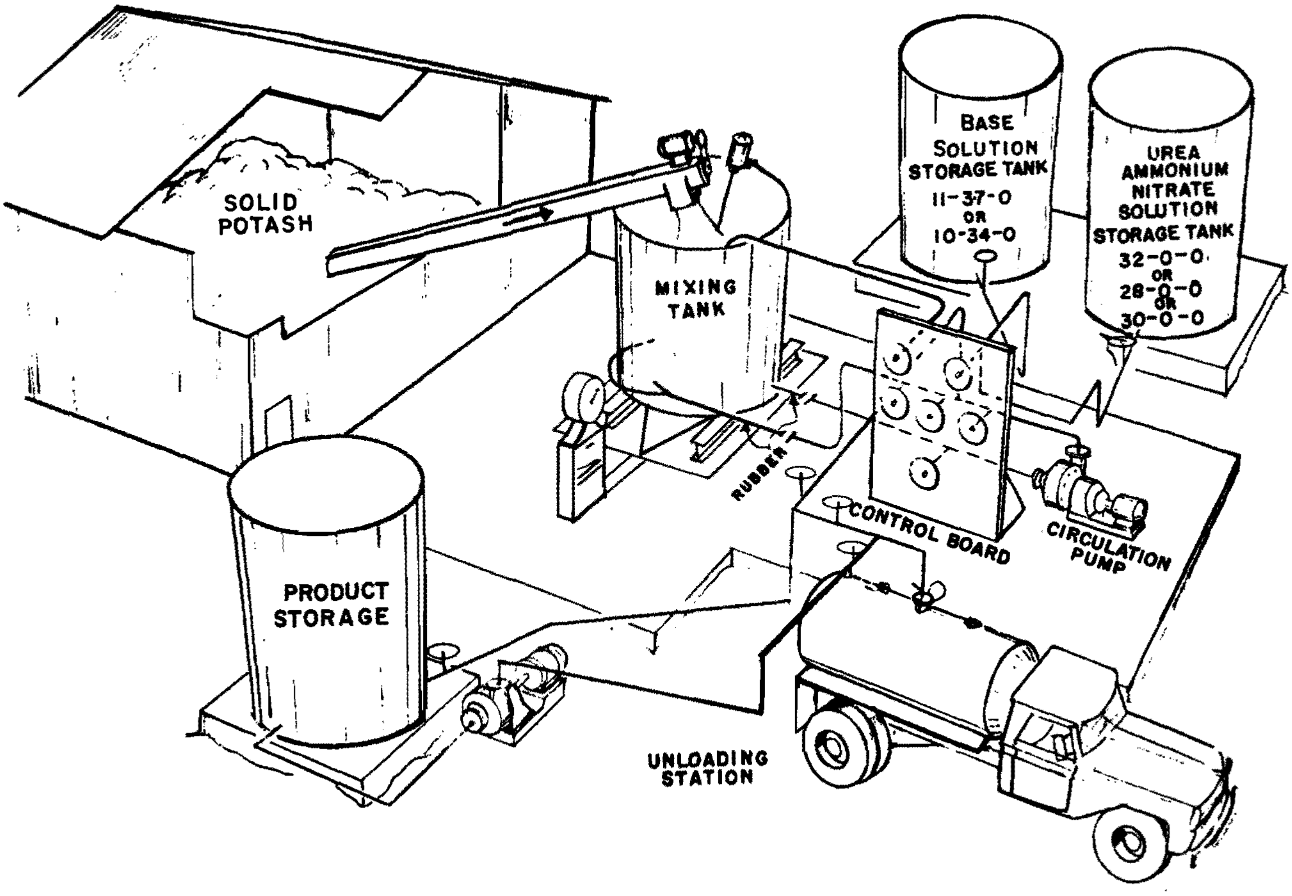


Figure 18. Liquid Fertilizer Mix Plant.

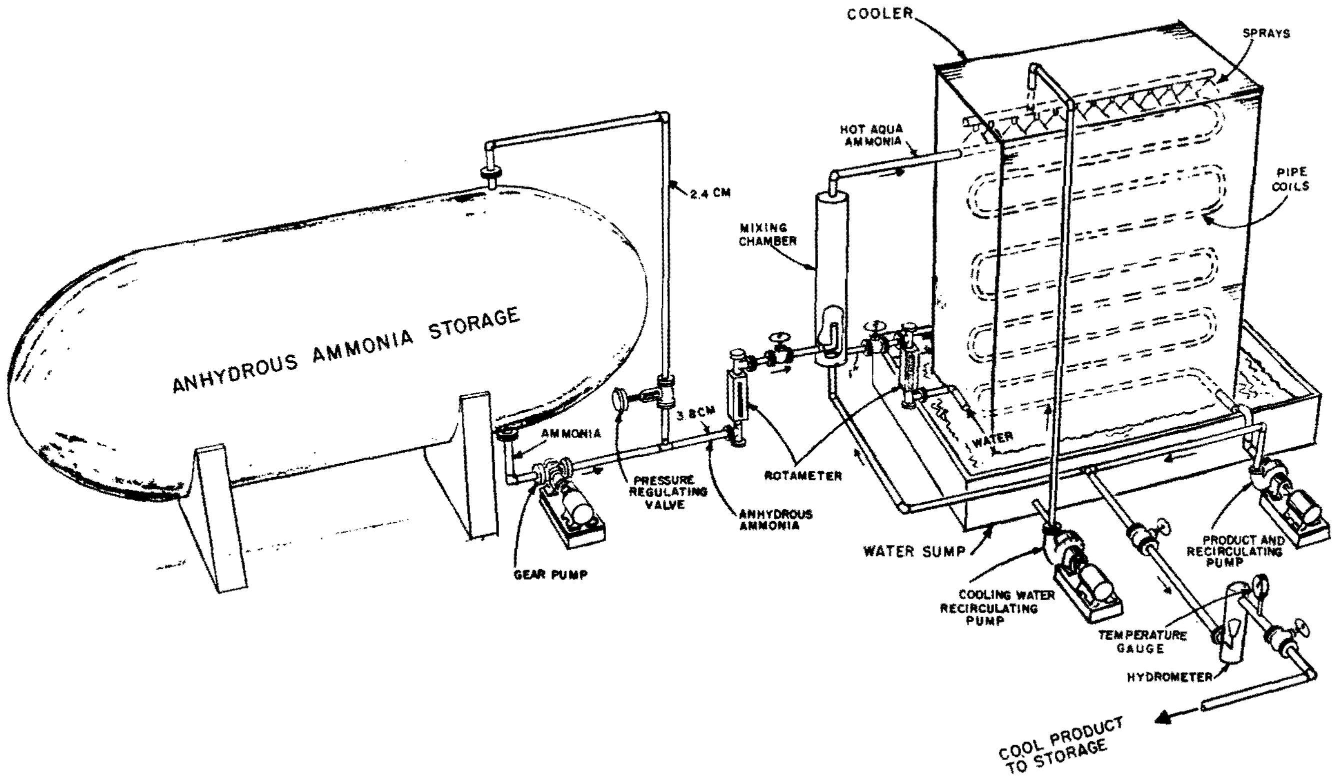


Figure 19. Continuous-Type Ammonia Converter.

water is added to adjust the specific gravity of the liquid to that of aqua ammonia containing 20% N. The curve in figure 20 shows this specific gravity at several temperatures. With this type of plant, a 50-ton tank car of anhydrous ammonia can usually be converted to 206 tons of aqua ammonia in approximately 5-8 hours. This rate of conversion is dependent upon the size of the cooler in the plant.

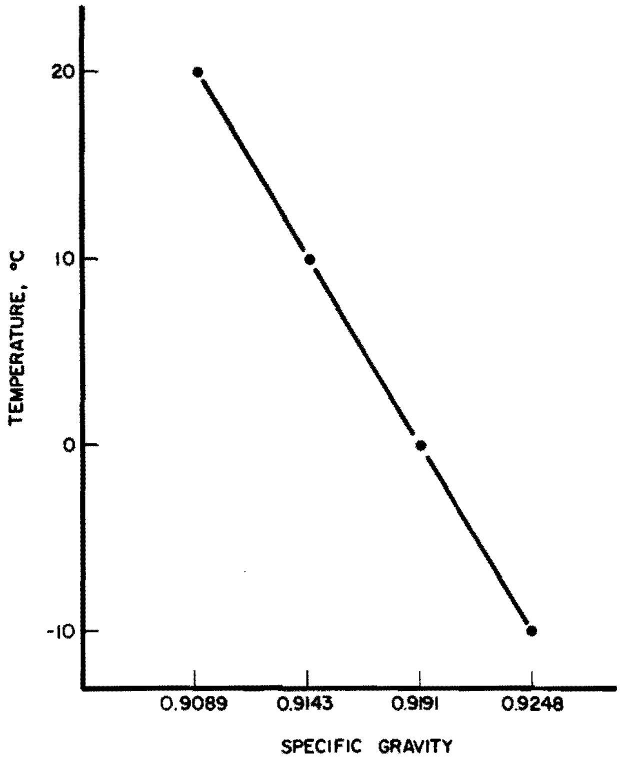


Figure 20. Specific Gravity Versus Temperature of 20%-N Aqua Ammonia (Ref. 4° C).

Because aqua ammonia has a low vapor pressure, it does not need to be injected as deeply into the soil as anhydrous ammonia. Most operators have found that they do not have excessive ammonia losses if they inject the aqua ammonia about 7.6-12.7 cm (3-5 in) beneath the surface of the soil. This is about half the depth of injection that is required for anhydrous ammonia. The applicators used for applying aqua ammonia are similar to those for anhydrous ammonia in that they have injection knives; however, since these knives travel at a shallower depth, much less energy is required to pull them. Also, aqua ammonia can be applied at a much faster rate than anhydrous ammonia because deep injection of this solution is not required. Many operators have found that they can apply the aqua ammonia in tilling operations, such as plowing, disking, etc., without high ammonia losses.

Pressure-Type Solutions

Many different pressure-type solutions have been used in the United States. Usually these solutions are made from a combination of ammonia and ammonium nitrate or urea or both. All of the solutions contain water; however, some of them have a water content as low as 0.5%. Table 1 shows some of the chemical and physical characteristics of typical ammonia-ammonium nitrate water solutions that have been used in the United States, and table 2 shows similar data for ammonia, ammonium nitrate-urea, and ammonia-urea solutions (5).

These solutions are produced in the same batch-type plant used to produce the nonpressure UAN solution (figure 14). The batch tank used in the production of these solutions is usually constructed so that it will withstand pressures up to 5.3 kg/cm^2 (75 psig). The same mixing procedure is used in the production of these solutions as is used for the nonpressure solution except that anhydrous ammonia is an extra ingredient which must be added, and the piping systems should be fabricated to withstand pressures of 5.3 kg/cm^2.

TABLE 1. AMMONIA-AMMONIUM NITRATE SOLUTIONS

Solution No.[a]	%				Specific Gravity, at 16°C	Gauge Pressure, kg/cm^2 at 40°C	Salt-Out Temp.,	
	Total N	Free NH_3	NH_4NO_3	H_2O			°F	°C
448(25-69-0)	44.8	25.0	69.0	6.0	1.124	1.20	6	-14
471(30-64-0)	47.1	30.0	64.0	6.0	1.103	1.90	-32	-36
466(25-74.5-0)	46.6	25.0	74.5	0.5	1.150	2.04	5	-15
490(34-60-0)	49.0	34.0	60.0	6.0	1.042	3.37	-52	-47
414(19-74-0)	41.4	19.0	74.0	7.0	1.186	0.56	64	18
440(28-60-0)	44.0	28.0	60.0	12.0	1.083	1.76	-36	-38
370(16.6-66.8-0)	37.0	16.6	66.8	16.6	1.182	0.07	48	9
410(26.3-55.5-0)	41.0	26.3	55.5	18.2	1.079	1.20	-25	-32
452(29.9-59.0-0)	45.2	29.9	59.0	11.1	1.070	1.83	-27	-33
452(26-68-0)	45.17	26.0	68.0	6.0	1.12	1.97	6	-14

a. In the solution numbering code, the first number is the percentage of total N (in tenths of percent); the numbers in parentheses are the percentages of free ammonia, ammonium nitrate, and urea, respectively.

TABLE 2. AMMONIA-AMMONIUM NITRATE-UREA AND AMMONIA-UREA SOLUTIONS

Solution No.[a]	%					Specific Gravity, at 16°C	Gauge Pressure, kg/cm^2 at 40°C	Salt-Out Temp.,	
	Total N	Free NH_3	NH_4NO_3	Urea	H_2O			°F	°C
449(28-40-15)	44.0	28.0	40.0	15.0	17.0	1.052	1.97	1	-17
444(25-55-10)	44.5	25.0	55.0	10.0	10.0	1.108	1.55	-23	-31
450(27-50-12)	45.2	26.7	50.0	12.0	11.3	1.085	2.11	-8	-22
490(33-43-13)	49.1	33.5	44.0	13.0	9.5	1.020	3.80	-26	-32
495(37-40-11)	49.5	37.0	40.0	11.0	12.0	1.039	4.22	-50	-46
515(40-40-10)	51.6	40.0	40.0	10.0	10.0	0.983	5.48	-3	-19
370(25-0-35)	37.1	25.0	-	35.3	23.3	1.090	1.69	34	1
450(37-0-32)	45.0	36.6	-	32.0	31.4	0.929	3.80	17	-8

a. In the solution numbering code, the first number is the percentage of total N (in tenths of percent); the numbers in parentheses are the percentages of free ammonia, ammonium nitrate, and urea, respectively.

Use of Pressure-Type Nitrogen Solutions

Some use of pressure-type solutions for direct application has been reported, but they are primarily used as a source of nitrogen and ammonia for use in ammoniation-granulation plants to produce compound fertilizers. The free ammonia of the solutions reacts with the superphosphates and acids which are also added to the granulator. These solutions also provide supplementary nitrogen as ammonium nitrate and/or urea to produce high nitrogen grades. The granulator is usually a TVA-type rotary granulator in which the nitrogen solutions are added beneath the rolling bed of material. The reaction of ammonia with other materials causes enough heat and liquid phase to be added to the granulator which cause the smaller size particles to be agglomerated into the desired size of granules for excellent storage, uniform application, and customer acceptance. Sometimes steam is also added to promote granulation. The most popular solution of this type is one that contains 44.8% total N, 25% free NH_3, 69% NH_4NO_3, and 6% H_2O. The next most popular solutions contain 47.1% total N, 30% free NH_3, 64% NH_4NO_3, and 6% H_2O. These solutions have been used to produce compound fertilizers, such as 15-15-15, 16-8-8, etc., in ammoniation-granulation plants; however, the trend in the United States is to replace them with anhydrous ammonia. Compound fertilizers will be discussed in chapter XIX in which the use of nitrogen solutions, anhydrous ammonia, and acids is covered. That chapter also covers the calculation of heats of reaction and liquid phase of granulation formulations to provide good granulation in typical granulation plants using the TVA ammoniator granulator.

These nitrogen solutions are being replaced by anhydrous ammonia because anhydrous ammonia is now readily available to the ammoniation-granulation plant at a lower cost than the nitrogen solutions. Therefore, most granulation plants now use much larger quantities of sulfuric acid and phosphoric acid to fix ammonia that is used in the formulations. Also, many of the nitrogen solutions are being replaced by byproduct ammonium sulfate. Recently, some companies have replaced the nitrogen solutions with low-cost urea. Usually, urea and anhydrous ammonia can be delivered to the ammoniation-granulation plants at a lower cost than the nitrogen solutions, and for this reason it is anticipated that these solutions will become less popular in the future as a source of both ammonia and nitrogen for granulation plants.

In addition to the solutions shown in tables 1 and 2, a low-pressure ammonia urea solution has been produced in Europe and shipped to Brazil for use in granulation plants (8). This solution does not exert a gauge pressure until its temperature reaches about 35°C (95°F), and at 41°C (105°F) it exerts a gauge pressure which is estimated to be only 0.35 kg/cm^2 (5 psig). The solution contains 33% N, 16% free ammonia, 44% urea, and 40% water.

The Brazilian company that received this solution found it safe to store the solution in a nonpressure storage tank formerly used for the storage of crude oil. No ammonia was lost from the solution when several inches of crude oil were allowed to cover the surface of the liquid in the tank. This solution was used to produce granular products in a granulation plant that contained both a rotary and a pan granulator. The experience of this company demonstrated that this solution probably could be used in developing countries.

Summary

Liquid nitrogen materials (anhydrous or aqua ammonia and nitrogen solutions) are major sources of nitrogen in the United States, Canada, Mexico, and Denmark; they are important and growing sources in several other countries. About 60% of the N applied in the United States is applied in fluid forms. The popularity of these materials has increased because they are usually one of the most economical sources of nitrogen. Also, the energy requirement for their manufacture is less than for solids. The nonpressure solutions have the greatest growth rate because of their ease in handling, storage, and application. Application with irrigation water is particularly popular. Also, they are excellent carriers of pesticides and micronutrients and are used as a source of supplementary nitrogen for fluid mixtures. The medium-pressure ammonia-ammonium nitrate and ammonia-ammonium nitrate-urea solutions appear to be losing their popularity as a source of ammonia and nitrogen for the production of compound granular fertilizers in ammoniation-granulation plants. They are being replaced by anhydrous ammonia and solid nitrogen materials.

Some of the developing countries have started using low-pressure nitrogen solutions, and a few of the Asian and Latin American countries have shown considerable interest in the application of anhydrous and aqua ammonia or other liquids.

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XI Some Factors Influencing Choice of Nitrogen Fertilizers

Introduction

The usual aim in choosing which nitrogen fertilizer or fertilizers should be produced and marketed is, or should be, to determine which products will produce the greatest increase in crop value per dollar spent. The problem is not a simple one; it involves estimation of the cost of manufacturing or procuring the products, the cost of marketing and distributing them, the agronomic effectiveness of the alternative products, and the value of the increased agricultural production. The answer may be different for different crops or regions. Often some compromise must be made between cost of manufacture and distribution on the one hand and agronomic effectiveness on the other. The question, whether to supply nitrogen in two or more forms to meet diverse requirements, needs to be considered in light of whether the additional benefit is worth the additional cost (if any). Finally, a decision is needed as to whether only straight nitrogen fertilizers should be produced or whether nitrogen should also be produced in the form of compound fertilizers. Most countries have found it useful to supply both types.

Agronomic Considerations

It is sometimes said that all nitrogen fertilizers are equally effective when used properly. This is not quite true unless one defines proper use as avoiding some types of uses in which certain products have inherently low effectiveness. Perhaps more to the point, one needs to consider how the products will be used. It is very difficult to change the habits or practices of a large number of farmers and, in fact, it may be uneconomical to do so if the proposed practices involve expenditures for equipment that small farmers cannot afford. Therefore, effectiveness of fertilizers should be evaluated on the basis of how the farmers are likely to use them rather than how they should be used for maximum effectiveness.

Nitrogen fertilizers may be classified into three groups according to whether the nitrogen is present in the ammoniacal form or the nitrate form or some mixture of the two. A fourth group could be added--complex organic compounds. Natural organic fertilizers do not fall within the scope of this manual while synthetic organic compounds other than urea will be discussed separately under controlled-release fertilizers (chapter XXI).

Ammoniacal fertilizers are anhydrous ammonia, aqua ammonia, and the ammonium salts--sulfate, phosphates, chloride, and carbonate or bicarbonate. Urea will be included in this group since it readily hydrolyzes in the soil to ammonium carbonate.

Nitrate fertilizers are sodium, potassium, and calcium nitrate. Fertilizers containing mixtures of ammoniacal and nitrate fertilizers are mainly ammonium nitrate and various combinations containing it, such as urea ammonium nitrate solution, ammonium phosphate nitrate, etc.

Ammoniacal fertilizers as a group have some characteristics in common. Most plants cannot utilize ammoniacal nitrogen effectively (rice is a notable exception), thus for most crops, utilization is dependent on conversion of the ammoniacal nitrogen to nitrate nitrogen in the soil. This conversion takes place through a series of microbiological processes and is usually quite rapid in warm soils. However, the reaction requires oxygen and cannot take place when air is excluded from the soil as, for example, by flooding. The rate of nitrification decreases as the soil temperature decreases, and at soil temperatures of 10°C and below the reaction practically ceases. For this reason fertilizers containing at least some nitrate are preferred for use in cold climates for those crops that make substantial growth in early spring when soil temperatures are low. Many farm crops such as maize and cotton will not germinate or grow in cold soil, thus the rate of nitrification is not likely to be a limiting factor for these crops.

Ammoniacal nitrogen is adsorbed by colloids in the soil and therefore is resistant to leaching. Because of rapid nitrification in most agricultural situations, this advantage is short-lived and hence relatively unimportant. There are two important exceptions:

1. When an ammoniacal fertilizer is placed in the reducing (anaerobic) zone of a flooded soil, it remains in the ammoniacal form and hence resistant to leaching as long as the zone remains anaerobic. Since the rice plant can utilize ammoniacal nitrogen efficiently, this situation provides an important opportunity for rice farmers to minimize nitrogen losses by leaching or volatilization.

2. Since ammoniacal nitrogen does not nitrify in cold soil, it may be applied in late autumn for fertilization of crops to be planted in the spring without danger of loss by leaching during the winter in those climates where the soil temperature remains below 10°C during the winter. This situation enables farmers to take advantage of a low price or abundant supply of fertilizer which may be available during the autumn and to apply the fertilizer during a less busy time than the spring planting season.

Surface-applied ammoniacal nitrogen is subject to more or less serious losses by volatilization of ammonia depending on the type of fertilizer, pH of soil, temperature, etc. Anhydrous ammonia would volatilize instantly if applied to the soil surface, thus it must be injected 10 cm or more below the surface to avoid heavy losses. The same is true of aqua ammonia of the usual concentration (25% NH_3). Dilute aqua ammonia (5% NH_3) can be surface applied without serious losses on some soils. Surface-applied urea may be subject to moderate to heavy losses, particularly in warm, humid climates or on calcareous soils. In the case of flooded rice, loss of ammonia by surface application of urea depends on the pH of the floodwater rather than that of the soil. When urea is applied to the surface of unflooded soil, ammonia loss depends on the rate of hydrolysis of urea to ammonia and carbon dioxide and can be largely prevented by working it into the soil soon after application or by timely rains or irrigation.

Ammonium bicarbonate is subject to serious loss of ammonia unless it is worked into the soil. Other ammonium salts are relatively free from ammonia loss problems; however, appreciable loss can occur with surface application on strongly alkaline soils or alkaline floodwater, especially with diammonium phosphate and even with ammonium sulfate.

All ammoniacal fertilizers are acid forming, but ammonium sulfate and chloride are the most strongly acid forming since both the nitrogen and the anion contribute to acidifying the soil. (For a discussion of the acid- and base-forming characteristics of fertilizers, see chapter XXII.) The acid-forming quality may be an advantage for use on alkaline soils or for crops that require acid soils (such as tea). In other cases the acidity is likely to be a disadvantage since eventually the soil may become so acid as to be unfit for agricultural use unless corrected by application of limestone.

The value of the anion of the ammonium salt must be considered. This is especially true of ammonium phosphates which are usually considered as phosphate fertilizers, since their $N:P_2O_5$ weight ratio ranges from 1:5 for MAP to 2:5 for DAP. However, they are capable of economically supplying a substantial amount of nitrogen, as will be pointed out in chapter XVII, and should be given due consideration in planning a nitrogen supply. Ammonium sulfate is often valued for its sulfur content since there are widespread deficiencies of this element (see chapter XX). However, its S:N ratio is far greater than needed for most situations, thus it is often used as an ingredient of compound fertilizers rather than as a straight nitrogen fertilizer. The chlorine content of ammonium chloride is beneficial in rare cases (see chapter VIII) but more often deleterious for some crops and soils. It leaches rapidly from well-watered soils and is not considered harmful in most cases except for specific crops that are sensitive to it or situations where chloride accumulations in the soil present a problem (such as semiarid soils).

Nitrates are generally agronomically effective and preferable for some crops (tobacco) or for rapid response in cool soils. Nitrates leach readily from some soils under conditions of heavy rainfall or irrigation. As pointed out previously, ammoniacal nitrogen is rapidly converted to nitrate in most situations, thus only in certain conditions can any specific advantage or disadvantage be attributed to the nitrate form. Nitrates are, of course, free from ammonia loss problems. In flooded or waterlogged soils, nitrate nitrogen may be reduced ("denitrified") first to nitrite then to N_2, N_2O, or NO and thus lost to the atmosphere. For this reason, nitrates are generally regarded as unsuitable for subsurface application to flooded rice.

Sodium, calcium, and potassium nitrate have a basic reaction in the soil which is an advantage for acid soils. The sodium content of sodium nitrate may be useful in increasing yields of certain crops, but it may be a disadvantage for soils that already have an excessive sodium content. Calcium nitrate finds use on saline soils since the calcium will replace sodium adsorbed on clay, permitting sodium to be washed out. The main disadvantage of calcium and sodium nitrates is their low analysis (15%-16%). Potassium nitrate is generally considered as a potash fertilizer (13-0-44), and its advantages will be discussed in chapter XVIII. However, it is also valued for its nitrate nitrogen content for use in some specialty fertilizers, such as tobacco fertilizer.

Ammonium nitrate contains both ammoniacal and nitrate nitrogen in equal amounts and therefore has some of the advantages and disadvantages of both forms. It is generally regarded as agronomically effective for a wide range of crops and soils with the notable exception of subsurface application on flooded rice. It is satisfactory for use on upland rice and in some cases for surface application on flooded rice. It is widely used in Europe and North America both as a straight nitrogen material and as an ingredient of compound fertilizers. The urea ammonium nitrate solution (UAN) and ammonium sulfate nitrate (ASN) contain one-quarter of their nitrogen in the nitrate form and three-quarters in the ammoniacal form.

Physical Properties and Safety

The physical properties of fertilizers are an important consideration and sometimes a deciding factor. The physical properties of solid fertilizers will be discussed in chapter XXII and in various other chapters dealing with specific products. Chapter X covered pertinent physical properties of nitrogen solutions, anhydrous ammonia, and aqua ammonia.

Some hazards are involved in storage, transportation, and use of ammonium nitrate and some compound fertilizers containing it, which were discussed in chapter VIII. In some countries where safe practices are difficult to enforce, these hazards could be a serious drawback. Likewise transportation, storage, and use of anhydrous ammonia involve hazards (chapter X) which can be reduced to an acceptable level only by enforcement of rigid specifications for the equipment and following safe practices. These conditions may be difficult to attain in some countries.

Manufacturing Considerations

The choice of nitrogen fertilizer to be produced within a country may be influenced by linkages with other industries or by the resources of the country. The manufacture of urea is not economical except when associated with an ammonia plant. For countries where importation of ammonia would be less expensive than indigenous production, a good choice could be use of imported ammonia for production of ammonium nitrate, ammonium phosphate, ammonium sulfate, or some combination of the three. Another possibility for using imported ammonia is production of nitrophosphate fertilizers, which would supply both nitrogen and phosphate fertilizers. In most cases it is better to plan the fertilizer industry as a whole rather than the nitrogen industry separately.

Ammonium sulfate is often available as a byproduct from other industries, such as coking operations, metallurgical extraction processes, and caprolactam production; low-cost byproduct sulfuric acid for use in making ammonium sulfate may be available from smelting industries. Also ammonium sulfate may be a convenient byproduct from pollution abatement facilities. Likewise, ammonium chloride may be produced economically as a coproduct of soda ash production or from byproduct hydrochloric acid from other industries.

Conversely, fertilizer production facilities often can supply raw materials for other industries; ammonia and urea have many industrial uses, and ammonium nitrate is widely used as a blasting agent in mining industries or in road building. Therefore, integrated planning of the industrial sector may influence the choice of nitrogen fertilizer products.

Economic Considerations

The usual aim in choosing a nitrogen fertilizer is to select a product or products that will result in the lowest average delivered cost per kilogram of N at the farm level, assuming that all sources of N are equally efficient. A later section of this manual will show illustrative comparative estimates of manufacturing costs. However, a comparison can also be made on the basis of actual delivered costs in a country where various nitrogen products are manufactured and marketed in competition with each other under free market conditions. Such a comparison is available for the United States. Data for the 10-year period 1968-77 are shown in table 1. Anhydrous ammonia has been the least expensive nitrogen source during this period; it costs only about one-half as much as urea or ammonium nitrate. Urea, ammonium nitrate, and nitrogen solutions have sold at about the same price during this period with a tendency toward relatively lower urea prices during recent years, perhaps because of increased supply of this product. Ammonium sulfate prices have ranged from about 25% to 40% higher than those of urea or ammonium nitrate.

TABLE 1. AVERAGE PRICES PAID BY U.S. FARMERS FOR NITROGEN FERTILIZERS, 1968-77 ($/kg OF N)

	Ammonium Sulfate	Ammonium Nitrate	Urea	Anhydrous Ammonia	N Solution (30% N)
1968	0.29	0.22	0.22	0.12	0.23
1969	0.28	0.20	0.20	0.10	0.20
1970	0.28	0.20	0.20	0.10	0.20
1971	0.28	0.21	0.20	0.11	0.21
1972	0.28	0.21	0.20	0.11	0.20
1973	0.30	0.23	0.22	0.12	0.21
1974	0.59	0.46	0.44	0.26	0.41
1975	0.81	0.61	0.59	0.36	0.56
1976	0.52	0.45	0.40	0.25	0.41
1977	0.55	0.47	0.41	0.24	0.44

Source: 1978 Fertilizer Situation, U.S. Department of Agriculture, Economic Research Service, December 1977 (original data converted to metric units).

The comparison is not necessarily transferable to other countries. The low delivered cost of anhydrous ammonia depends on a well-organized, large-scale (and expensive) distribution system that would be difficult to match in most countries. Distribution of nitrogen solution also has specialized requirements. However, the relative cost of the solid materials should be at least qualitatively relevant although their comparative cost would be affected by transportation costs. The price data for solid materials in table 1 are a composite of bulk and bagged products. In 1976, about 73% of the solid fertilizers sold in the United States was in bulk form. Delivery in bags would increase the relative cost of the lower analysis materials per kilogram of N.

Perhaps the lowest cost solid nitrogen fertilizer is diammonium phosphate. An illustration in chapter XVII shows that DAP is the lowest cost phosphate fertilizer when the nitrogen content is evaluated at the price of the equivalent amount of urea. The same data can be interpreted to show that when the value of the P_2O_5 content is based on the cost of TSP, the net cost of the nitrogen would be $0.26/kg versus $0.34/kg for urea. A similar comparison may be made on the basis of current world market prices as shown in "Fertilizer International" (July 1978). With TSP at $90/ton and DAP at $125/ton, the net cost of the N in DAP would be about $0.19/kg of N versus $0.26 for urea. This differential would be increased by transportation, storage, and bagging costs because DAP is more concentrated than TSP or urea.

Unfortunately, most crops require a higher ratio of $N:P_2O_5$ than that of DAP, thus additional nitrogen must be supplied from another source. This can be done by adding ammonium nitrate, ammonium sulfate, or urea to make APN, APS, or UAP compounds or by using supplemental straight nitrogen at the farm level.

Evaluation of the economic advantage of improved agronomic efficiency would be relatively simple if a clear-cut agronomic advantage could be shown. For instance, if the response ratio of wheat to fertilizer A averages 10:1 and the response ratio to fertilizer B is 11:1, the additional 10% efficiency of fertilizer B will result in 1 additional ton of wheat per ton of N wherever fertilizer B is used rather than fertilizer A. If a ton of wheat is valued at $120 and a proposed plant will produce 300,000 tons of N annually, then an additional annual farm income of $36 million will result from choice of fertilizer B rather than A. This example illustrates the importance of choosing the most effective type of fertilizer. Unfortunately, it is seldom possible to demonstrate a clear-cut general superiority of one nitrogen fertilizer over another. Differences of 10% in response ratios are often not statistically significant; results are often variable from year to year, from one crop to another, and from one soil to another. In particular, relative efficiency is often influenced by method, timing, or placement, leading to the conclusion that superiority or inferiority of nitrogen fertilizers is seldom an intrinsic property of the material itself but more closely related to how it is used. Therefore, planners are confronted with the alternatives of selecting a product that will do best with prevalent farmers' use practices or teaching millions of farmers how to use a given product more effectively.

Estimated Cost and Gate Sale Price of Urea, Ammonium Nitrate, and Ammonium Sulfate

The following comparative cost estimates are intended to be illustrative and to provide a comparison between products rather than provide absolute values. They are based in part on published figures and in part on information received from engineering firms and contractors. In each case plant investment costs are shown for a range of capacities. Production costs are calculated for a "base case" which is for current (1978) conditions in an industrial location of a developed country (United States or Europe). The creditability of these estimates can be judged by comparison with current world market prices. Further estimates will then indicate the effect of higher capital charges that are likely to be incurred in developing countries, the effect of scale of operation, the effect of percentage capacity utilization, and the effect of raw material costs. General assumptions used in all cost estimates in this manual are listed and discussed in chapters VI and XXV and will not be repeated here.

Estimated Cost of Urea Production

The approximate capital requirements for urea plants in a developed country as related to capacity in the range of 500-1,700 tpd are shown in figure 1. Battery-limits costs range from about $13 million at 500 tpd to $27 million at 1,700 tpd. Total plant costs are taken as 1.5 times battery-limits cost.

Table 2 shows the estimated production cost of prilled urea for a base case in a developed country for a plant of 1,000-tpd capacity operating at 90% of rated capacity. The cost of storage facilities is based on 45 days' production for bulk storage at $50/ton of dehumidified storage capacity plus 10 days' storage of bagged product at $75/ton. Carbon dioxide is assumed to be available at no charge from an adjacent ammonia plant. Assuming that ammonia is available at $120/ton, the estimated bulk urea production cost is about $111/ton. Allowing 10% return on investment, the bulk gate sale price is about $123/ton. This is in line with current world market prices. Assuming a cost of $12/ton for bags and bagging, the gate sale price of bagged urea is $135/ton. The cost of bags depends on the type of bag. The allowance of $12/ton is considered adequate for 50-kg bags consisting of a woven

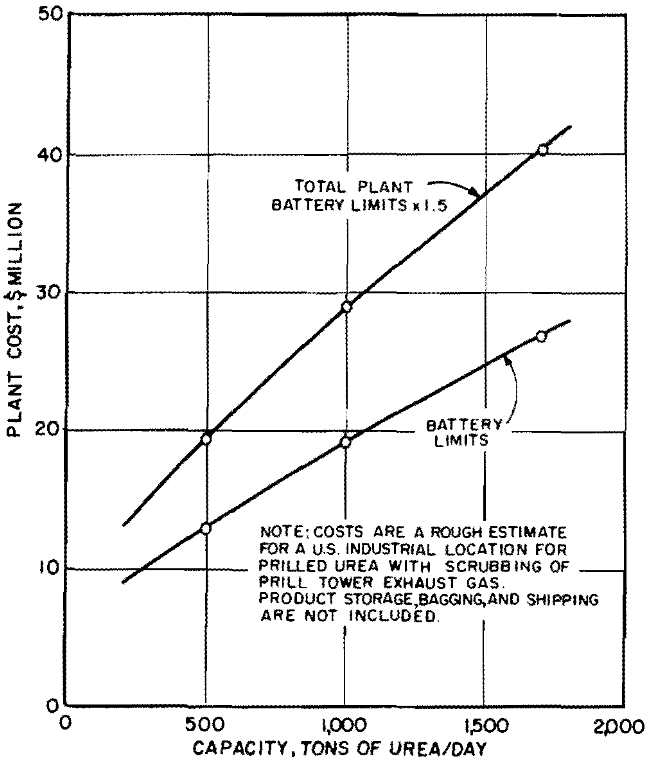

Figure 1. Estimated Investment Cost of Urea Plants as Related to Capacity.

polypropylene outer bag with a polyethylene film inner bag.

The effect of scale of production is indicated in table 3 and figure 2. In calculating the production cost at capacities other than the base cost, the following assumptions were made:

1. The cost of raw materials, utilities, and supplies would remain constant per ton of product.
2. Labor-related costs (labor, overhead, and chemical control) per year would increase as the 0.6 power of capacity.
3. Capital-related costs per year (depreciation, maintenance, interest, taxes, and insurance) would be directly proportional to the capital investment.

The results of the calculation indicate that increasing the scale of operation from 500 to 1,700 tpd would lower the bulk production cost from $118 to $105/ton and the gate sale price from $132 to $114/ton. Thus, the economies of scale are moderate. However, as pointed out previously, the economies of scale of ammonia production are quite important. Therefore, in an ammonia-urea complex where urea is the sole end product, the combined economies of scale of the two plants would be very important. On the other hand, a decision to make two or more end products from the output of a single ammonia plant might not increase the cost of the end products by a substantial percentage and might have compensating advantages.

The effect of ammonia cost on the production cost of urea is shown in figure 3 for a plant capacity of 1,000 tpd. The figure was estimated on the basis that the urea cost would vary from that in the base case in proportion to the difference in ammonia cost times 0.575 times 1.05. The 0.575 factor represents the amount of ammonia required to produce 1 ton of urea. The 1.05 factor increases the administrative and miscellaneous expense as the cost of ammonia and, hence, urea increases and thereby allows for increased interest on working capital. Increasing the ammonia cost from $100 to $200/ton would increase the production cost of urea from $100 to $160/ton. The gate sale price would increase from $111 to $171/ton.

Urea plants are invariably located adjacent to an ammonia plant and, hence, the effect of location on

TABLE 2. ESTIMATED PRODUCTION COST OF UREA (BASE CASE) PRILLED (46% N)

Capacity--1,000 tpd; Capacity Utilization--90%
Annual Production--300,000 tpy
Plant Investment--$31 million
Storage Facilities--$3 million

Item	Quantity	Unit Cost	$/ton of Urea
Raw Materials			
Ammonia	0.575 ton	$120	69.00
CO_2	0.760 ton	no charge	
Formaldehyde	3.5 kg	0.38	1.33
Utilities			
Water	70 m^3	0.01	0.70
Steam	1.2 tons	4.00	4.80
Electricity	125 kWh	0.02	2.50
Labor	0.40 man-hour	7.00	2.80
Overhead	100% of labor		2.80
Chemical control	20% of labor		0.56
Maintenance	5% of investment		5.67
Taxes and insurance	2% of investment		2.67
Depreciation and interest	10.67% of investment		12.09
Miscellaneous supplies			1.00
Subtotal			105.92
Adm. and misc. expense	5% of subtotal		5.30
Production cost (bulk)			111.22
Bags and bagging			12.00
Production cost (bagged)			123.22
Return on investment, 10%			11.33
Gate sale price (bulk)			122.55
Gate sale price (bagged)			134.55

TABLE 3. EFFECT OF CAPACITY ON PRODUCTION COST AND GATE SALE PRICE OF BULK UREA (90% CAPACITY UTILIZATION)

	500-tpd Plant	1,000-tpd Plant[a]	1,700-tpd Plant
Plant cost, $ million	19.5	31.0	40.2
Storage facilities, $ million	1.5	3.0	5.1
Total investment, % million	21.0	34.0	45.3
Cost, $/ton of urea			
Raw materials, utilities, and supplies	79.33	79.33	79.33
Labor-related costs	8.12	6.16	4.98
Capital-related costs	24.74	20.43	15.70
Subtotal	112.19	105.92	100.01
Adm. and misc. expense 5%	5.61	5.30	5.00
Production cost	117.80	111.22	105.01
ROI, 10%	14.00	11.33	8.88
Gate sale price, bulk	131.80	122.55	113.89

a. Base case.

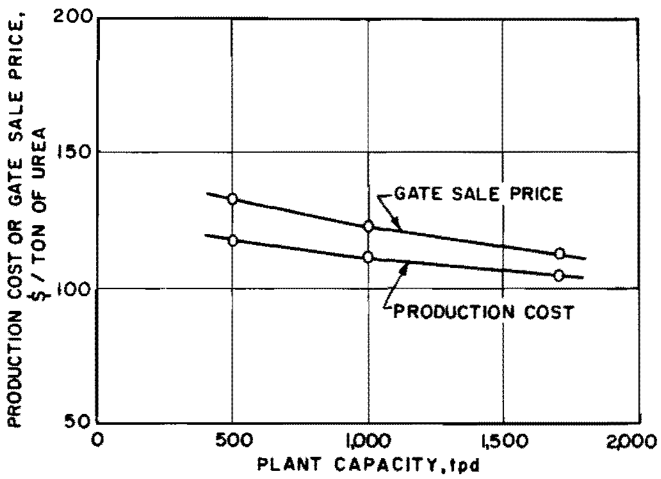

Figure 2. Effect of Plant Capacity on Production Cost and Gate Sale Price of Urea.
(Developed Country, 90% Capacity Utilization, Ammonia Cost – $120/ton).

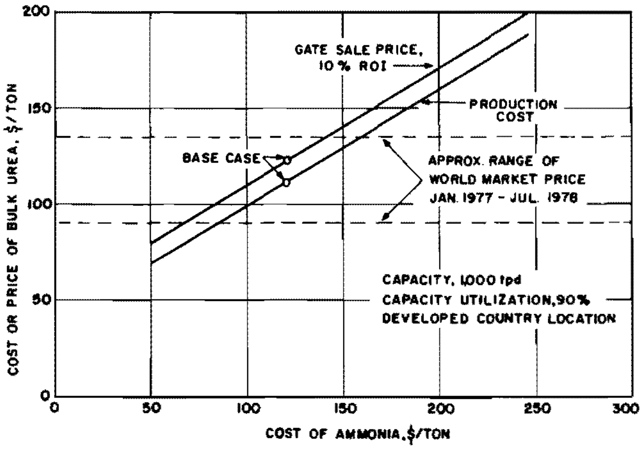

Figure 3. Effect of Ammonia Cost on Production Cost and Gate Sale Price of Urea.

urea costs is primarily related to the effect of location on ammonia cost. It is technically possible to produce urea from imported ammonia by using carbon dioxide from some other source. For instance, carbon dioxide could be extracted from stack gas from a lime kiln, a cement plant, or a fuel-fired electric generating plant by using CO_2 absorbent solutions such as MEA (see chapter VI, "CO_2 removal").

Since 0.76 ton of CO_2 is required per ton of urea, if CO_2 could be obtained at a cost of $20/ton, the cost per ton of urea would be $15.20. There may be cases in which this alternative should be considered. The location also affects the urea cost by affecting the investment cost. A location in a developing country or in a remote part of a developed country (such as Alaska or Siberia) results in higher investment costs because of higher construction cost, need for more auxiliary and supporting facilities, etc. In the base case (table 2), capital-related costs totaled $20.43/ton of urea, and return on investment was $11.33. The effect of increasing the capital costs by 25% and 50% is shown in the following tabulation.

Effect of Increased Capital Cost on Production Cost and Gate Sale Price of Urea (Bulk)

Increase in Capital Investment, %	Production Cost, $/ton of Urea	Gate Sale Price (10% ROI), $/ton of Urea
0 (base case)	111.22	123.22
25	116.33	130.49
50	121.44	138.44

The effect of operating at a lower percentage of capacity than 90% (assumed in the base case) is to increase the cost per ton of product since capital-related and labor-related costs remain the same on an annual basis and, hence, they are greater per ton of product. In the base case the sum of the capital- and labor-related costs amounted to $26.59 per ton of urea. The following tabulation illustrates the effect of capacity utilization on costs.

Effect of Capacity Utilization on Production Cost and Gate Sale Price of Urea (1,000-tpd, 330,000-tpy Capacity)

Capacity Utilization, %	Production Cost, $/ton	Gate Sale Price (10% ROI), $/ton
100	108.56	118.76
90 (base case)	111.22	122.55
80	114.54	127.29
70	118.82	133.39
60	124.51	141.51

Thus, the increased cost caused by below-capacity operation is rather moderate. However, in an ammonia-urea complex, below-capacity operation will increase the ammonia cost sharply and hence the urea cost. On the other hand, if the complex contains an alternative use for ammonia or if the ammonia can be sold, failure to operate the urea plant at a high percentage of rated capacity would be far less serious.

Estimated Cost of Ammonium Nitrate Production

Ammonium nitrate production facilities are almost invariably operated in conjunction with a nitric acid plant but not necessarily in conjunction with an ammonia plant. The estimated capital cost of battery-limits nitric acid plants as related to capacity and type is shown in figure 4. For the base case, a capacity of 1,070 tpd of HNO_3 is assumed which is sufficient to produce 1,353 tpd of ammonium nitrate (34% N). This is equivalent to 460 tpd of N which is the same as for the 1,000-tpd urea plant that was used as the base case in the preceding section. The base case assumes the use of a high-pressure process with a battery-limits capital cost of $15.3 million and a total cost of $23 million which should be sufficient to allow for 10 days' intermediate storage of nitric acid as well as other auxiliary and supporting facilities. It probably would not be sufficient to allow for a large ammonia terminal and storage facility in case ammonia was imported from overseas sources.

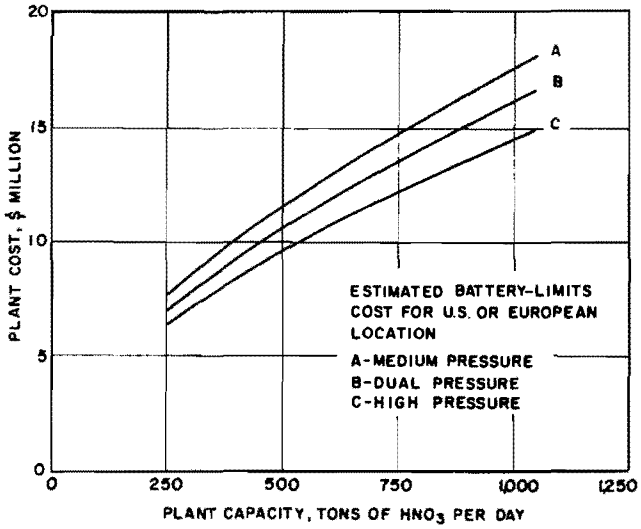

Figure 4. Effect of Type of Process and Plant Size on Capital Cost of Nitric Acid Plants.

The estimated production cost of nitric acid for the base case is shown in table 4. Assuming that ammonia is available at $120/ton, the estimated production cost is $53.40/ton. The effect of capacity on production cost is shown in table 5. As the capacity increases from 250 to 1,070 tpd, the production cost decreases from about $65 to $53/ton. Figure 5 shows the effect of ammonia cost and nitric acid capacity on the production cost of nitric acid. Further discussion of the economics of nitric acid production will be combined with that of ammonium nitrate.

The estimated production cost and gate sale price of ammonium nitrate (34% N) for the base case are shown in table 6. The assumptions are the same as for the urea base case which permits the following direct comparison.

	Urea		Ammonium Nitrate	
	$/ton	$/kg of N	$/ton	$/kg of N
Production cost, bulk	111.22	0.24	85.29	0.25
Production cost, bagged	123.22	0.27	97.29	0.29
Gate sale price, bulk	122.55	0.27	96.25	0.28
Gate sale price, bagged	134.55	0.29	108.25	0.32

The comparison indicates that urea is $0.01 to $0.03 less expensive per kilogram of N than ammonium nitrate. This is well within the limits of accuracy of the estimates. However, distribution costs would be higher per kilogram of N for ammonium nitrate because of its lower analysis. Ammonium nitrate has a higher density than urea, thus the nitrogen content per unit volume is about the same. Therefore, costs that are proportional to volume, such as storage costs, would be about the same while costs that are

TABLE 4. ESTIMATED PRODUCTION COST OF NITRIC ACID

Capacity--1,070 tpd (100% HNO_3 basis); Capacity Utilization--90%
Annual Production--321,000 tpy
Plant Investment--$23 million (includes 7 days' storage)
Process--High Pressure, Extended Absorption

Item	Quantity	Unit Cost	$/ton of 100% HNO_3
Raw materials			
Ammonia	0.288 ton	$120	34.56
Catalyst (Pt)	150 mg	$9/g	1.35
Utilities			
Steam (credit)	-0.4 ton	4.00	-1.60
Cooling water	87 m^3	0.01	0.87
Boiler feedwater[a]	8.5 m^3	0.13	1.10
Electricity[b]	9.5 kWh	0.02	0.19
Labor	0.08 man-hour	7.00	0.56
Overhead	100% of labor		0.56
Chemical control	20% of labor		0.11
Maintenance	5% of investment		3.58
Taxes and insurance	2% of investment		1.43
Depreciation and interest	10.67% of investment		7.65
Miscellaneous supplies			0.50
Subtotal			50.86
Adm. and misc. expense	5% of subtotal		2.54
Production cost			53.40

a. Includes water to absorption tower.
b. Does not include electricity for mechanical refrigeration of absorption tower coolant (not always required).

TABLE 5. EFFECT OF CAPACITY ON PRODUCTION COST OF NITRIC ACID

	250-tpd Plant	500-tpd Plant	1,070-tpd Plant[a]
Cost, \$/ton of HNO_3			
Raw materials, utilities, and supplies	36.97	36.97	36.97
Labor-related costs	2.22	1.67	1.23
Capital-related costs	22.97	17.22	12.66
Subtotal	62.16	55.86	50.86
Adm. and misc. expense 5%	3.11	2.79	2.54
Production cost	65.27	58.65	53.40

a. Base case.

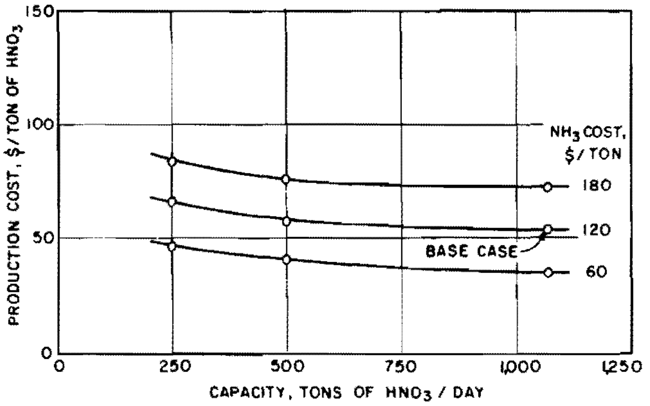

Figure 5. Effect of Plant Capacity and Ammonia Cost on Production Costs of Nitric Acid.

proportional to weight would be 35% greater for ammonium nitrate.

World market prices of bulk ammonium nitrate are not available for comparison, but recent bids on bagged ammonium nitrate delivered in Alexandria, Egypt, ranged from \$130 to \$143/ton as compared with bagged urea at \$160-\$173/ton ("Fertilizer International," No. 110, August 1978). The lowest bids corresponded to \$0.38 and \$0.35/kg of N for ammonium nitrate and urea, respectively. Since freight costs are included in the bid prices, they are not directly comparable with estimated gate sale prices.

According to the present estimates the capital investment cost for the base case is lower for urea than for ammonium nitrate (including nitric acid)--\$34 million for urea versus \$44 million for ammonium nitrate. However, one advantage of ammonium nitrate is that it does not require a coexisting ammonia plant. As an example of this advantage, if ammonia could be

TABLE 6. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIUM NITRATE (PRILLED 34% N)

Capacity--1,353 tpd; Capacity Utilization--90%
Annual Production--405,900 tons
Plant Investment--\$17.5 million
Storage--\$4.0 million

Item	Quantity	Unit Cost, \$	\$/ton of Product
Raw materials			
Ammonia	0.210 ton	120	25.20
Nitric acid	0.773 ton	53.40	41.27
Stabilizer	4 kg	0.25	1.00
Utilities			
Steam	0.2 ton	4.00	0.80
Water	8 m^3	0.01	0.08
Electricity	20 kWh	0.02	0.40
Labor	0.17 man-hour	7.00	1.19
Overhead	100% of labor		1.19
Chemical control	20% of labor		0.24
Maintenance	5% of investment		2.65
Taxes and insurance	2% of investment		1.06
Depreciation and interest	10.67% of investment		5.65
Miscellaneous supplies			0.50
Subtotal			81.23
Adm. and misc. expense	5% of subtotal		4.06
Production cost (bulk)			85.29
Bags and bagging			12.00
Production cost (bagged)			97.29
Return on investment, 10% of \$44.5 million			10.96
Gate sale price (bulk)			96.25
Gate sale price (bagged)			108.25

imported at a cost of $120/ton and if indigenous production of ammonia would cost $200/ton, then production of ammonium nitrate from imported ammonia would have a clear advantage over production of urea from domestically produced ammonia. This possibility may be of interest to countries that have no economical feedstock for producing ammonia.

Another advantage of ammonium nitrate over urea is that the ammonium nitrate unit can operate independently of the nitric acid unit and both are independent of the ammonia plant since storage of the intermediate products, ammonia and nitric acid, is feasible. A urea plant, on the other hand, cannot operate when the associated ammonia plant is not in operation since it is not economically feasible to store the CO_2 required for urea production. This degree of independence of plant operation should result in higher capacity utilization for ammonium nitrate than for urea. For example, if two independently operated units each have a reliability of 90%, the plant as a whole will have a reliability of 90% if adequate intermediate storage is provided, but two dependent units each with a reliability of 90% will have a reliability as a whole of only 81%.

The estimated cost of producing ammonium nitrate on scales of 323 and 647 tpd, corresponding to 250 and 500 tpd of HNO_3, is shown in table 7. The estimated bulk gate sale price decreases from $124 to $96/ton of bulk product as the capacity increases from 323 to 1,353 tpd. These results are shown in figure 6, which also shows the effect of ammonia cost on the gate-sale price of ammonium nitrate.

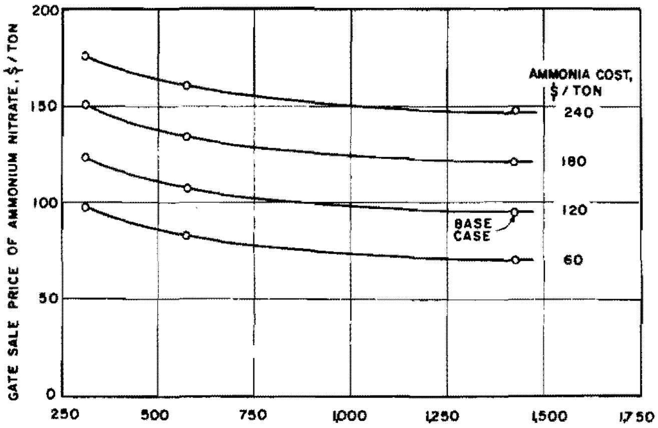

Figure 6. Effect of Plant Capacity and Ammonia Cost on Gate Sale Price of Bulk Ammonium Nitrate (34% N) for Nitric Acid-Ammonium Nitrate Complexes.

Estimated Cost of Ammonium Sulfate Production

Straight ammonium sulfate seldom is produced from sulfuric acid and ammonia unless one of the two raw materials is a byproduct, thus it may not be relevant to most situations to estimate a production cost on this basis. Ammonium sulfate often is produced as an ingredient of granular compound fertilizers by including ammonia and sulfuric acid in the formulation (see chapter XIX). In this case the cost of the two materials is part of the formulation cost, with possibly some credit for the heat of reaction, which assists in drying the product or in some cases eliminates the need for drying.

The following estimates of the cost of producing straight, crystalline ammonium sulfate may be helpful even though the raw material cost is not likely to fit a specific circumstance since the estimate can be readily adjusted to any raw material cost.

Figure 7 shows the estimated battery-limits cost for ammonium sulfate plants in the range of 100-500 tpd. The lower curve is for a crystallization plant using sulfuric acid and ammonia. The upper curve is for a crystallization plant using a byproduct ammonium sulfate solution of 40% concentration. The latter plant requires more equipment to evaporate water and, hence, is somewhat more expensive. Production cost estimates for the two types of plants

TABLE 7. ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIUM NITRATE AS AFFECTED BY SCALE OF OPERATION

Capacities--323, 647, and 1,353 tpd; Capacity Utilization--90%
Annual Production--96,900, 194,100, and 405,900 tpy

Item	Quantity	Unit Cost, $	Cost, $/ton of Ammonium Nitrate		
			323 tpd	647 tpd	1,353 tpd[a]
Ammonia	0.210 ton	120/ton	25.20	25.20	25.20
Nitric acid	0.773 ton	See table 5	50.45	45.34	41.27
Stabilizer	4 kg	0.25/kg	1.00	1.00	1.00
Utilities		See table 6	1.28	1.28	1.28
Labor-related costs[b]			4.66	3.48	2.62
Capital-related costs[c]			16.65	12.44	9.36
Miscellaneous supplies			0.50	0.50	0.50
Subtotal			99.74	89.24	81.23
Adm. and misc. expense, 5% of subtotal			4.99	4.46	4.06
Production cost (bulk)			104.73	93.70	85.29
Bags and bagging			12.00	12.00	12.00
Production cost (bagged)			116.73	105.70	97.29
ROI, 10%[d]			19.50	14.54	10.96
Gate sale price (bulk)			124.23	108.24	96.25
Gate sale price (bagged)			136.23	120.24	108.25

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a. Base case.
b. Annual labor cost assumed to vary as the 0.6 power of capacity.
c. Based on 17.67% of $9.13, $13.67, and $21.5 million.
d. Based on total capital costs for nitric acid and ammonium nitrate plants of $18.9, $28.3, and $44.5 million.

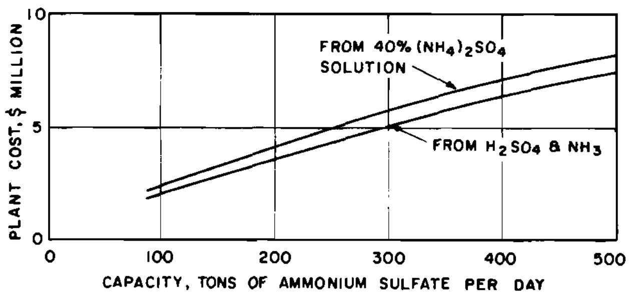

Figure 7. Cost of Battery-Limits Plants for Producing Crystalline Ammonium Sulfate.

are shown in tables 8 and 9. The estimated cost of producing bulk ammonium sulfate from ammonia priced at $120/ton and from sulfuric acid priced at $35/ton is about $82/ton, and the gate sale price is $90.

The economics of utilizing a byproduct solution depends on what value is placed on the solution. In the estimate in table 9, it is assumed that the solution is valued at the cost of an equivalent amount of ammonia at $120/ton and the estimated production cost of the bulk product is about $63/ton. Adding a 10% ROI gives a gate sale price of about $72/ton, which is equivalent to about $0.34/kg of N. The current world market price (June 1978) is in the range of $0.31 to $0.36/kg of N. Because of its low analysis (21% N), the delivered cost of ammonium sulfate is likely to be much higher per kilogram of N.

When ammonia and sulfuric acid are used in a granulation plant as a part of the formulation for compound fertilizers, the purpose may be to assist granulation, to avoid drying expense, and to supply sulfur for agronomic reasons as well as to supply nitrogen. If the ammonia is charged at $120/ton and the sulfuric acid at $35/ton, the cost of these two materials is equivalent to $57/ton of ammonium sulfate or $0.27/kg of N.

TABLE 8. ESTIMATED PRODUCTION COST OF AMMONIUM SULFATE (BASE CASE), CRYSTALLINE, 21% N

Capacity--400 tpd; Capacity Utilization--90%
Annual Production--120,000 tpy
Plant Investment--$9.4 million
Storage Facilities--$1.0 million

Item	Quantity	Unit Cost, $	$/ton of Product
Ammonia	0.258 ton	120	30.96
Sulfuric acid	0.744 ton	35	26.04
Electricity	36 kWh	0.02	0.72
Water	50 m^3	0.01	0.50
Fuel		0.25	
Labor	0.2 man-hour	7.00	1.40
Overhead	100% of labor		1.40
Chemical control	20% of labor		0.28
Maintenance	5% of investment		4.33
Taxes and insurance	2% of investment		1.73
Depreciation and interest	10.67% of investment		9.25
Miscellaneous supplies			1.00
Subtotal			77.86
Adm. and misc. expense	5% of subtotal		3.89
Production cost, bulk			81.75
ROI, 10%			8.67
Gate sale price, bulk			90.42

TABLE 9. ESTIMATED PRODUCTION COST OF AMMONIUM SULFATE PRODUCTION FROM AMMONIUM SULFATE SOLUTION FROM CAPROLACTAM PRODUCTION OR POLLUTION ABATEMENT SCRUBBING OPERATIONS

Assumption: Ammonium sulfate solution at 40% concentration is available at a cost equal to the cost of the ammonia content. Solution preparation is charged to pollution abatement or caprolactam production.

Capacity--400 tpd; Capacity Utilization--90%
Annual Production--120,000 tpy
Plant Investment--$10.5 million
Storage Facilities--$1.0 million

Item	Quantity	Unit Cost, $	$/ton of Product
Solution, 40% AS	2.5 tons	12.38	30.96
Electricity	36 kWh	0.2	0.72
Water	50 m^3	0.1	0.50
Fuel			0.25
Steam	1.6 tons	4.00	6.40
Labor	0.2 man-hour	7.00	1.40
Overhead	100% of labor		1.40
Chemical control	20% of labor		0.28
Maintenance	5% of investment		4.79
Taxes and insurance	2% of investment		1.92
Depreciation and interest	10.67% of investment		10.22
Miscellaneous supplies			1.00
Subtotal			59.84
Adm. and misc. expense	5% of subtotal		2.99
Production cost, bulk			62.83
ROI, 10%			9.58
Gate sale price			72.41

PART THREE

PHOSPHATE FERTILIZERS

XII Phosphate Rock and Sulfuric Acid

Introduction

Phosphate rock and sulfuric acid are the two major raw materials for manufacture of phosphate fertilizers. Nearly all commercial phosphate fertilizers are derived from phosphate rock; the major exception is basic slag which derives its phosphorus indirectly from phosphate minerals that are present in iron ore or deliberately added to the iron blast furnace charge. Minor exceptions are materials of organic origin such as bones and guano. While recycling of organic matter is still an important means for conserving the soil phosphorus, the recycling is not primarily done by inclusion in commercial fertilizers.

Sulfuric acid is a necessary raw material in the most popular phosphate production processes. The major exceptions are basic slag and some nitrophosphate processes. Minor exceptions will be noted in chapter XVI, "Other Phosphate Fertilizers." Sulfuric acid is also a raw material for producing some nonphosphate fertilizers, mainly ammonium and potassium sulfates and sulfates of micronutrient elements.

World reserves and current production of phosphate rock and of raw materials for sulfuric acid production were discussed in chapter V. Data for production of these materials by country are also given in chapter V. Quality factors affecting the suitability of phosphate rock for use in chemical processing are discussed under each process (chapters XIII, XIV, and XV). The present chapter will describe briefly the world phosphate rock industry, the mineralogy of phosphate rock, and its use for direct application. The chapter will also discuss production of sulfuric acid as related to fertilizer manufacture.

Phosphate Rock

The commercial production and use of phosphate rock began in the 19th century. The first recorded statistical data were for 1847 when 500 tons was mined in Suffolk, England, although it is likely that there was some commercial production earlier. World production increased rapidly to 5,000 tons in 1850, 10,000 tons in 1853, over 100,000 tons in 1865, over 1,000,000 tons in 1885, over 10,000,000 tons in 1928, and over 110,000,000 tons in 1974 (1).[1] Production in 1977 was about 116 million tons. Based on projected fertilizer consumption with allowances for other uses, it is likely that annual phosphate rock production will be of the order of magnitude of 300 million tons by the year 2000 (2).

Although phosphate rock has many uses, probably as much as 85% of the world's production is used for fertilizer manufacture, including direct application to the soil. The grade of commercial phosphate rock may be expressed as its P_2O_5 content; the usual range is 28%-38% P_2O_5. In recent years the world average has ranged from 32.7% to 32.5% P_2O_5 for commercial phosphate rock sold or used by the producer.

The grade is also commonly expressed in terms of tricalcium phosphate, $Ca_3(PO_4)_2$, known in the trade as "bone phosphate of lime" or BPL. This term originated when tricalcium phosphate was thought to be the main constituent of bone and phosphate rock. It is now known that the phosphatic component of both bone and most phosphate rock is apatitic compounds. Conversion factors are:

P_2O_5 → BPL x 0.4576
BPL → P_2O_5 x 2.1852

"Commercial" phosphate rock usually refers to any rock containing a high percentage of phosphate minerals that can be used for commercial purposes such as fertilizer manufacture, direct application to the soil, or manufacture of industrial phosphorus compounds. The term usually applies to a product obtained by mining and beneficiation although in some cases the rock as mined can be used without beneficiation.

"Deliveries" of phosphate rock (domestic and export) amounted to about 103 million tons in 1976 of which about 40% was exported from the country of origin (3). The following tabulation shows a breakdown of the rock exported by grade:

Grade, % BPL	% of Total Exports
65 and under	3.7
66-68	12.0
69-72	35.1
73-77	22.2
78 and over	27.0
	100.0

The price varies with grade, location, and other factors. Listed prices in January 1977 ranged from $44/ton for 80%-82% BPL BuCraa rock to $35.25 for 70%-72% BPL Youssoufia (Morocco) rock. For Florida rock the range was from $31 for 75% BPL rock to $25 for 68% BPL rock. Most phosphate rock is sold by contract at prices below listed prices. (Listing of prices was discontinued in 1977.) According to U.S. Bureau of Mines' estimates, the average price of 70% BPL rock, f.o.b. Tampa, or Jacksonville, Florida, was $25/ton in July 1978, including $1.27 severance tax.

Many countries exported phosphate rock, but 57.5% of all rock exported came from Morocco and the United States. The percentage of total exports by country follows (3):

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[1] All tons in this manual are metric tons unless otherwise specified.

Country of Origin	% of Total Exports (1976)
Morocco	35.5
United States	22.0
U.S.S.R.	11.8
Togo	4.8
Tunisia	4.4
Jordan	4.0
Senegal	3.7
Israel	1.5
Algeria	1.3
Egypt	0.4
All others	10.6
	100.0

Phosphate rocks may be classified according to their origin as sedimentary, metamorphic, or igneous. About 85% of the phosphate rock used commercially is of sedimentary origin; the remainder is mainly igneous.

Apatitic Phosphates

Most commercial phosphate rocks contain fluorapatite as the primary and usually the only source of phosphorus. The formula for pure fluorapatite is $Ca_{10}F_2(PO_4)_6$. However, pure fluorapatite is relatively rare. The apatite structure is amenable to many substitutions of which the most common are Mg, Sr, and Na for Ca; OH and Cl for F; As and V for P; and CO_3 + F for PO_4.

A large percentage of the sedimentary rocks fall into the group called francolite or carbonate apatites. Lehr and McClellan give the following general empirical formula for the francolite group (4):

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

where: "a" represents the molar substitution of Na for Ca, "b" represents the molar substitution of Mg for Ca, and "x" is the molar substitution of CO_3 and F for PO_4.

The authors have demonstrated that as x, the extent of carbonate substitution, increases the reactivity increases. The value of x may range from nearly zero up to about 1.2 in commercial phosphate rock. The P_2O_5 content of pure fluorapatite is 42.2%; the P_2O_5 content of the carbonate apatites decreases with increasing carbonate substitution to a minimum of about 34% in the most highly substituted apatites.

A significant number of phosphate rocks show substantial substitution of OH (hydroxyl) for F. These include phosphates from Nauru, Christmas Island, and Curacao and Brazilian igneous apatites. Some of these phosphates also have substantial carbonate substitution. An extreme example is Curacao phosphate. It contains only about 20% of the stoichiometric fluorine for fluorapatite. Presumably hydroxyl substitution accounts for most of the remaining 80%. It also has a substantial proportion of carbonate substitution for phosphate. The island phosphates are presumably formed by reaction of coral limestone with phosphate leached from guano deposits; they are included with sedimentary ores for convenience.

Most Brazilian apatites of igneous origin are fluorine deficient. Typical samples contain one-third to two-thirds of the stoichiometric quantity; they may be classified as hydroxy-fluorapatites.

Aluminous Phosphates

Deposits in which the principal phosphate minerals are aluminous are fairly widespread. The deposits in Thies in Senegal and C-grade ore in Christmas Island are presently being mined and used. The extent of utilization of the C-grade ore is small at present, but it occurs in a stratum overlying the apatitic ore so that most of it is mined and stockpiled awaiting an economic utilization process while the apatitic ore is being marketed. A similar situation exists in Florida where a "leached zone" containing aluminum phosphates overlays the pebble phosphate matrix. Since the "leached zone" is low grade and variable in composition, no attempt has been made to stockpile it.

The principal aluminum phosphate minerals are crandallite, millisite, and wavellite. The chemical composition of these minerals is somewhat variable, but the following formulas are typical:

Wavellite	$4AlPO_4 \cdot 2Al(OH)_3 \cdot 9H_2O$
Crandallite	$CaO \cdot 2Al_2O_3 \cdot P_2O_5 \cdot 5H_2O$
Millisite	$2CaO \cdot Na_2O \cdot 6Al_2O_3 \cdot 4P_2O_5 \cdot 17H_2O$

As in apatites, various substitutions are possible: Fe for Al is one common substitution.

The aluminous phosphate ores contribute only a very small percentage to present world use. However, they can be used for fertilizer manufacture by a nitrophosphate technique or, in some cases, for direct application after calcining. Aluminum phosphate minerals also occur as accessory minerals in some apatitic deposits.

Accessory Minerals

Phosphate deposits contain a wide variety of accessory minerals; the value of the deposit often is related to the amount and character of the accessory minerals and the ease or difficulty of separating them from the phosphate. Perhaps the most common are silica, which may be present as quartz or cristobalite, or in hydrous forms such as chert or opal; clays and other silicate minerals such as feldspar, mica, etc.; and carbonates, mainly calcite and dolomite.

Physical Properties

The physical properties of the deposit are often a controlling factor in determining whether the deposit can be mined and beneficiated economically. Such factors include whether the ore is consolidated (cemented together) or unconsolidated, the size of the phosphate particles and accessory minerals, and their hardness. If the ore is consolidated, the type of cementing agent and degree of consolidation affect beneficiation potentialities. Extent of weathering and crystal size of component materials are often important. A detailed treatment of this subject is far beyond the scope of this manual.

Factors that Influence Economic Potential

The economic potential of a deposit will depend on many factors, including market price or value, extent and grade of the deposit, location, estimated cost of mining and beneficiation, quality and grade of the beneficiated product, and environmental factors. In recent years increasing importance has been given to environmental problems, and several proposals to mine new deposits have been postponed or abandoned because of objections of environmentalists who claim that the mines would harm wildlife, destroy esthetic values, or pollute (or deplete) natural water supplies.

When a deposit is to be mined for domestic use, the potential economics is related to the alternative of using imported ore or imported fertilizer. A complete study is needed to determine whether phosphate fertilizer can be manufactured and delivered to domestic farmers at a lower cost using domestic ore as compared with imported ore. The value of foreign exchange needs to be taken into account. Also, the stability of price and supply of imported rock must be evaluated. Recent fluctuations in world market price do not inspire confidence in stability.

List prices in 1972 were about \$10-\$14/ton, f.o.b. Florida and Morocco ports, for 72% BPL phosphate rock. Starting in 1973, the price rose sharply and reached \$48 and \$65/ton in 1975 for Florida and Morocco rock, respectively. Thereafter, the price declined, and in January 1977 the following listed prices were reported for 72% BPL rock:

Source	\$/ton
Morocco, Khouriba	38.00
Morocco, Youssoufia	35.25
Florida	28.50[a]

a. Increased to \$34, July 1977.

The average grade of U.S. phosphate rock exported in 1977 was 32.1% P_2O_5 (about 70% BPL), and the average value at the mine was \$21.81. The overall average grade of marketable production of phosphate rock in the United States was 30.8% P_2O_5 (67.3 BPL), and its average value was \$17.39 (5).

Direct Application of Phosphate Rock

Ground phosphate rock is not classified as a fertilizer in most countries and is not included in fertilizer consumption statistics reported by most countries. However, FAO reports consumption of ground rock phosphate separately; in 1976 reported consumption was equivalent to 1.2 million tons of P_2O_5, about 5% of phosphate fertilizer consumption. Over 70% of the reported use was in the U.S.S.R.; the remainder was widely distributed among many countries.

It is likely that actual consumption of phosphate rock for direct application is substantially higher than reported due to unreported consumption or, in some countries, inclusion with fertilizer use. For instance, use of ground rock phosphate is believed to be a substantial part of China's P_2O_5 consumption, but no statistics are available.

Considerable difference of opinion exists as to the merits of ground rock phosphate as a fertilizer. In many countries, the chemical phosphate fertilizer industry perceives ground rock as a threat to its prosperity and has urged government restrictions of its use. In other cases, industry or government authorities have promoted its use.

Some of the factors that contribute to the difficulty of making an impartial appraisal of the merits of direct application of ground rock phosphate are:

1. Phosphate rocks vary widely in their reactivity, hence their agronomic value.
2. The agronomic response to rock phosphate strongly depends on the type of soil and, to some extent, on the crop and climatic factors.
3. The response depends on timing, method of application, and particle size.
4. The residual value of a single application or cumulative value of repeated applications is important with all phosphate fertilizers, but this is not easily evaluated. Ground rock phosphate often has a more favorable long-term than short-term effect.
5. Agronomic and economic studies of long-term use on food crops are generally lacking.

The principal advantage of ground rock phosphate is its low cost. When both must be imported, ground rock may cost about half as much as TSP; when indigenous rock is available, the cost differential may be greater. Other advantages are:

1. A very low capital investment is required for processing.
2. No particular technical skills are required.
3. The energy requirement is small.
4. There is little or no loss in processing.
5. Rocks unsuitable for chemical processing are in some cases suitable for direct application.
6. The long delay involved in constructing chemical processing plants can be avoided.
7. Economy of scale is relatively unimportant.
8. Ground phosphate rock has a liming value on acid soils which needs to be studied further.

The main disadvantages are uncertainty as to agronomic value; inconvenience of handling and applying the fine, dusty material; and relatively low P_2O_5 content compared with TSP or ammonium phosphates.

It is generally agreed that ground phosphate rock is effective only on acid soils (pH 6 or less). This statement applies to apatitic rocks, not to calcined aluminum phosphate ores which are effective on neutral or calcareous soils.

Phosphate rocks are also more effective in warmer climates, in moist soils, and on crops of fairly long-term growing patterns. They are less effective for short-season crops grown under cool soil temperatures, particularly in the first year of application.

It is generally agreed that the rock should be finely ground and well mixed with the soil. However, there is some difference of opinion as to the usefulness of very fine grinding. The majority opinion seems to be that there is little to be gained by grinding finer than about 90% through 100-mesh (0.147 mm), although there are some who claim that very fine grinding such as 80% through 320-mesh (0.043 mm) is worthwhile.

Ground rock that has been granulated after grinding has given rather poor first crop results even when the granules disintegrate in the soil, presumably because granulation reduces the area of contact with the soil. However, in most of the tests, the granules have been in the range of 1-4 mm. Tests are in progress at IFDC with "minigranules" (0.1-0.5 mm) that give promise of overcoming dustiness of ground rock without significantly impairing its effectiveness.

While it is generally agreed that the reactivity is important, there is some disagreement as to how important it is and how to measure it. Chemical methods for evaluating reactivity are discussed later. The importance of reactivity is greatest for the first crop or season; the long-term or residual effectiveness does not seem to be closely related to reactivity. Rocks of relatively low reactivity have shown good long-term effectiveness.

Some investigators have related the response to phosphate rock to an annual rainfall; better results were obtained on well-watered soils.

In the early part of the 20th century, several long-term experiments were conducted in the United States with ground phosphate rock from Tennessee, which is one of the less reactive sedimentary rocks. Hopkins has reported results from experiments in four states of the United States which show that the increased value of crops grown in a rotation with rock phosphate added exceeded the cost of the rock phosphate by factors ranging from about 5:1 to 10:1 (6). When superphosphate was used the ratio of the value of increased yield to cost was much lower, mainly because the superphosphate cost was about four times as much per ton of P_2O_5 as the cost of ground rock phosphate.

As a result of these tests, use of ground rock phosphate increased in the United States to a maximum of well over 1 million tpy in 1953. However, more recently use has decreased sharply and, in 1976, amounted to only about 41,000 short tons, including "colloidal phosphate" a fine material recovered from Florida waste ponds.

The decreased use is attributed to two factors. First, large-scale production of high-analysis phosphates (TSP and DAP) has brought the delivered cost of these materials down to the point that ground rock phosphate has little cost advantage, particularly when transported over long distances. Secondly, the granular phosphates are much easier to handle and apply to the soil than the finely ground rock phosphate.

Ground phosphate rock has been advocated and used for reclaiming low-phosphorus soils of abandoned farms or of new (previously uncultivated) land of low native phosphorus fertility. For this purpose a heavy application is recommended, such as 1-3 tons/ha, which may be repeated at 5- to 10-year intervals. Also, phosphate rock is used in Europe as a replacement for basic slag to maintain soil fertility, usually by relatively large applications at intervals of several years. In either case there may be supplemental application of soluble phosphate fertilizers, depending on the crop needs.

In tests with single-season crop results, the most reactive phosphate rocks have shown effectiveness nearly equal to superphosphate with some crops and soils.

Methods for Measuring the Reactivity of Phosphate Rock

Numerous chemical methods have been tried experimentally, and several are used commercially for evaluating the reactivity of phosphate rock for direct application.

The principal extractants that have been used for evaluating the reactivity of phosphate rock are citric acid, formic acid, neutral ammonium citrate, and alkaline ammonium citrate. The latter is used mainly for evaluating calcined aluminum phosphates.

Most of these reagents were not originally intended to evaluate reactivity of phosphate rocks. For instance, the neutral and alkaline ammonium citrate solutions originally were intended to separate chemical reaction products in superphosphate and other fertilizers from unreacted rock on the assumption that unreacted rock was insoluble in these reagents. Citric acid extraction was developed to evaluate basic (Thomas) slag, a popular fertilizer material in European countries. Formic acid extraction apparently was developed specifically for phosphate rock.

Nearly all extraction methods use a ratio of sample weight to extraction volume of 1 g:100 ml. Extraction times usually are 30 minutes to 1 hour. Extraction temperatures and agitation during extraction may be specified. For instance, the AOAC method used neutral ammonium citrate of specified concentration (1 g of sample, 100 ml of solution) with extraction for 30 minutes at 65°C. The Wagner method used 2% citric acid solution and 30 minutes extraction time at 17.5°C.

Variations of the extraction conditions have been tried experimentally, including temperature, sample: extractant ratio, time of extraction, and concentration of solution in an effort to match more closely the values obtained with agronomic data. Successive extractions of the same sample also have been tried.

One disadvantage of all of these methods is that the percentage of P_2O_5 extracted depends on the grade of the rock, especially when the rock contains inert gangue minerals such as silica. For instance, in a series of tests with mixtures of North Carolina rock and quartz in ratios ranging from 91:9 to 50:50, the amount of P_2O_5 extracted from a 1-g sample of the mixture was nearly constant (5.5%-6.0% of the sample), but the percentage of the total P_2O_5 extracted increased from 21.0 to 36.9 as the grade of the mixture decreased. Thus, if the reactivity is taken as percentage of the P_2O_5 extracted, the apparent reactivity increases as the grade decreases. This situation tends to discourage efficient beneficiation since, when a higher grade is attained, the apparent reactivity is lowered. It is also possible that unscrupulous merchants may deliberately lower the grade by addition of worthless diluent in order to increase the apparent reactivity.

In order to eliminate the adventitious effect of grade, Lehr and McClellan have developed the concept of "absolute citrate solubility" in which the P_2O_5 dissolved is expressed as a percentage of the P_2O_5 content of the gangue-free apatite (4). The latter can be estimated by X-ray data or by complete chemical and mineralogical characterization. The disadvantages of this method are:

1. The estimation of the P_2O_5 content of the apatite requires equipment and skills that are not commonly available.
2. The P_2O_5 content of the apatite varies from about 34% to 42% so that the method introduces a variable that is not clearly related to reactivity.

Some minerals that often occur in phosphate rock depress the solubility of P_2O_5 in the various extractants. The most important of these are calcite and dolomite. Also, gypsum or any soluble calcium salt affects P_2O_5 solubility in the neutral ammonium citrate methods. These materials can be removed by the use of appropriate solvents before the P_2O_5 solubility is determined.

When six calcite-free phosphate rocks were extracted with neutral ammonium citrate, the average amount of P_2O_5 extracted was 5% of the sample weight or about 16% of the total P_2O_5. Additions of 1%, 2%, and 4% calcite reduced the P_2O_5 extraction as follows:

Calcite addition, %	0	1	2	4
P_2O_5 extracted, % of total P_2O_5	16	12	10	9

Thus, even a very small amount of calcite in phosphate rock causes a large percentage reduction of P_2O_5 solubility in neutral ammonium citrate. Calcite also affects P_2O_5 solubility in citric acid and formic acid; in one test the solubility reduction caused by 10% calcite was from 37% to 26% for citric acid and from 59% to 47% for formic acid.

Table 1 shows solubility results obtained with four extraction methods with samples of phosphate rock from six U.S. sources. The method using acidic ammonium citrate (pH 3) is a promising experimental method that has been used by TVA and IFDC. The other three methods are used commercially in some countries. The results of these and other tests have been compared with the results of various agronomic tests. A fairly good correlation was obtained between agronomic efficiency for the first crop in two greenhouse experiments and solubility values by any of the extraction methods; the pH 3 method gave the best correlation. However, in some tests with long-season crops there was little difference in effectiveness of rocks from different sources. Also, correlation of solubilities with residual responses was less satisfactory.

TABLE 1. SOLUBILITY OF PHOSPHATE ROCKS IN VARIOUS EXTRACTANTS COMPARED WITH AGRONOMIC EFFICIENCY[a]

	Rock Source					
	North Carolina	North Florida	Central Florida	Tennessee	Idaho	Missouri
Total P_2O_5	30.5	32.4	32.7	30.7	32.5	34.7
	% of Total P_2O_5 Extracted					
Ammonium citrate, pH 7[b,c]	26.1	20.4	16.2	14.9	11.5	1.4
Citric acid, 2%	49.6	29.7	25.7	25.3	23.8	6.0
Formic acid, 2%	85.8	30.3	28.0	21.3	33.1	5.0
Ammonium citrate, pH 3[b]	81.1	48.4	42.3	31.5	27.9	5.3
	Relative Agronomic Efficiency, TSP = 100[d]					
Rice[e]	84	46	37	6	24	0
Corn[f]	77	41	34	10	33	1

a. From unpublished cooperative studies by IFDC and TVA.
b. Ammonium citrate solution concentration was equivalent to 185 g of citric acid per liter.
c. Extracted 30 minutes at 65°C (AOAC method). All others extracted 1 hour at room temperature.
d. Yield response expressed as percent of response to TSP.
e. Greenhouse experiment: Engelstad, O.P., A. Jugsujinda, and S. K. De Datta. 1974. Soil Science Society of America Proceedings, 38:524-529.
f. Greenhouse experiment: Khasawneh, F. D., TVA unpublished information.

The general conclusions were:

1. All extraction methods gave a reasonably good correlation with the relative agronomic efficiency (RAE) for the first crop in this particular experiment. In this and other experiments, extraction with acidic ammonium citrate (pH 3) gave the best correlation.
2. None of the methods correlated well with the residual effectiveness or long-term agronomic value.

In another experiment, a group of phosphate rocks was used in greenhouse and field experiments in Colombia (7). The reactivities, as indicated by P_2O_5 solubility in various reagents, are shown in table 2.

TABLE 3. RELATIVE DRY MATTER YIELD OF CROP RESPONSE TO SEVEN PHOSPHATE ROCKS

	Relative Dry Matter Yield, %		
Rock Sample	Guinea Grass[a]	Beans[b]	Cassava[b]
Huila	44	82	90
Pesca	30	60	88
Sechura	100	92	-
Gafsa	85	90	100
North Carolina	88	100	98
Central Florida	57	78	92
Tennessee	38	67	86
No P (check)	0	43	41

a. Greenhouse experiment.
b. Field experiment.

TABLE 2. REACTIVITY SCALES OF THE PHOSPHATE ROCKS AS MEASURED BY VARIOUS METHODS

		Soluble P_2O_5, % of Rock					
		Neutral Ammonium Citrate					
Rock Source	Total P_2O_5 in Rock, %	1st	2nd	2% Citric Acid	2% Formic Acid	pH 3 Ammonium Citrate	Absolute Citrate Solubility, %[a]
Huila, Colombia	20.9	0.8	3.4	5.2	6.2	10.5	12.2
Pesca, Colombia	19.8	1.9	1.9	7.0	5.3	8.5	9.7
Sechura, Peru	30.0	5.3	5.4	15.2	21.8	24.1	14.9
Gafsa, Tunisia	30.0	4.9	5.6	14.1	22.4	21.1	18.5
North Carolina	29.9	7.2	6.7	15.9	25.7	24.8	19.8
Central Florida	32.7	3.0	3.2	8.4	8.2	14.0	10.1
Tennessee	30.1	2.6	2.7	8.8	6.9	9.8	5.1

a. Solubility of P_2O_5 in neutral ammonium citrate as determined by a method described in reference (4).

A comparison of agronomic results obtained in these tests is shown in table 3. In the field test with cassava, there was a good response to all phosphate rocks but no statistically significant difference between the different rocks. Correlation coefficients of solubility versus yield for the other two experiments are shown in table 4. In these tests the three most reactive rocks (Gafsa, Sechura, and North Carolina) were always at least 80% as effective as the comparison standard which was basic slag for the guinea grass and cassava tests and triple superphosphate for the test with beans.

The best correlation was obtained with the pH 3 method when the P_2O_5 solubility was expressed as a percentage of the sample. When expressed as a percentage of the total P_2O_5, the correlation was poor because the low-grade rocks gave a relatively high apparent reactivity.

The fact that there was little difference in the effectiveness of the different rocks in the cassava experiment illustrates that rock reactivity is not always a highly important factor.

TABLE 4. CORRELATION OF VARIOUS REACTIVITY SCALES OF THE PHOSPHATE ROCKS AND THE DRY MATTER YIELDS OF GUINEA GRASS AND BEANS

Method of Evaluation	Correlation Coefficient, r	
	Guinea Grass	Beans
Neutral ammonium citrate[a]	0.867	0.778
Neutral ammonium citrate[b]	0.927	0.961
2% citric acid	0.921	0.774
2% formic acid	0.944	0.879
Ammonium citrate, pH 3	0.984	0.910
Absolute citrate solubility	0.811	0.874

a. First extraction.
b. Second extraction.

The field experiment with beans was continued for 3 crops covering a period of about 18 months. The results showed that the relative agronomic efficiency (RAE) of the phosphate rocks, as compared with TSP, increased with time (8).

	RAE of Phosphate Rocks		
	High Reactivity	Medium Reactivity	Low Reactivity
1st crop	90	71	29
2nd crop	105	65	40
3rd crop	115	95	85
Total, 3 crops	105	77	51

It was concluded that an effectiveness rating based on one cropping period is not sufficient.

Lehr and McClellan have examined several hundred samples of phosphate rock from the principal world sources (4). One noteworthy finding is that the reactivity of different samples from the same geographic location may vary widely. In some cases, samples of rock from different strata of the same mine may have different reactivities.

While there is a need for an improved chemical method for evaluating reactivity of phosphate rocks for direct application, it is evident that reactivity is only one of several factors that affect the agronomic and economic usefulness. Therefore, reactivity values are useful only as a general guide; where and how the rock is used is equally important.

Calcined Aluminum Phosphate

Ores consisting mainly of hydrated aluminum phosphate minerals are useful for direct application after being calcined at a controlled temperature. The calcining may be done in a rotary kiln or in a fluidized bed calciner. Calcining drives off the combined water and thereby increases the grade and destroys the crystallinity of the phosphate minerals, which improves the reactivity of the phosphate.

At present, only two aluminum phosphate ores are known to be used for direct application after calcining. One of these is in Senegal near Thies. The ore, as mined, contains about 29% P_2O_5 on a dry basis; after calcination it contains over 34% P_2O_5. A partial analysis of the calcined product is:

P_2O_5	34.6%
Al_2O_3	35.9%
CaO	10.9%
Fe_2O_3	9.1%
SiO_2	2.9%
TiO_2	1.9%
MgO	0.3%

After calcination, the ore is ground to about 95% minus 100-mesh and marketed for direct application under the trade name "Phospal." About 75% of the P_2O_5 is soluble in alkaline ammonium citrate. Field tests showed that fertilizer effectiveness of the product was approximately equal to that of superphosphate on calcareous, neutral, and acid soils (9). Superphosphate was marginally better immediately after application while Phospal was better in long-term tests. The product is used mainly in France and in Senegal and some nearby countries.

A similar ore occurs in the upper stratum ("C-grade") of the phosphate deposit on Christmas Island. The C-grade ore contains about 25% P_2O_5 dry basis; after being calcined the composition range is:

P_2O_5	29%-33%
Al_2O_3	29%-24%
CaO	15%-21%
Fe_2O_3	11%-19%
CO_2	0.9%-1%
F	0.6%-0.8%

Calcination is carried out in a fluidized bed. Experiments showed that maximum citrate solubility was obtained in the range of 400°-600°C. The maximum P_2O_5 solubility is about 75% in either neutral or alkaline ammonium citrate solution; the solubility in 2% citric acid solution is much lower, about 20%-30%. The product is used for direct application after being ground to pass a 100-mesh (0.15 mm) screen.

Both the Phospal from Senegal and the Christmas Island product may be shipped in bulk after calcination to be ground in the importing country.

Some of the ground product is used in mixtures with other fertilizer materials. However, if the mixture is granulated into granules of the usual size (1-4 mm), the agronomic effectiveness is lower, at least for the first season after application.

TVA has carried out experiments with Florida "leached-zone" ore which also contains a high percentage of aluminum phosphate minerals--millisite, crandallite, and wavellite (10). It was found that maximum P_2O_5 citrate solubility of 70%-79% was obtained by calcining at 500°-600°C. However, the leached zone material is low grade and variable in composition and hence poorly suited for commercial utilization.

Sulfuric Acid

Sulfuric acid is an important raw material for phosphate fertilizer production and to a much lesser extent for nitrogen and potassium fertilizers. World production of sulfuric acid was about 121 million tons in 1977 (11). Probably about half of this production was used in fertilizer production.

About 58% of the world's production was based on elemental sulfur, 25% on pyrite, and 17% on other sources. Of the other sources, the principal one was byproduct sulfuric acid recovered from smelting operations.

In general terms, sulfuric acid is produced by catalytic oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3), which is subsequently absorbed in water to form sulfuric acid (H_2SO_4). In practice the SO_3 is absorbed in sulfuric acid which is kept at a controlled concentration (usually 98%) by water addition.

There are no major variations of commercial interest on this basic chemistry. There are alternatives as to source of SO_2 and method of conversion to SO_3.

The two principal processes for conversion of the SO_2 are known as the chamber and the contact processes. The older chamber process, which was introduced in Europe near the middle of the 18th century, uses nitrogen oxides as oxygen-carrying catalysts for the conversion of SO_2 to SO_3 (12, 13). The reactions which produce the SO_3 and sulfuric acid take place within huge lead chambers (from which the process is named) or in packed towers that may be substituted for the chambers. Major disadvantages of the chamber process are limitations in throughput, quality, and concentration (usually 60° Bé, or about 78% H_2SO_4). All known new plants use the contact process, although some older chamber process plants may still be in use.

In the contact process SO_2 is converted to SO_3 by use of a metal or metal-oxide catalyst. Platinum was once widely used as the catalyst but because of its excessive first cost and susceptibility to "poisoning," it has been largely replaced by vanadium oxide (14). The SO_3 is passed to an absorption tower where it is absorbed in recirculating concentrated acid. There are many variations in the contact process depending upon the types of raw materials available and other considerations; also, a number of engineering variations are in use by the many different design/construction firms offering services in this field. Main advantages of the contact process are that concentrated acid (98% H_2SO_4) of high purity can be produced directly and that compact plants of quite high capacity have now become rather commonplace, and capacities up to about 2,000 tpd are not unusual.

Sulfuric Acid from Elemental Sulfur

Elemental sulfur, also called "brimstone," is the preferred source of sulfuric acid whenever it is available at reasonable cost. The elemental sulfur may be mined by the well-known Frasch process, recovered from volcanic ores, recovered from "sour" natural gas, or recovered from oil. It is also possible and sometimes commercially feasible to produce elemental sulfur from pyrites and other sulfide ores and from coal.

Commercial sulfur usually is 99.5% or higher in purity. "Dark" sulfur contains hydrocarbon impurities up to about 0.5%; "bright" sulfur contains less than about 0.1% (measured as carbon). Dark sulfur causes difficulties in some types of sulfur-burning plants. However, methods for using dark sulfur without difficulty have been developed. Another quality factor is the ash content, which should be quite low to avoid dust that will accumulate in the catalyst bed. Solid impurities can be removed from molten sulfur by filtration (15). Alternatively, by using a hot gas filter, dust arising from ash in the sulfur can be removed from the hot gas leaving the sulfur burner.

Most sulfur-burning plants are designed to use sulfur in liquid form, although plants with solid feed have been used. In many cases the sulfur is transported in liquid form by ships, barges, or railcars that are specially equipped for that purpose. In this case, the sulfur is stored in liquid form at the plant receiving terminal until it is used. When the sulfur is received in solid form, it usually is melted before use.

In production of sulfuric acid from sulfur, heat is released in various steps of the process as follows (16):

Reaction	Heat Released, kcal/mole of H_2SO_4
$S + O_2 = SO_2$	70.9
$2SO_2 + O_2 = 2SO_3$	23.5
$SO_3 + H_2O = H_2SO_4$	32.8
Total reaction	
$S + 1\text{-}1/2\ O_2 + H_2O = H_2SO_4$	126.2

Some additional heat is released by dilution of the sulfuric acid to the usual concentration of 98% or 93%, but this is relatively small. The total heat released is equivalent to about 1.3 million kcal/ton of H_2SO_4. Recovery of a maximum portion of this heat as usable energy is an important objective.

In a typical sulfuric acid plant (figure 1), the molten sulfur is burned with dry air. The air is dried in a drying tower by contact with concentrated sulfuric acid. The sulfur is burned in a refractory-lined combustion chamber with excess air at a temperature of 950°-1100°C producing a combustion gas containing about 10% SO_2. The gas is cooled in a boiler, which generates steam, to about 420°C, the desired inlet temperature to the catalytic converter. Some of the excess air may be bypassed around the burner and boiler to control the combustion chamber temperature and to decrease the required size of the boiler. Alternatively, excess air may be added between catalyst beds to control the temperature during conversion.

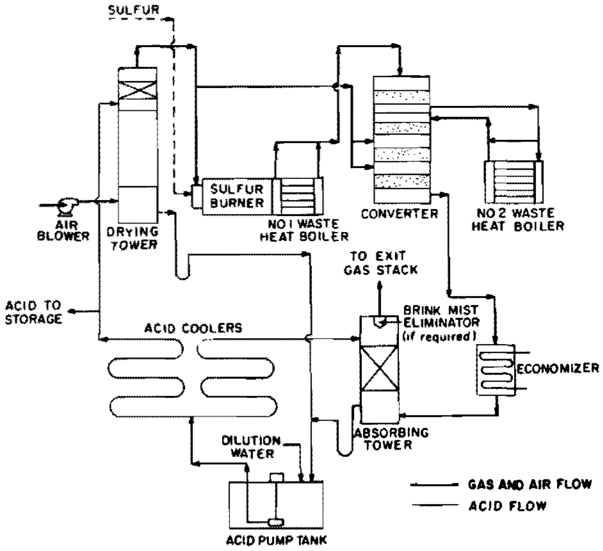

Figure 1. Sulfur-Burning, Single-Contact Sulfuric Acid Plant.

The catalytic conversion of SO_2 to SO_3 usually is carried out in three or more steps (catalyst beds) with cooling of the gas between steps to keep the temperature within the desired range of 420°-450°C. The conversion steps are carried out by contact of the gas with successive beds of vanadium oxide catalyst which are often arranged in sections of a single tower.

The gas leaving the first catalyst bed may be at a temperature of 580°-600°C and must be cooled to a range of 420°-450°C to promote efficient conversion in the second bed because of unfavorable equilibrium at higher temperatures. Cooling may be done by injecting cool air or by heat exchange to produce more steam. Likewise, cooling between the second, third, and successive beds is required, but the temperature rise is less than for the first bed.

The gas leaving the tower is cooled further in a heat exchanger (economizer) before entering the absorption tower where the SO_3 is absorbed in a recirculated stream of concentrated sulfuric acid. The sulfuric acid is maintained at the desired concentration (usually 98% H_2SO_4) by water addition, and its temperature is controlled in the desired range of 70°-90°C measured at the tower inlet by cooling the recirculated acid. Some of the acid goes to the air-drying tower mentioned previously where moisture from the incoming air supplies some of the water needed in the reaction. Since the heat released in this step is at a low temperature level, little use can be made of it.

In the above-described single absorption process, the recovery of sulfur as sulfuric acid is 97%-98%; the remainder is lost to the atmosphere as SO_2. In most countries the discharge of this amount of SO_2 to the atmosphere is environmentally unacceptable. Therefore, most plants use a double-contact, double-absorption (DC/DA) system as shown in figure 2. The gas, after passing through three catalyst beds, goes to the first absorption tower where the SO_3 is removed. The gas is then reheated to about 420°C, passed through the fourth catalyst bed, and then cooled and sent to a second absorption tower.

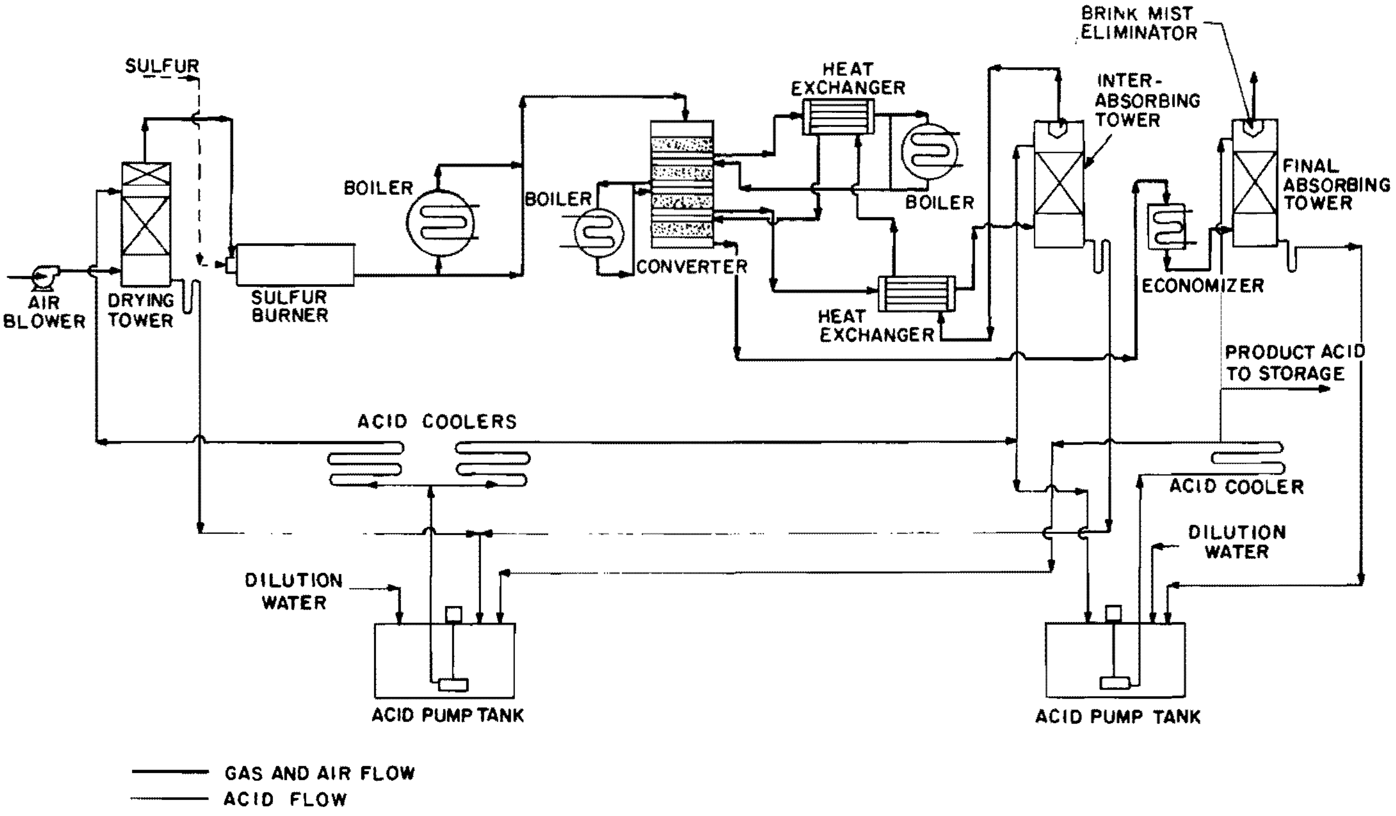

Figure 2. Sulfur-Burning, Double-Contact, Double-Absorption Sulfuric Acid Plant.

In the reaction,

$$2SO_2 + O_2 \rightarrow 2SO_3$$

removal of the reaction product, SO_3, facilitates more efficient conversion in the last catalyst bed. The DC/DA process reduces the SO_2 loss to less than 2 kg of SO_2/ton of H_2SO_4. High-efficiency mist eliminators are also required to limit the loss of H_2SO_4 mist to less than 0.05 kg/ton of H_2SO_4. Thus, the recovery in a DC/DA plant should be at least 99.7%.

The use of the DC/DA system adds 10%-15% to the cost of the plant in comparison with the older single absorption process. It also uses more energy and produces less steam or other recoverable energy. An alternative, which is said to be less expensive, is to recover the SO_2 from a single absorption plant by ammonia scrubbing (17). Scrubbing the gas with ammonia solution produces an ammonium sulfite/bisulfite solution which is then acidulated with sulfuric acid. The liberated SO_2 is returned to the sulfuric acid plant, and a concentrated ammonium sulfate solution remains which may find use in a fertilizer plant. Alternatively, the ammonium sulfite-bisulfite solution may be acidulated with phosphoric acid, producing an ammonium phosphate solution. There are numerous other tail-gas scrubbing processes that produce various byproducts or waste products.

Operation of a sulfuric acid plant under pressure has some advantages; the equipment is smaller and less expensive, less catalyst is required, and equilibrium conditions and reaction rates are more favorable in the conversion and absorption steps. The first pressure plant was built by Produits Chimiques Ugine Kuhlmann near Lyon, France. It began operation in 1972. Its capacity is 550-575 tpd. A recent article describes its operating history and gives the process flowsheet (18). The plant utilizes a double-contact, double-absorption process and operates at 5-atm pressure, measured at the air compressor exhaust. The conversion efficiency was 99.80%-99.85% during the first 5 years of operation. It was estimated that the investment cost was 10% less than for a conventional (nonpressure) plant, but for larger capacities up to 2,000 tpd, an investment saving of up to 17% is possible. About two-thirds of the energy required for compression is recovered by expansion of the reheated tail gas in a turbine that drives the compressor. Operating results are summarized below (18):

Sulfur consumption	330 kg/ton
Electric power	65 kWh/ton
Byproduct steam (at 40 atm)	990 kg/ton
Process and cooling water	Same as conventional processes
Maintenance	3%-4% of capital cost
Operating labor	2 men/shift
Acid concentration	99.0%-99.5% H_2SO_4

It was noted that the plant was designed in 1970 before the energy crisis, and some improvements in heat and energy recovery would be possible and economically desirable under current conditions.

Another recently developed pressure process is called the CIL process (Chemetics International, Ltd., a Canadian organization). The process operates at 8 atm and uses a single-contact, single-absorption system. The unique feature of the process is that SO_2 remaining in the gas leaving the converter is absorbed in the sulfuric acid in the absorption tower. The acid containing dissolved SO_2 then goes to the air-drying tower where the dissolved SO_2 is stripped from the acid into the airstream and thereby recycled through the sulfur burner to the converter.

The solubility of SO_2 in sulfuric acid increases with increase of pressure and with decrease in temperature. In a conventional plant operating at 1-atm pressure and with an acid temperature of 110°C, the solubility of SO_2 in sulfuric acid is only 8 ppm. However, by increasing the pressure to 8 atm and lowering the temperature to 49°C, the SO_2 solubility is increased to 190 ppm. Under these conditions, a substantial amount of SO_2 can be transferred in the acid stream to the air-drying tower and then to the incoming airstream. Cameron, et al., point out that there is no theoretical limit to the amount of SO_2 that can be recovered and recycled; it depends on the rate of recirculation of acid between the absorber and air-drying towers (19). In a conventional plant, each tower has its own acid recirculation system (see figure 1) with only enough interchange between the systems to maintain the acid concentrations at the desired level. In the CIL system, most of the recirculation is between the two systems. It is claimed that this system can readily attain or exceed the 99.7% efficiency that is required to meet U.S. pollution control standards.

The CIL process would have the advantages of a pressure process, which were pointed out in describing the Kuhlmann process, and the additional advantage of requiring only single-contact and single-absorption equipment which would obviously decrease capital costs and simplify plant operation. However, maintaining the relatively low acid temperature (about 50°C) in the absorber tower would require more cooling. It is not known to what extent the CIL process is used in commercial practice.

Capital Costs--The estimated capital cost of DC/DA sulfuric acid plants based on elemental sulfur is shown in figure 3. The lower curve shows a battery-limits cost for an industrial country. The estimate is based on early 1977 costs and does not allow for future inflation; it includes an allowance for 4 weeks' storage of sulfur and sulfuric acid. It does not allow for a cooling tower for reuse of cooling water. The upper curve is based on a battery-limits cost plus 50% to allow for auxiliary and support facilities, site preparation, etc; these costs will vary with location and coexisting facilities. When the sulfuric acid plant is part of an industrial or fertilizer complex, this allowance probably is adequate. For location in a developing country, costs should be increased by 25% or more to provide for the increased cost of delivery and construction.

The plant normally produces enough steam to drive the main air supply compressor and boiler feedwater pumps plus about 1.2 tons of additional steam per ton of H_2SO_4. This excess steam can be used for generation of electricity or for concentration of phosphoric acid or other purposes.

Production Costs--An illustrative estimate of the cost of producing sulfuric acid from sulfur in a plant rated at 600 tons of H_2SO_4/day and operated at full capacity, 330 days/year, is given in table 5.

Assuming a sulfur cost of $50/ton delivered at the plant, the estimated production cost of sulfuric acid would be $26.74/ton of H_2SO_4 for a developed country location or $28.98 for a developing country, assuming that the plant capital cost is 25% higher. If 10% return on investment is added, the captive use cost is $31.79 and $35.29 for developed and developing countries, respectively.

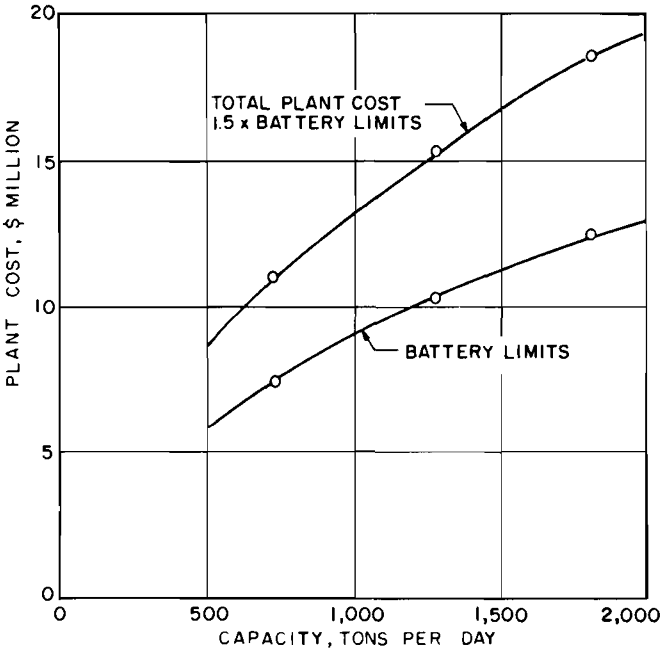

Figure 3. Capital Cost of Sulfur-Burning Sulfuric Acid Plants, Double Contact, U.S. or European Location, 1977.

Table 6 shows the estimated effect of scale of production on production cost and transfer price. The results of the calculation, assuming 100% capacity utilization, are summarized below.

Capacity, tons of H_2SO_4/day	Cost or Price, \$/ton of H_2SO_4			
	Developed Country		Developing Country	
	Production Cost	Transfer Price[a]	Production Cost	Transfer Price[a]
600	26.74	31.79	28.98	35.29
1,200	23.48	27.02	25.37	29.98
1,800	22.69	25.79	23.79	27.66

a. Includes 10% return on investment.

While sulfuric acid plants in general are not difficult to operate at full capacity for extended periods, maintaining a high capacity utilization depends on the reliability of production units that use the product and many other factors. Table 7 shows the effect of capacity utilization on transfer price, assuming a sulfur cost of $50/ton and a return on investment of 10% which is usually about the minimum that can be regarded as acceptable. It is evident that low capacity utilization can increase the cost significantly. For instance, operation at 60% of capacity increases the transfer price by about $10/ton in comparison with operation at 90% capacity utilization for a 600-tpd plant in a developing country location. Since about 3 tons of sulfuric acid is required per ton of P_2O_5 produced as phosphoric acid, the effect of low capacity utilization can be quite serious in a plant where the two units are interdependent.

Production of Sulfuric Acid from Pyrites or from Smelter Operations

When the source of the SO_2-containing gases is roasting of pyrites (FeS_2), pyrrhotite (approximately Fe_5S_6), or nonferrous sulfide ores, the sulfuric acid plant is similar to that described above (figures 1, 2) with the following exceptions:

1. The sulfur-burning furnace is omitted.
2. The incoming gas must be cooled and scrubbed or otherwise cleaned to remove all impurities that might poison the conversion catalyst or clog the catalyst bed.

TABLE 5. PRODUCTION COST OF SULFURIC ACID

Plant capacity, 600 tpd, 198,000 tpy
Capital cost, developed country, $10.0 million; developing country, $12.5 million

Item	Quantity	Unit Cost, %	Cost/ton of H_2SO_4
Sulfur	0.34 tons	50	17.00
Boiler feedwater	1.25 tons	0.32	0.40
Cooling water	25.8 tons	0.01	0.26
Electricity	35 kWh	0.02	0.70
Steam (excess)	1.2 tons	2.50	-3.00
Labor-related costs[a]	0.16 man-hours	15.40	2.46
Subtotal			17.82

	Developed Country	Developing Country
Operating costs	17.82	17.82
Capital-related costs[b]	8.92	11.16
Total production cost	26.74	28.98
Return on investment, 10%	5.05	6.31
Transfer price[c]	31.79	35.29

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a. Includes overhead, chemical control, and miscellaneous supplies.
b. Capital-related costs:

Depreciation, 15 years	6.67% of capital costs/year.
Interest at 8% of 1/2 capital cost	4.00% of capital costs/year.
Maintenance	5.00% of capital costs/year.
Taxes and insurance	2.00% of capital costs/year.

c. Captive use in-plant transfer price.

TABLE 6. EFFECT OF PLANT CAPACITY ON COST OF SULFURIC ACID (ANNUAL PLANT CAPACITY ASSUMED TO BE 330 x DAILY CAPACITY)

	Developed Country			Developing Country		
Capacity, tpd	600	1,200	1,800	600	1,200	1,800
Plant cost, $ million[a]	10.0	14.6	18.4	12.5	18.25	23.00
	Cost, $/ton of H_2SO_4					
Sulfur	17.00	17.00	17.00	17.00	17.00	17.00
Labor-related costs[b]	2.46	1.87	1.59	2.46	1.87	1.59
Capital-related costs[c]	8.92	6.25	5.74	11.16	8.14	6.84
Other costs[d]	-1.64	-1.64	-1.64	-1.64	-1.64	-1.64
Production cost	26.74	23.48	22.69	28.98	25.37	23.79
Return on investment[e]	5.05	3.54	3.10	5.68	4.61	3.87
Transfer price	31.79	27.02	25.79	34.66	29.98	27.66

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a. Capital costs for developed countries from figure 3; cost for developing countries assumed to be 25% higher.
b. Annual labor-related costs assumed to be proportional to the 0.6 power of plant capacity.
c. See table 5, footnote b.
d. Electricity, boiler feedwater, cooling water, and steam credit.
e. Assuming 10% return on plant cost.

3. The gas must be dried in a tower that uses sulfuric acid as the drying agent.
4. The clean, dry gas must be heated to conversion temperature (about 420°C). There is usually enough heat generated in the conversion step to preheat the incoming gas by heat exchangers.
5. Since the SO_2 concentration of the gas often is lower than that from sulfur burning, all equipment must be correspondingly larger.

As in the case of sulfur-burning plants, the sulfuric acid plant may use double-contact or tail-gas scrubbing to conform to pollution control requirements. A plant using sulfur dioxide from sulfide roasting is likely to cost about 50% more than a sulfur-burning plant including gas cleaning but excluding the roasting operation. Heat recovery depends mainly on how much heat can be recovered from the roasting operation. In general, the amount of heat recovered as steam or in other useful forms is somewhat less for a pyrites-based plant than for a sulfur-burning plant.

Pure pyrite (FeS_2) contains 53.4% S and 46.6% Fe. However, unlike sulfur, pyrite ores contain numerous impurities which affect their value, either positively or negatively. After mining and (usually) beneficiation, a commercial grade of pyrite may contain 40%-50% S. The most common valuable elements associated with pyrite are copper, lead, and zinc. However, the ore may contain many other elements (usually as sulfides) such as nickel, cobalt, cadmium, bismuth, arsenic, and small percentages of silver and gold.

A partial analysis of Spanish pyrite follows:

TABLE 7. EFFECT OF CAPACITY UTILIZATION ON TRANSFER PRICE OF SULFURIC ACID, \$ PER TON OF H_2SO_4[a]

Rated Capacity, tpd: Capacity Utilization, %	600	1,200	1,800
	Developed Countries		
100[b]	31.79	27.02	25.79
90	33.62	28.32	26.95
75	37.28	30.91	29.27
60	42.75	34.79	32.74
	Developing Countries		
100[b]	35.29	29.98	27.66
90	37.50	31.60	29.03
75	41.93	34.85	31.76
60	48.57	39.73	35.86

[a] Calculated from the data of table 6, assuming that labor-related and capital-related costs are constant on an annual basis and that sulfur and utilities costs and steam credit are constant per ton of sulfuric acid.

[b] Annual capacity = 330 x daily capacity.

	Composition of Spanish Pyrite (13)	
	Crude Pyrite	Floated Pyrite
Sulfur (S)	48%	48%
Copper (Cu)	0.8%-1.2%	0.3%
Lead (Pb)	0.5%-1.5%	0.3%
Zinc (Zn)	1.5%-2.5%	0.4%
Gold (Au)	1 g/ton	1 g/ton
Silver (Ag)	30 g/ton	30 g/ton

The recovery of the valuable metals and of the iron plays an important part in the economics of processing pyrites. Arsenic is an undesirable impurity; it tends to form volatile compounds during roasting which foul heat exchangers and ducts. However, methods of dealing with this problem have been developed.

When the pyrites are relatively rich in copper or other valuable metals, the ore may be separated by beneficiation to provide a concentrate of nonferrous sulfides which is treated separately. Alternatively, the cinder (residue) after roasting may be treated by one of several methods to extract valuable elements. Since the cinder mainly consists of iron oxide, it may be used by the steel industry as an iron ore. However, since several impurities are objectionable for use as iron ore, treatment after roasting may serve a dual purpose of recovering valuable elements and purifying the cinder for use in the steel industry.

Figure 4 shows a simplified flow diagram for production of sulfuric acid from pyrites. The diagram shows a single-contact, single-absorption process. In most locations either stack gas scrubbing or a second contact-absorption stage would be necessary to prevent atmospheric pollution. The treatment or disposal of the cinder, although important, is beyond the scope of this manual.

The capital cost of the plant including the pyrite roasting step is about 2.6 times the cost of an equivalent sulfur-burning plant (20). Based on the estimates in table 6, the capital-related operating costs would be higher than for a sulfur-based plant by about \$13/ton of H_2SO_4 for a 1,200-tpd plant in a developing country. Labor and other costs would also be higher. Assuming a total differential is \$15/ton of H_2SO_4, it is evident that, for equal production costs, the cost per ton of sulfur contained in pyrites would have to be \$45 less than for elemental sulfur unless some value is assigned to the cinder.

Lasaosa presented data showing that the net cost of producing sulfuric acid from Spanish pyrites, after allowing credit for byproducts, was less than from sulfur in 1972 (20). No generalized conclusion can be drawn because of wide variation in quality of pyrites, value of byproducts, and local conditions.

The recovery of byproducts from pyritic ores

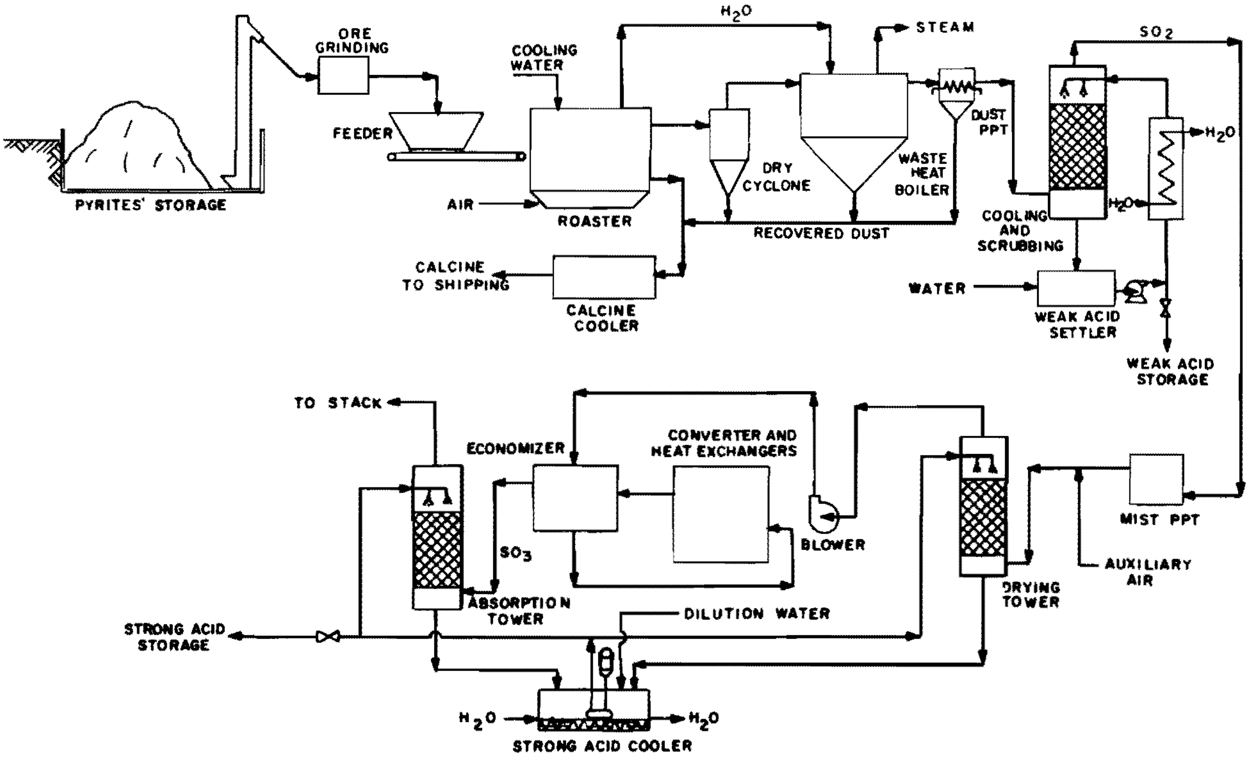

Figure 4. Simplified Flow Diagram for Plant to Produce Sulfuric Acid from Pyrites.

requires a high level of technology and may be a difficult undertaking for a developing country. Some countries that rely mainly on pyrites as a source of sulfuric acid are Finland, Norway, Sweden, Spain, Portugal, Italy, China, and the U.S.S.R. Some other countries, such as Japan, have a large production of sulfuric acid from smelting operations. The classification between pyrites and nonferrous ores is ill defined. In some countries a company that processes ore containing 1% copper might be classified as a copper smelter producing byproduct sulfuric acid; a similar operation in another country might be classed as a sulfuric acid producer with byproduct copper production.

The Outokumpu process which was developed in Finland consists of flash roasting pyrites in a nonoxidizing atmosphere in a fluidized bed. About half of the sulfur content is recovered as elemental sulfur, and the remainder is in the residue, pyrrhotite, a magnetic iron sulfide. The pyrrhotite may be roasted in an oxidizing atmosphere to recover the remaining sulfur as sulfur dioxide.

Production of Sulfuric Acid from Calcium Sulfate

Several plants have produced sulfuric acid from gypsum or anhydrite, with production of portland cement as a byproduct. A simplified flow diagram of the process is shown in figure 5. The process is carried out in a rotary kiln which is similar to cement kilns. When gypsum is used, it is first dehydrated in a separate kiln. When phosphogypsum is used, part of the fluorine is driven off and may be recovered or disposed of. When anhydrite is used, this precalcination step is unnecessary.

The charge to the rotary kiln consists of anhydrite (or calcined gypsum), coke, silica, and shale or other sources of iron and aluminum oxide. The charge must be proportioned precisely to give the required ratios of CaO, SiO_2, Al_2O_3, and Fe_2O_3 required for good quality cement.

The charge is mixed, ground, and pelletized to avoid dust losses. The kiln may be fired with coal, oil, or gas. The maximum temperature in the kiln is just short of fusion which may be of the order of 1400°C. The cement clinker is discharged to a cooler; then it is finely ground and mixed with about 5% gypsum (a set retarder).

The sulfur is driven off from the charge as sulfur dioxide and emerges in the kiln exhaust gas, which also contains oxygen, nitrogen, carbon dioxide, water vapor, and a substantial amount of dust. The gas is cleaned and cooled in a system of cyclones, dry electrostatic precipitators, wet scrubbers, and wet electrostatic precipitators. Then air is added for oxidation of SO_2 to SO_3. At this point the SO_2 content of the gas is about 5.5%. The gas is dried, reheated to conversion temperature, and passed through the sulfuric acid plant which is similar to that described previously under "Sulfuric Acid from Pyrites." Due to the lower concentration of SO_2 in the inlet gas, all equipment must be larger. The sulfuric acid is produced at the usual concentration, 96%-98% H_2SO_4.

The overall reaction by which sulfur is volatilized from calcium sulfate is:

$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$$

The reaction is believed to proceed in two stages. First, part of the calcium sulfate reacts with the carbon (coke) to form calcium sulfide:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$

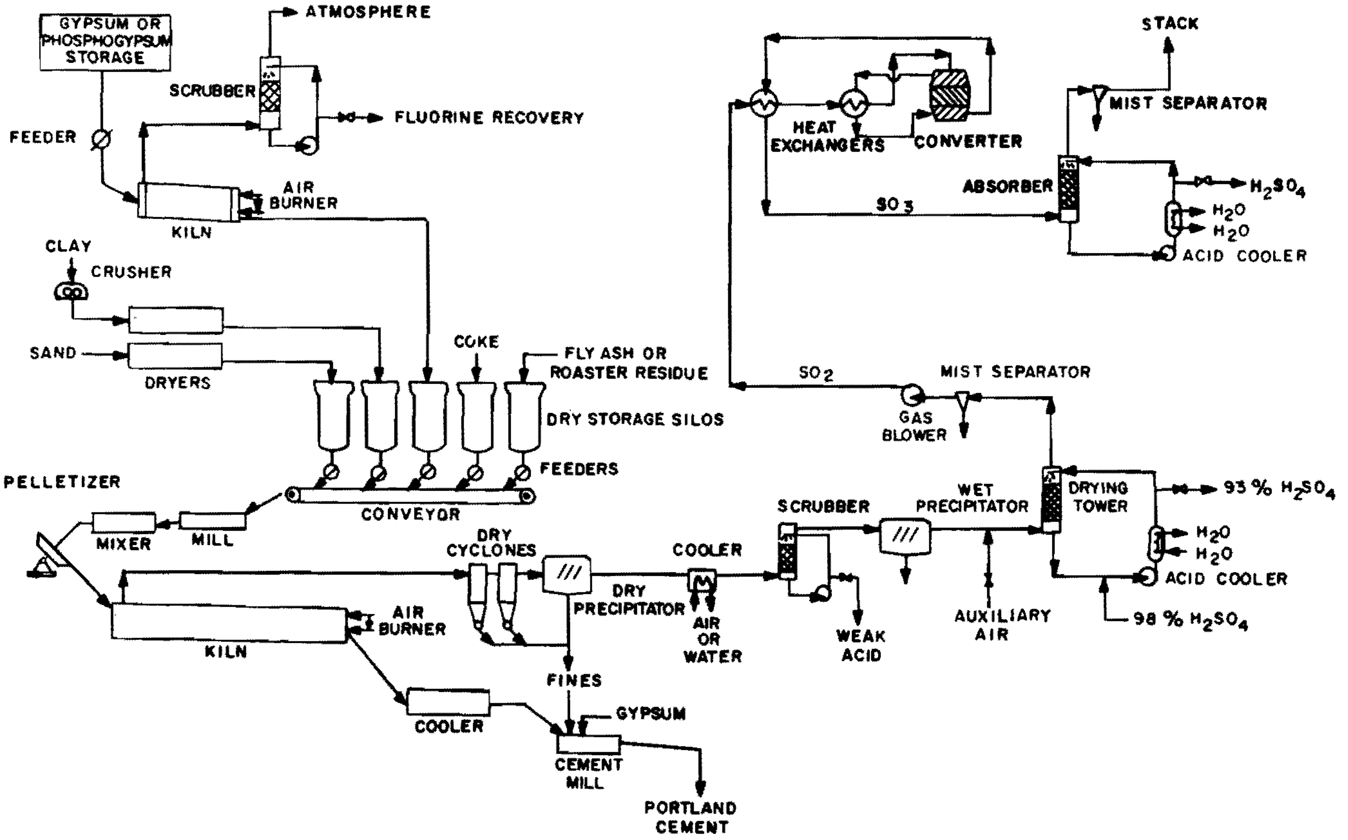

Figure 5. Simplified Flow Diagram for Plant to Produce Sulfuric Acid and Portland Cement from Gypsum or Phosphogypsum.

At somewhat higher temperatures the calcium sulfide reacts with the rest of the calcium sulfate:

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$$

At still higher temperatures, the CaO reacts with the other charge ingredients to form the desired compounds in portland cement, mainly tricalcium silicate, dicalcium silicate, tricalcium aluminate, and calcium ferrite.

Ashburner gives the approximate requirements for the process which are shown below together with their equivalents in the metric system (21):

Item	Requirement	
	Per Short Ton of H_2SO_4	Per Metric Ton of H_2SO_4
Anhydrite or	1.6 to 1.7 short tons	1.6 to 1.7 mt
Gypsum[a]	2.0 to 2.2 short tons	2.0 to 2.2 mt
Shale	0.29 short tons	0.29 mt
Sand	0.06 short tons	0.06 mt
Coke	0.10 short tons	0.10 mt
Fuel for anhydrite	6 million Btu	1.5 million kcal
Fuel for gypsum	10 million Btu	2.5 million kcal
Cooling water (circulating)	14,000 gal	58 mt
Electricity	228 kWh[b]	251 kWh
Labor	0.82 man-hours	0.90 man-hours

Capital cost: $50 million for 1,000 mtpd[c]

a. Does not include gypsum for addition to cement.
b. Includes 38 kWh for grinding cement clinker.
c. Basis: West Europe location, 1976, battery limits (22).

The process produces approximately equal quantities of cement and sulfuric acid. The largest kiln operating in 1968 at the Marchon plant, Whitehaven, England, had an annual capacity of 100,000 short tons of sulfuric acid and the same quantity of cement (21). The plant which used native anhydrite had five kilns with a total production capacity of 440,000 short tons of sulfuric acid and of cement. In the 1960s another large plant was in operation at Billingham, England, and a third in Wolfen, Germany, all based on anhydrite. A fourth plant located in Austria used natural gypsum or at times a mixture of natural gypsum and phosphogypsum. Also, plants located in France and Poland have been reported (23).

At that time (1968) no plant was known to have used phosphogypsum exclusively for extended periods of operation, although some plants had done so for short periods. Since then most of the plants have been closed for economic reasons, but plants using phosphogypsum are reported to be in operation in Austria, South Africa, East Germany, and Poland. Some details about these operations have been published recently (22). The requirements of the process developed by Chemie Linz (Austria) are in general agreement with those listed above.

In commenting on the use of phosphogypsum in the cement-sulfuric acid process, Ashburner made the following points (21):

1. The byproduct, phosphogypsum, usually contains 15%-25% free moisture in addition to about 21% combined water (dry basis). Thus, the weight ratio of water to $CaSO_4$ is between 0.38 and 0.58 (assuming no impurities). Removal of this water substantially increases the fuel requirement in comparison with anhydrite which is quite dry as mined.
2. The P_2O_5 content of phosphogypsum should be quite low because P_2O_5 has a deleterious effect on the setting properties of cement. The upper limit is not precisely known, but a maximum level of 1% P_2O_5 in the cement has been set by one organization (22). To attain this level the phosphogypsum should contain not more than about 0.5%. This level is difficult to reach in dihydrate plants but may be attained by recrystallization in dihydrate-hemihydrate or hemihydrate-dihydrate processes (chapter XIII). Thorough washing to remove soluble P_2O_5 is necessary.
3. Fluorine is undesirable in the cement kiln charge since it lowers the melting point and may cause ring formation in the kiln. A specification of 0.15% F in the phosphogypsum is suggested (22). Most of the fluorine may be removed by drying and calcining the phosphogypsum which is necessary in any case to drive off its water content. Also, fluorine compounds in the kiln gases should be completely removed before they enter the sulfuric acid plant to prevent impairment of the effectiveness of the vanadium oxide catalyst.
4. Other impurities commonly present in phosphogypsum such as silica and aluminum compounds are not objectionable, but they need to be taken into account in formulating the kiln charge which must be controlled very precisely.

The main advantage of sulfuric acid and cement from phosphogypsum is that the byproduct phosphogypsum is automatically available at a phosphoric acid plant at no cost. However, some additional source of sulfur would be needed to offset losses in recycling. Also, use of phosphogypsum would avoid a disposal problem. Developing countries often need both cement and phosphate fertilizer. In developed countries where cement production is already adequate, an additional supply might upset the market balance. In countries where alternative sources of sulfuric acid are very expensive and fuel costs are low, the process might well be considered. In special cases there may be advantages favoring use of phosphogypsum that are difficult to evaluate such as:

1. Saving in foreign exchange.
2. Independence from foreign sources.
3. Stimulation of domestic employment.
4. Lack of an environmentally acceptable alternative means for disposal of phosphogypsum. (Some other methods for utilizing phosphogypsum will be discussed in chapter XIII.)

The main disadvantages of the sulfuric acid cement process are the high capital cost and high energy (fuel) requirement. A comparison should be based on separate production of sulfuric acid and cement if both are needed. The fuel requirement for cement production from phosphogypsum is about 2.5 times that required for cement production from the usual raw materials (limestone, shale, etc.). Whereas production of sulfuric acid from sulfur produces a substantial amount of energy, usually in the form of byproduct steam, there is no export steam from the gypsum-based plant. No exact comparison of capital cost is available, but it is evident that the combination would be more expensive than separate plants since both the cement kiln and sulfuric acid plant would need to be larger and more complicated in the combined process than in separate production of cement from limestone and sulfuric acid from sulfur. Estimates of the total capital investment for the combined process range from a ratio of 5:1 to 10:1 when compared with sulfuric acid from sulfur (none of the investment assigned to cement) (21, 22, 24). A TVA study comparing the economics of producing sulfuric acid from sulfur, pyrites, and gypsum in Morocco, India, and Uruguay concluded that phosphogypsum would not be an economical alternative in any of the three countries under 1971 conditions (24).

It is evident that calcium sulfate is unlikely to be an economical source of sulfuric acid except perhaps in unusual circumstances. This situation might be changed in the future if the price of sulfur should increase substantially or if new technological developments should result in a better process. One possibility is the production of elemental sulfur and lime by heating calcium sulfate with a reducing agent such as coal in a neutral atmosphere. This reaction takes place in two steps:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$

$$3CaS + CaSO_4 \rightarrow 4CaO + 4S$$

The reactions take place at a lower temperature than that required for cement production.

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XIII Phosphoric Acid

Introduction

In the past few years phosphoric acid has been the source of perhaps 90% of the new phosphate fertilizer production, and this trend is expected to continue in the foreseeable future. Forecasts by the UNIDO/FAO/World Bank Working Group on Fertilizers indicate that in the period, 1976-81, phosphoric acid supply will increase from 15.9 to 21.9 million tons of P_2O_5, an increase of 38% (1). In the same period fertilizer P_2O_5 supply from all other sources was estimated to increase only slightly from 12.6 to 13.0 million tons. Thus, in 1981 phosphoric acid would constitute 63% of the total fertilizer P_2O_5 supply.

While other phosphate fertilizers as a group are expected to increase only slightly, some increase in nitrophosphate production is expected which will be offset by declines in SSP and basic slag. The study did not include any prediction about future use of ground phosphate rock for direct application since it is not classified as a manufactured fertilizer.

There are two basic types of processes for the production of phosphoric acid--furnace processes and wet processes. Furnace processes include the blast-furnace process and the electric-furnace process. The blast-furnace process has not been used commercially since 1938. However, the electric-furnace process is used extensively to make elemental phosphorus; most of this phosphorus is converted to phosphoric acid for nonfertilizer uses. Since it is unlikely that furnace processes will be competitive for producing phosphoric acid for fertilizer use except possibly in unusual circumstances, these processes will be described only briefly.

Wet processes may be classified according to the acid used to decompose phosphate rock. Sulfuric, nitric, and hydrochloric acid are used in commercial processes. Processes using nitric acid will be described under "Nitrophosphates," (chapter XV). Processes using hydrochloric acid are not competitive for fertilizer purposes except under unusual conditions and will be described briefly in this chapter. Processes using sulfuric acid are by far the most common means of producing phosphoric acid for fertilizer use (and sometimes for other uses); therefore, these processes will be described in more detail. However, the scope of this manual precludes extensive detail of even the most important processes. For more detail, readers should consult Phosphoric Acid, edited by A. V. Slack (2), and other references listed at the end of this chapter.

Production of Phosphoric Acid by Wet Processes Using Sulfuric Acid

Chemistry of Process

The main chemical reaction in the wet (sulfuric acid) process may be represented by the following equation using pure fluorapatite to represent phosphate rock:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4\ nH_2O + 6H_3PO_4 + 2HF$$

where n = 0, ½, or 2, depending on the hydrate form in which the calcium sulfate crystallizes.

The reaction represents the net result of two stages. In the first stage, phosphoric acid reacts with the apatite forming monocalcium phosphate, and in the second stage monocalcium phosphate reacts with sulfuric acid to form phosphoric acid and calcium sulfate. These two stages do not necessarily require two reaction vessels; they usually take place simultaneously in a single reactor.

As mentioned in chapter XII, phosphate rock contains many impurities both in the apatite itself and in accessory minerals. These impurities participate in numerous side reactions. Most phosphate rocks have a higher $CaO:P_2O_5$ ratio than pure fluorapatite. The additional CaO consumes more sulfuric acid and forms more calcium sulfate. The HF formed by the reaction reacts with silica and other impurities (Na, K, Mg, and Al) to form fluosilicates and other more complex compounds. A variable amount of the fluorine is volatilized as SiF_4, HF, or both. The amount volatilized and the form depend on phosphate rock composition and process conditions.

As a result of side reactions, numerous impurity compounds (some of them very complex) are formed. For a complete discussion of the nature of impurities, see Phosphoric Acid by A. V. Slack (2).

Heat Released in Reaction

The reaction involved in producing phosphoric acid from fluorapatite and sulfuric acid by the dihydrate process may be represented by the following equation:

$$Ca_{10}F_2(PO_4)_6\ (s) + 10H_2SO_4\ (liq.) + 20H_2O\ (liq.) \rightarrow 10CaSO_4 \cdot 2H_2O\ (s) + 2HF\ (aq.) + 6H_3PO_4\ (aq.)$$

The heat of reaction may be calculated by use of the following heats of formation of reactants and products.

Compound	Heat of Formation at 25°C, kcal/g-mole	Reference
$Ca_{10}F_2(PO_4)_6$ (crystalline solid)	3,267.2	Farr and Elmore (3)
H_2SO_4 (liquid)	193.91	National Bureau of Standards (4)
H_2O (liquid)	68.317	National Bureau of Standards (4)
$CaSO_4 \cdot 2H_2O$ (crystalline solid)	483.06	National Bureau of Standards (4)
H_3PO_4 (aqueous, 30% P_2O_5)	308.25	Egan and Luff (5)
HF (aqueous)	75.56	National Bureau of Standards (4)

The heat of reaction so calculated is 256.94 kcal/g-mole of apatite which is equivalent to 255 kcal/kg of apatite or about 600 kcal/kg of P_2O_5. The heat required to raise the temperature of the gypsum ($C_p = 0.272$) and phosphoric acid (30% P_2O_5; $C_p = 0.703$) from 25° to 82°C (77° to 180°F) is calculated to be 197 kcal/kg of P_2O_5 (6, 7). Thus, about 403 kcal/kg of P_2O_5 remains to be dissipated, and most processes provide a means of removing the excess heat. In practice, some of the heat is lost by convection and conduction. On the other hand, some heat may be brought in by use of heated wash water or, if the wash water is not heated, some of the heat in the gypsum is transferred to the recycled weak acid and thus returned to the reaction. Additional heat will be generated by reaction of additional sulfuric acid with impurities in the rock. Most phosphate rock contains 10%-20% more calcium than that required to form pure fluorapatite with the phosphorus in the rock, which may result from substitution of carbonate for phosphate in the apatite or presence of calcite or both. Reaction of this amount of calcium with sulfuric acid to form gypsum would increase the net heat of reaction per kilogram of P_2O_5 by about 11%-16%.

Hydrogen fluoride is shown as a product of reaction in the first equation. It reacts with the silica present as an impurity in phosphate rock to form fluosilicic acid which, in turn, forms fluosilicates and other compounds with impurities in the rock. The thermal effect of these reactions is negligible.

The net heat of reaction is influenced appreciably by the concentration of the sulfuric acid used, as shown by the following tabulation.

Concentration of Sulfuric Acid, % H_2SO_4	Net Heat of Reaction, kcal/g-mole of Apatite	Excess Heat to be Dissipated, kcal/kg of P_2O_5
100	256.94	403
98	247.54	385
93	224.54	329
90	211.54	299
85	191.94	253
80	174.24	211
75	160.74	180

If the conditions are such that the calcium sulfate crystallizes in the form of anhydrite or hemihydrate rather than gypsum, the excess heat to be dissipated is about 100 kcal/kg of P_2O_5 less than the values given above.

Types of Processes

Commercial wet processes may be classified according to the hydrate form in which the calcium sulfate crystallizes:

Anhydrite - $CaSO_4$
Hemihydrate - $CaSO_4 \cdot \frac{1}{2}H_2O$
Dihydrate - $CaSO_4 \cdot 2H_2O$

The hydrate form is controlled mainly by temperature and acid concentration. At present there is no commercial use of the anhydrite process, mainly because the required reaction temperature is high enough to cause severe corrosion difficulties. Processes in commercial use follow:

Crystal Form(s)	Number of Separation Steps[a]	Usual Conc. of Product Acid, % P_2O_5	Usual Temp., °C	
			Reactor	Recrystallizer
Dihydrate	1	26-32	70-85	-
Hemihydrate	1	40-50	85-100	-
Hemihydrate-dihydrate	1	26-30	90-100	50-60
Hemihydrate-dihydrate	2	40-50	90-100	50-65
Dihydrate-hemihydrate	2	35-38	65-70	90-100

a. Filtration or centrifuging steps.

At present, straight dihydrate processes are by far the most popular and, hence, will be described in the most detail. However, there is increased interest in two-stage processes that involve crystallization in the hemihydrate form followed by recrystallization in the dihydrate form (or vice versa), with or without intermediate separation by filtration or centrifuging. These processes will be described briefly.

Straight dihydrate processes are the most popular worldwide because they are relatively simple and adaptable to a wide range of grades and types of phosphate rock. In the case of some of the newer processes, experience has been limited to rock from a few sources, and the versatility of the processes has not been demonstrated.

Hemihydrate processes have the advantage of producing phosphoric acid of a relatively high concentration. This means that the concentration step can be eliminated if the concentration is high enough for the desired use, which will result in lower capital and operating costs. Since phosphoric acid plants often have onsite sulfuric acid production facilities that supply byproduct steam for phosphoric acid concentration, the advantage of eliminating the concentration step may depend on whether the steam can be profitably utilized for other purposes. Hemihydrate processes also claim the advantage of a sludge-free acid product and some decrease in the amount of impurities (especially aluminum) extracted from the rock and appearing in the product acid. The main disadvantages are the higher reaction temperature which increases corrosion and the increased complexity of some of the processes.

Hemihydrate-dihydrate processes without intermediate filtration are widely used in Japan. The Nissan "H" process is typical. One advantage is that the gypsum byproduct is pure enough for industrial uses without extensive treatment. This advantage is important in Japan where all natural gypsum is imported and expensive. The process also provides a very high recovery of P_2O_5 from the rock since losses in the gypsum are very low. The value of the 2%-3% increase in P_2O_5 recovery depends on the cost of the rock. The disadvantages are the higher cost and increased complexity of the process. Also some phosphate rock contains impurities that stabilize the hemihydrate, thereby preventing recrystallization to gypsum at an acceptable rate.

Hemihydrate-dihydrate processes with two filtration steps have the same advantages as the above-described single-stage Japanese process, plus the added advantage of producing phosphoric acid of relatively high concentration. Processes of this type that are in commercial use include the Fisons' HDH process and the new Nissan "C" process. The extra filtration step increases the cost and complexity of the plant, but this disadvantage may be offset by decreasing or eliminating the concentration step.

The dihydrate-hemihydrate process has about the same advantages and disadvantages as hemihydrate-dihydrate except that the hemihydrate byproduct may be more useful than gypsum in some cases. The Central Prayon process is the only one known to be in commercial use (in Belgium). On the other hand, the product acid concentration is somewhat lower.

In the following step-by-step general description of phosphoric acid production, it will be assumed that a standard dihydrate process is used unless otherwise stated. The discussion will be divided into the following steps:

1. Selecting phosphate rock,
2. Selecting source of sulfuric acid[1],
3. Receiving and storing raw materials,
4. Grinding and otherwise preparing of the rock,
5. Reacting the phosphate rock and sulfuric acid,
6. Filtering to separate phosphoric acid from gypsum[2], and
7. Concentrating and clarifying the phosphoric acid.

Description of Process

Selection of Phosphate Rock--Many phosphoric acid plants are built in countries where phosphate rock must be imported. The plant is often designed on the basis of some standard phosphate rock. However, it is often prudent to build into the plant sufficient flexibility to permit use of rocks from different sources. This versatility will enable the producer to take advantage of competitive situations and to avoid disruption of supply when the intended source is inadequate or interrupted by hostilities, disasters, or other circumstances. Many plants find it advantageous to use a blend of rocks from different sources. The extra expense in making the plant more versatile usually can be repaid many times over by savings resulting from freedom of choice in the world market. Some examples of steps to increase versatility of the plant are:

1. Extra grinding capacity for harder rock,
2. Extra filtration capacity to provide for rocks that cause less rapid filtration,
3. Slurry handling systems that will cope with acid-insoluble impurities in the rock, and
4. More corrosion-resistant construction for rocks that have corrosive impurities.

When the plant is built at or near the mine, there is still the likelihood that the rock composition will vary. In addition, there are other questions to be considered relating to the economic optimum balance between cost of extra beneficiation as compared with the cost of utilizing lower grade rock.

The selection of a phosphate rock source is sometimes viewed as a simple matter of obtaining a given amount of P_2O_5 in the rock delivered to the plant at the lowest price. However, phosphate rock is a very complex raw material which affects the plant operation in numerous ways, some of which may be unpredictable. Therefore, a thorough evaluation of all quality factors should be made before selecting a phosphate rock or changing from one source to another.

A complete chemical and mineralogical analysis of a phosphate rock is helpful in evaluating its usefulness for making phosphoric acid. However, this information is not sufficient in itself; trial runs in a plant or pilot plant are needed for a reliable evaluation unless the rock is one that has been used extensively in other similar plants with known results.

The following quality factors may provide a general guide for selection of phosphate rock for phosphoric acid production. The economic effect of many of the factors can be evaluated quantitatively to arrive at a comparative value of alternative sources of phosphate rock.

Starting with a standard grade of rock, the more common quality factors for wet-process phosphoric acid production and their effect are:

1. Lower grade (% P_2O_5) means that more tonnage must be bought, transported, handled, and (usually) ground.
2. An increase in the $CaO:P_2O_5$ weight ratio increases the sulfuric acid requirement. (Any CaO present as $CaSO_4$ should be excluded in calculating this ratio.)
3. Magnesium oxide forms precipitates with fluorine in the reactor which may blind the filter cloth; therefore, high MgO content is considered undesirable. When phosphoric acid is used to produce ammonium phosphates or polyphosphates, water-insoluble (but citrate-soluble) magnesium ammonium phosphate compounds may be formed. These compounds form troublesome impurities in liquid fertilizers.
4. Increases in the Fe_2O_3 + Al_2O_3 content above 2%-3% decrease the plant capacity, often decrease the P_2O_5 recovery, and cause post-precipitation problems (sludge). However, up to about 5% may be tolerable.
5. It is desirable to have enough reactive silica (SiO_2) to form SiF_4 and/or fluosilicates so as to avoid formation of free HF, which is corrosive. Excessive silica or other acid-insoluble impurities may cause erosion of equipment and possible accumulations in digestion vessels depending on particle size, character, and plant design. Also, a high percentage of silica in the rock would increase the required filter area.
6. Chlorine contents above about 0.01% cause increased corrosion of stainless steel. More expensive alloys may tolerate a Cl content of 0.10% or perhaps higher.
7. High organic matter may increase foaming problems (by stabilizing the foam), increase viscosity, and hinder filtration. The effect depends on both the character and quantity of organic matter. Some rocks must be calcined to remove organic matter to make them usable.
8. Carbon dioxide (CO_2) contributes to foaming and increases consumption of antifoam reagents.
9. All commercial phosphate rocks contain fluorine (F); no special effect has been noted due to variations in fluorine content within the range of experience. Effects of fluorine on scaling, corrosion, and post-precipitation are related to other elements that combine with fluorine, including Na, K, Al, Mg, and Si.
10. Some rocks which contain sulfides release hydrogen sulfide (H_2S) upon acidulation. This gas is toxic. Also sulfides tend to increase corrosion.
11. Many other less common impurities may be present in sufficient quantity to require consideration (TiO_2, SrO, BaO, Cd, etc.).
12. Hardness is a factor in that harder rocks require more grinding capacity.
13. The particle size of the rock as received affects the amount of crushing and grinding required. Very fine particle size may lead to dust losses in handling.
14. Low reactivity of the rock may require finer grinding.
15. Filterability of the rock-acid slurry is one of the most important characteristics of a phosphate rock for use in phosphoric acid production. Factors influencing filterability are complex and not completely understood. However, if a plant is to be designed to use a specific rock, an acceptable filtration rate can usually be attained through experimental means by adjusting operating condi-

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[1] Sulfuric acid production was described in chapter XII.

[2] Disposal of gypsum and fluorine byproducts will be dealt with in chapter XXIII (Pollution Control).

tions, addition of crystal modifiers, or pretreatment of the rock.

Table 1 shows the range of composition and median values of a group of 15 phosphate rocks from commercial sources. Although the group is representative, compositions outside this range have also been used.

TABLE 1. TYPICAL ANALYSIS OF COMMERCIAL PHOSPHATE ROCKS

Constituent	% by Weight	
	Range	Median
P_2O_5	29-38	33
CaO	46-54	51
SiO_2	0.2-8.7	2
$Al_2O_3 + Fe_2O_3$	0.4-3.4	1.4
MgO	0.1-0.8	0.2
Na_2O	0.1-0.8	0.5
CO_2	0.2-7.5	4.5
F	2.2-4.0	3.7
Cl	0.0-0.5	<0.02
SO_3	0.0-2.9	1.0
$CaO:P_2O_5$ weight ratio	1.35-1.70	1.5

Assuming 94% overall P_2O_5 recovery, the number of tons of phosphate rock required per ton of P_2O_5 recovered as phosphoric acid is:

	Grade of Rock, % P_2O_5	Rock Requirement, Tons/Ton of P_2O_5 in Acid
Low	29	3.67
Median	33	3.22
High	38	2.80

Calculation of Sulfuric Acid Requirement--Although the sulfuric acid requirement for production of phosphoric acid from any given rock is best obtained experimentally, it is sometimes necessary to calculate it from the chemical analysis of the rock. For a first approximation the sulfuric acid requirement may be equated to that required to combine with the calcium in the rock to form calcium sulfate. This calculated value is often close enough for planning purposes. The requirement per ton of P_2O_5 recovered should be adjusted according to the expected recovery. The overall recovery is seldom more than 94% if mechanical and sludge losses are included.

If a complete analysis of the rock is available, a more exact calculation may be made. The method is illustrated in table 2 and is explained below:

1. Assuming 94% overall P_2O_5 recovery, 1,064 kg of rock P_2O_5 is required per ton of P_2O_5 recovered.
2. If the rock contains 33% P_2O_5, 3,224 kg of rock is required.
3. The CaO content of the rock is calculated. If the rock contains any other cation that forms an insoluble sulfate (such as barium), its CaO equivalent should be added.
4. The CaO equivalent of the SO_3 content (not total S) should be taken into account.
5. Typical filter cake contains about 3.3% of the input P_2O_5 in insoluble forms of which 1% may be unreacted rock and 2.3% $CaHPO_4$ cocrystallized with gypsum. The aggregate weight ratio of CaO combined with P_2O_5 is about 1.0.
6. The empirical assumption is that 15% of the fluorine combines with CaO to form CaF_2. Actual reactions are much more complex; $Ca_4SO_4SiF_6AlF_6(OH)\cdot 12H_2O$ is an example of a complex insoluble compound found in filter cake.
7. Items 4, 5, and 6 are totaled.
8. Item 7 is subtracted from 3 to give net CaO for reaction with H_2SO_4.
9. The H_2SO_4 equivalent of the CaO is calculated.

TABLE 2. CALCULATION OF H_2SO_4 REQUIRED PER TON OF P_2O_5 RECOVERED AS PHOSPHORIC ACID USING MEDIAN ROCK ANALYSIS (TABLE 1)

Item	Kg per Ton of P_2O_5 Recovered
1. P_2O_5 required in rock at 94% recovery, $\frac{1,000}{0.94}$	1,064
2. kg of rock required per ton of P_2O_5 recovered, $\frac{1,064}{0.33}$	3,224
3. CaO in rock, 3,224 x 0.51	1,644
4. CaO equivalent to SO_3, 3,224 x 0.01 x $\frac{56}{80}$	22.6
5. CaO combined with P_2O_5 in filter cake, .033 x 1,064	35.1
6. CaO combined with fluorine, 0.15 x 0.037 x 3,224 x $\frac{56}{19x2}$	26.4
7. Total CaO not combined with sulfate	84.1
8. Net CaO for reaction with H_2SO_4, 1,644 - 84.1	1,559.9
9. H_2SO_4 required for $CaSO_4$, 1,559 x $\frac{98}{56}$	2,729.8
10. Excess H_2SO_4, $\frac{1.5}{30}$ x 1,000	50.0
11. Total H_2SO_4 required	2,779.8
Short Calculation	
12. H_2SO_4 required based on CaO only, 1,644 x $\frac{98}{56}$	2,877

10. The amount of excess H_2SO_4 is calculated by assuming that the 30% P_2O_5 acid contains 1.5% free H_2SO_4.

11. Total H_2SO_4 requirement is item 9 plus item 10.

12. A simplified calculation based on H_2SO_4 equivalent to total CaO is shown in table 2.

In the following tabulation the sulfuric acid requirement for median-grade rock is taken from table 2 (2.78 tons of H_2SO_4 per ton of P_2O_5), and requirements for rocks of other Ca:P_2O_5 ratios are estimated in proportion to that ratio.

	High	Median	Low
Grade of rock, % P_2O_5	38	33	29
Rock requirement, tons/ton of P_2O_5	2.80	3.22	3.67
CaO:P_2O_5 ratio in rock	1.70	1.50	1.35
H_2SO_4 requirement, tons/ton of P_2O_5	3.15	2.78	2.50

Source of Sulfuric Acid--Although sulfuric acid production is discussed in chapter XII, some aspects of the source of the acid will affect plans for phosphoric acid production. Most, but not all, phosphoric acid plants have onsite facilities for producing sulfuric acid from sulfur or pyrites. In this case, heat is recovered from the sulfuric acid plants in the form of steam which is available for concentrating phosphoric acid and other uses.

Recently, double-absorption processes have been used in sulfuric acid plants to control emission of SO_2. This practice adds appreciably to the cost and decreases the amount of steam available for export. An alternative is to use an ammonia scrubbing system to recover SO_2 from the tail gas of a single absorption plant followed by acidulation with sulfuric, phosphoric, or nitric acid to release a concentrated stream of SO_2 for return to the sulfuric acid plant and a solution of ammonium sulfate, phosphate, or nitrate for use in a fertilizer plant (see chapter XII).

Finally, sulfuric acid from pyrites, smelter operations, or other byproduct sources may contain impurities that may or may not be deleterious for phosphoric acid production. In at least one case, zinc in smelter acid proved useful since the fertilizer produced from phosphoric acid contained enough zinc, mainly derived from the smelter acid, to improve crop yields in zinc-deficient areas.

Receiving and Storing Raw Materials--An efficient system for bulk handling and storing phosphate rock and other raw materials is necessary for a modern phosphoric acid plant. (Other raw materials are discussed elsewhere.) The criteria to be met are:

1. Rapid unloading of ships or other delivery units;
2. Negligible loss of rock;
3. Easy storage with ability to separate shipments or to blend shipments as desired;
4. Efficient retrieval from storage;
5. Protection against wind, rain, snow, and freezing weather;
6. Protection from contamination with other raw materials, windblown dust, soil, etc.; and
7. Provision for expansion if future needs warrant.

When phosphate rock is received dry, it is usually desirable to keep it dry by covered storage, especially if it is to be used in a dry grinding system in order to avoid the expense of redrying. If open storage is used, wind or heavy rains can cause losses of rock that may amount to several percent if it contains much fines. However, relatively coarse rock can be stored in open piles, particularly if it is to be wet ground. The storage capacity should be at least 1½ times the largest shipment to allow for delays. Even larger storage capacity may be advantageous for blending shipments.

Rock Grinding and Preparation--The choices in rock grinding seem to be dry grinding, wet grinding, or no grinding. Several processes claim the ability to use rock without grinding if it is finer than 35-mesh or in some cases 20-mesh (Tyler) screen size (0.417 or 0.833 mm). Somerville suggests that such coarse rock is suitable for single tank digester processes when sulfate control is good, but finer grinding is needed for multicompartment digesters and when sulfate control is poor (8). Houghtaling states that older Prayon-type plants (which use multicompartment digesters) required grinding to 60% minus 200-mesh (0.074 mm). Newer plants of the same type specify only 25% minus 200-mesh, 60% minus 100-mesh, and all minus 35-mesh (Tyler) (9).[3]

Most of the older plants and some of the new ones use dry grinding. Ring roller mills or ball mills are often used with air classification. The power requirement naturally depends on the initial size of the rock, its hardness, and the desired particle size. For grinding Florida rock to 55% minus 200-mesh, a requirement of 15-20 kWh/ton of rock has been suggested, including air classification and pneumatic conveying to ground rock storage. Softer rocks may require one-half to two-thirds as much power.

There is a general tendency toward wet grinding in newer plants that are located near the mine. The wet grinding is done in a ball mill; a slurry containing 62%-70% solids is produced and fed to the digester via a surge tank. Advantages of wet grinding are 30%-40% reduction in power requirement and elimination of dust losses, atmospheric pollution by dust, and the necessity of drying the rock. The main disadvantages are somewhat faster wear of the balls and mill lining and a decrease in the amount of recycled water that can be used elsewhere in the plant. It is also necessary to maintain reasonably close control of the water:solids ratio in grinding.

The power requirement for wet-grinding 180 short tons per hour of Florida rock to minus 35-mesh was given by Shearon as 2,500 hp for closed circuit grinding and 3,800-4,000 hp for open circuit grinding (10). The corresponding power consumption is 11.4 kWh and about 18 kWh/mt for closed- and open-circuit wet grinding, respectively.

There is some difference of opinion about the need for fine grinding of very unreactive rocks such as igneous apatite. Lutz and Pratt (11) suggest that such rock should be ground to 80% minus 200-mesh; whereas Somerville considers that rock reactivity is not a major factor. According to Somerville, unground Meramec (Missouri) apatite (minus 150-mesh) is satisfactory. The explanation of this difference of opinion probably lies in the type of digester used (8).

Calcining of phosphate rock usually is considered part of beneficiation. However, some phosphoric acid producers who purchase rock also calcine it to eliminate organic matter or to decrease carbonate content or both. One purpose in calcining is to improve the color of products such as liquid fertilizer or nonfertilizer products such as sodium tripolyphosphate. However, Stern stated that one phosphoric acid plant was able to increase production by 30%-40% by switching from uncalcined to calcined rock (12). A saving in foam-control reagents is another advantage.

Reaction System--There are so many types of reaction systems in use throughout the world that no

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[3] A table comparing Tyler sieve sizes with other systems is given in chapter XXII.

attempt will be made to identify all of them. The objective in designing the reaction system is to carry out the reaction between phosphate rock and sulfuric acid in such a way as to recover a maximum percentage of the P_2O_5 originally in the rock as product phosphoric acid in the simplest and least expensive manner. Since the filtration step is the most critical and expensive step in the process, a primary objective in the reaction step is to form gypsum crystals of such size and shape that the filtration and washing can be carried out rapidly and efficiently.

Maximizing recovery means minimizing losses. Three types of P_2O_5 losses are recognized: (1) unreacted phosphate rock, (2) P_2O_5 cocrystallized with gypsum through isomorphic substitution of HPO_4^{--} for SO_4^{--}, and (3) phosphoric acid lost in the gypsum due to incomplete washing. Perhaps a fourth source of loss should be mentioned--mechanical losses due to spillage; leakage; washing of filter cloth, piping, and equipment for scale removal; and losses as sludge.

Although the objectives of the reaction step are clear, the means for attaining them may seem complicated. To the uninitiated, it might seem that the best way to carry out a chemical reaction would be to mix the two reactants directly. In practice, however, reaction systems are designed to prevent direct contact between the two reactants, phosphate rock and sulfuric acid. One purpose of this arrangement is to ensure slow growth of gypsum crystals to a relatively large size rather than formation of many small ones. Also, a high concentration of free sulfuric acid will result in coating the phosphate rock with calcium sulfate reaction product, thus blocking further reaction. A serious case of "reaction blocking" in a phosphoric acid plant can take several hours or even days to correct. On the other hand, a high concentration of calcium ions (low sulfate) in the slurry will increase the amount of phosphate cocrystallized with the gypsum. Hence, the aim of designers and operators of reaction systems is to maintain a uniform composition of the slurry, avoiding pockets of high sulfate or calcium concentration. The liquid phase usually consists of phosphoric acid (about 30% P_2O_5) with about 1.5% free sulfuric acid; the optimum concentration of free sulfuric acid varies with rock composition. The solid phase is mainly gypsum. The proportion of solids in the slurry is about 35%-45%. Phosphate rock particles introduced into this slurry dissolve rapidly in the phosphoric acid in the liquid phase causing supersaturation with calcium sulfate, which results in the growth of gypsum crystals.

To approach this ideal situation, the incoming streams of sulfuric acid and phosphate rock are mixed with the slurry (directly or indirectly) as rapidly and completely as possible, and the slurry in the reaction system is agitated to ensure homogeneity.

A simplified flow diagram of a modified Prayon system (Davy Powergas) is shown in figure 1. The "attack" tank is divided into four to eight compartments, depending on the size of the plant. The sulfuric acid is premixed with recycled weak phosphoric acid and discharged into the first, second, or third compartment depending on the type of rock. The rock slurry from wet grinding is discharged into the first, second, or third compartments or divided among them. For temperature control, a portion of the slurry is withdrawn to a vacuum flash cooler. Part of the cooled slurry is returned to the "attack" system, and part is sent to the digester system. A large volume of slurry is recirculated through the attack system from the last compartment to the first.

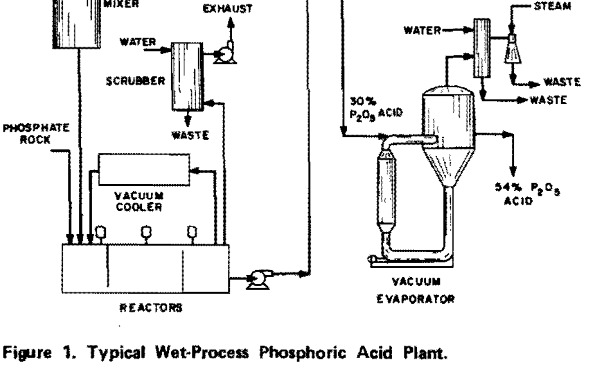

Figure 1. Typical Wet-Process Phosphoric Acid Plant.

The "digester" tanks permit completion of reactions and lowering of any supersaturation under mild agitation. Also small adjustments can be made here by the addition of sulfuric acid or phosphate rock. Plants of the type illustrated have been built with capacities as high as 1,140 tons of P_2O_5 per day in a single train.

In other dihydrate processes, the phosphate rock may be premixed with recycled weak phosphoric acid or with recycled reaction slurry. Sulfuric acid may be sprayed on the surface of the slurry in the reactor vessel.

In many older plants, the sulfuric acid was diluted, sometimes to 55%-60% H_2SO_4, and cooled in a heat exchanger before use. Most modern plants use the sulfuric acid at the concentration at which it is received, usually 93% H_2SO_4.

When strong sulfuric acid is premixed with weak recycled phosphoric acid, much heat is released, and this is accompanied by evaporation of water and volatilization of fluorine compounds (mainly SiF_4 and HF). In some plants this step is carried out in a flash vacuum cooler, providing a rich stream of fluorine compounds in the vapor which can be recovered as fluosilicic acid for sale or further processing.

Several processes use a single-tank reactor. One of these is known as the Gulf Design Isothermal Process, using a Swenson crystallizer as a reactor. A diagram of the reactor system is shown in figure 2.

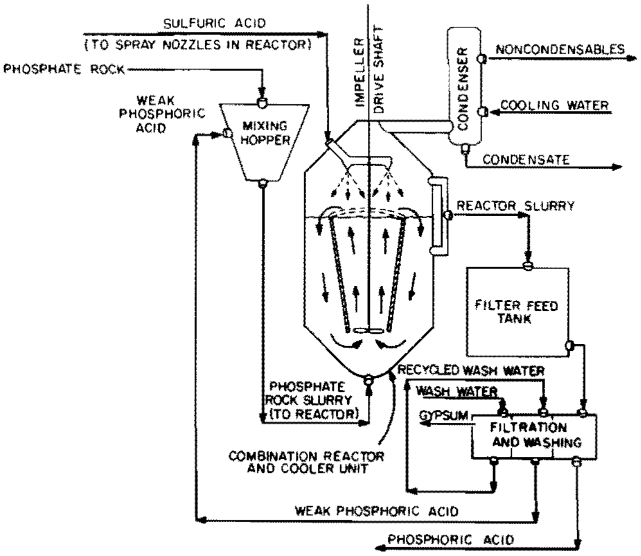

Figure 2. Phosphoric Acid via the Swenson—Gulf Design Isothermal Reactor System.

It should be noted that strong sulfuric acid is sprayed on the surface of the slurry in the top of the reactor, while the phosphate rock is premixed with recycled phosphoric acid and pumped in at the bottom of the vessel. The entire vessel is under reduced pressure, thereby controlling the temperature by evaporation. The circulation pattern is controlled by an agitator in a draft tube. It is claimed that the temperature varies less than 0.3°C from one part of the reactor to another. The plant illustrated in figure 2 is rated at 640 tpd, using unground Florida flotation concentrates (0.10-0.41 mm). Advantages claimed are use of wet, unground rock; lower capital, operating, and maintenance costs; and excellent control of atmospheric pollution.

Another type of reaction system is described by Somerville and illustrated in figure 3. In this process, phosphate rock (0.5 mm or smaller) is mixed with recycled slurry in a cone mixer and discharged to the reactor. Sulfuric acid is premixed with recycled phosphoric acid, and the mixture is discharged into a vacuum cooler. A relatively small flow of slurry is drawn from the reaction vessel to the vacuum cooler and recycled to the reactor to control the reaction temperature. Typical operating temperatures are 84°C in the reactor and 73°C in the cooler. By minor modifications the system can be operated as a hemihydrate process in which case the temperatures are about 100°C in the reactor and 83°C in the cooler.

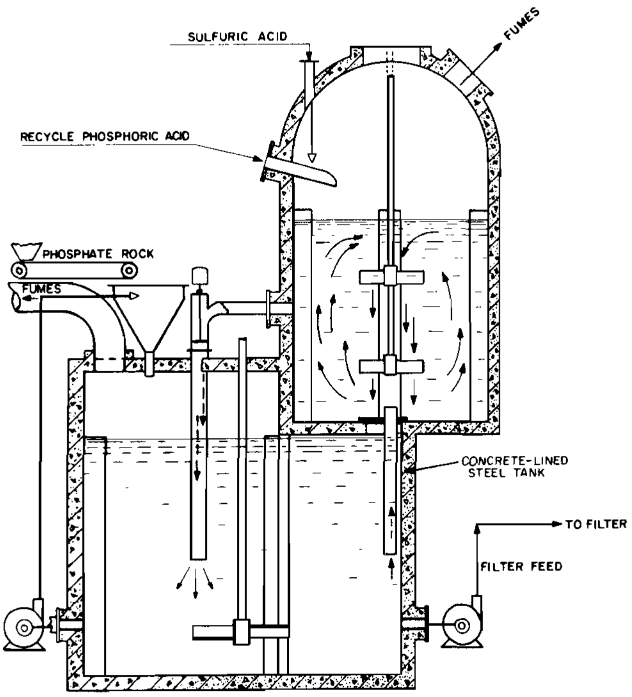

Figure 3. Somerville Phosphoric Acid Reaction System.

The arrangement shown is recommended for plants with capacities of approximately 360 tons or less of P_2O_5 per day. For larger plants (720-tpd), two vacuum coolers are recommended with sulfuric acid feed going to one and filter feed drawn from the other.

Some advantages claimed are better gypsum filtration, lower P_2O_5 losses in the gypsum, and lower capital and operating costs. Also, it is claimed that low-cost, small plants (20-50 tpd) may be economical for some situations.

One interesting cost-saving practice advanced by Somerville is the extensive use of concrete as a material of construction for reactor and cooling vessels. Based on 25 years' experience, Somerville claims that concrete, with proper design and installation, is inherently resistant to wet-process phosphoric acid attack, provided it is made with acid-resistant aggregate such as siliceous sand and gravel. Also repair or replacement costs are low.

Another process employing a single tank reactor is the Rhone-Poulenc process, illustrated in figure 4.

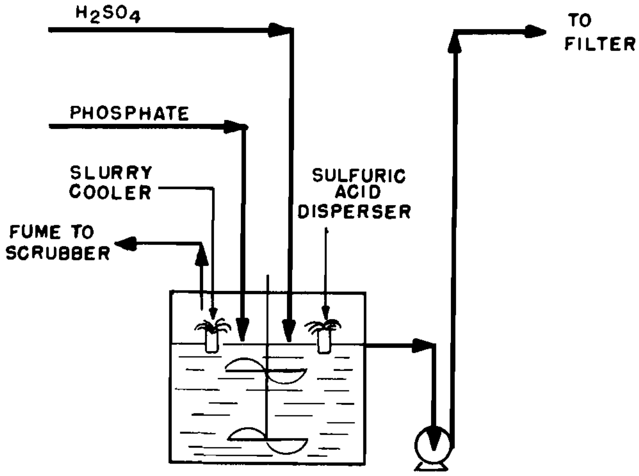

Figure 4. Rhone-Poulenc Phosphoric Acid Reaction System.

One feature of this process is that the temperature in the reactor is controlled by a flow of air over the surface of the slurry in the reactor. To assist in evaporative cooling, special spray-like devices pick up some of the slurry from the surface and shower it in droplets through the air-swept space in the reactor above the slurry level. Sulfuric acid is also added as a spray at the top of the reactor. Phosphate rock is introduced through a center well to a zone of maximum agitation. The system has been used in units producing 100-800 tons of P_2O_5 per day.

No attempt will be made to describe or even mention all of the phosphoric acid processes that are available or in use throughout the world.

The processes described above are believed to be fairly representative of dihydrate processes. The Kellogg-Lopker process (used in England) employs a novel two-tank reactor system. One unusual feature is the short retention time--about 1.5 hours--compared with about 8.0 hours for most other systems. Fisons Ltd., Nissan, and the Dorrco Division of Jacobs Engineering offer dihydrate, hemihydrate, and two-stage processes. Most major fertilizer plant engineering and construction firms offer phosphoric acid processes either of their own origin or under license from the developers.

While most plants operate with a small excess of sulfuric acid, it is possible to operate with a deficiency of sulfuric acid but with an excess of SO_4 by replacing part of the sulfuric acid with an equivalent amount of ammonium sulfate (or other soluble sulfate). Up to about 10%-15% of the sulfuric acid can be replaced by ammonium sulfate. This process modification may be advantageous for utilizing small amounts of byproduct ammonium sulfate. A further advantage is lower corrosion rates. A disadvantage is longer reaction time (up to 18 hours). Also the phosphoric acid produced by this process contains ammonium phosphate; therefore, its use is limited to production of ammonium phosphate or compound fertilizers.

In other process modifications free sulfuric acid may be neutralized (partially or entirely) after digestion or filtration with ammonia or calcium phosphate to render it less corrosive in subsequent steps. In case of neutralization with calcium phosphate, additional calcium sulfate is formed and can be removed. Elimination or reduction of sulfate in phosphoric acid makes it possible to make higher analysis fertilizer products.

Reaction Time and Retention Time--Somerville states that the average life of a phosphate rock particle in a typical reaction system may range from 15 seconds to 3 minutes. Nevertheless, retention times in industrial plants range from 1.5-12.0 hours or more (8). One of the reasons is connected with the formation of good gypsum crystals, as discussed previously. Another reason is the difficulty of close control of free sulfuric acid (SO_4^{--}) content of the liquid phase when the reaction time is short. Close control of this value is extremely important. Although the optimum level of control may depend on the character of the rock, a level of about 1.5% is typical. Serious upsets can occur when the SO_4 level varies appreciably from the optimum. Obviously, the shorter the reaction time, the faster (and more often) one can get into trouble. The success of the 1½-hour reaction time in the Kellogg-Lopker process is likely related to the use of an automatic sulfate analysis instrument that permits close control and rapid adjustments.

Filtration--The function of the filtration step is to separate the gypsum (and any insoluble materials derived from phosphate rock or formed in the reaction) from the phosphoric acid product as completely, efficiently, and economically as possible. All modern plants use continuous filters, although batch filters have been used in small plants in the past.

The most popular types of filters are the tilting-pan rotary filters, traveling pan filters, horizontal table filters, and belt filters. In each of these filters, the cycle proceeds through the following steps: (1) deposition of the phosphoric acid-gypsum slurry on the filter, (2) collection of product acid by application of vacuum; (3) two or three countercurrent washes to complete the removal of phosphoric acid from the gypsum; (4) discharge of the washed gypsum; and (5) washing of the filter cloth to prevent accumulations of scale-forming materials. The sequence of operations is illustrated in figure 1. In the washing sections, successively weaker solutions of phosphoric acid are collected. The last wash is with fresh water or sometimes with water recycled from a gypsum pond or from sumps that collect cloth-washing water and spillage or drippings. The very weak acid collected in the last section is returned to the preceding section with the filtrate from the first wash being recycled to the reaction vessels. Some of the product acid also may be recycled to the digestion step to control the percentage of solids in the slurry at a manageable level, usually 40%-45%.

Filters are usually rated according to their active surface area, which may range up to about 170 m^2. The rate of rotation (in a rotary filter) or the rate of travel (in a belt filter) is variable to permit adjustments as required by the filtration characteristics of the slurry and other factors.

The production rate may vary widely, but a common design factor is 6.5 tons of P_2O_5/m^2/day. The filtration rate is affected primarily by the size and shape of gypsum crystals which, in turn, are affected by conditions in the reaction section including the type of phosphate rock, use of crystal shape modifiers, control of reaction conditions, etc. Insoluble impurities in the rock, such as clay, may affect filtration rates adversely. The filtration rate is also affected by the temperature, concentration, viscosity of the acid, and the desired recovery. While many plants strive for maximum recovery, in specific plants there is often an economic optimum operating rate, at which increased production is attained at some sacrifice of recovery.

Filtration rates also depend on the design of the filter, amount of vacuum, and numerous other factors. Moraillon, et al., give illustrations ranging from 2 to 18 tons/m^2/day (13). Shearon mentions rates ranging from 0.8 to 1.0 short ton/ft^2/day (7.8 to 9.8 mt/m^2/day) for Florida plants (10).

Concentration and Clarification of Phosphoric Acid--Phosphoric acid produced by most dihydrate processes contains 26%-32% P_2O_5 (filter acid). Acid of this concentration can be used in some fertilizer processes, but for most purposes it is economically preferable to concentrate it by evaporation of part of the water content. The desired concentration depends on the use; some illustrations follow.

Use	Acid Concentration, % P_2O_5
Triple superphosphate - den process	50-54
Triple superphosphate - slurry process	38-40
Diammonium phosphate	about 40
Monoammonium phosphate (depending on process)	40-54
Shipment (merchant grade)	54[a]
Superphosphoric acid for shipment or liquid fertilizer production	69-72

a. Although 54% P_2O_5 is the usual standard for merchant-grade acid, variations are in the range of 50%-60%.

The above concentrations are merely guides to standard practice; it is quite possible to use other concentrations in most cases. For instance, 30% P_2O_5 acid has been used for TSP production by a process requiring extensive drying of the product. However, energy is usually more efficiently used by concentrating the acid than by drying the product with high rates of recycle. This is especially true when energy is available in the form of steam from an adjacent sulfuric acid plant.

Precipitates form in phosphoric acid before, during, and after concentration. Compounds precipitating before concentration are likely to be mainly calcium sulfate and fluosilicates. A wide variety of compounds may form during and after concentration, depending on acid concentration. These compounds are collectively known as "sludge" and cause many difficulties in handling and use of the acid. They also form scale in evaporators. Therefore, many manufacturers clarify the acid and either recycle the sludge or use it in fertilizer products where it causes the least trouble. Acid for shipment, in particular, should be well clarified. Phosphoric acid produced by hemihydrate processes (40%-50% P_2O_5) is reported to be relatively free from sludge.

Much of the fluorine is volatilized during evaporation and must be recovered to prevent pollution. In some cases salable fluorine byproducts are produced such as fluosilicic acid, fluosilicates, cryolite, or aluminum fluoride.

Phosphoric acid concentrators may be classified as direct-fired or indirectly heated. In direct-fired evaporators, combustion gases come into direct contact with the acid, as in a spray tower or submerged combustion evaporators. Use of this type is declining because of the difficulty of cleaning the exhaust gases to recover acid mist and fluorine compounds. As an exception superphosphoric acid is produced in several plants by concentrating 54% P_2O_5 acid to 69%-72% P_2O_5 in a direct-fired evaporator similar to a submerged combustion evaporator. Figure 5 shows a diagram of a TVA pilot plant of this type. Subsequent improvements and modifications have been made in commercial-scale units, one of which is known as the Oxy-Nordac evaporator. Somewhat similar evaporators have been developed by Prayon, Nordac, and others for concentrating filter acid from 30% to 50%-55% P_2O_5. The fuel requirement for concentrating from 30% to 54% P_2O_5 is about 1,400,000 kcal/ton of P_2O_5. Also, about 70 kWh of electrical energy is required per ton of P_2O_5. Any solid or gaseous fuel may be used, and some types of coal can be used. Concentration from 54% to 70% P_2O_5 requires about 600,000-800,000 kcal/ton of P_2O_5.

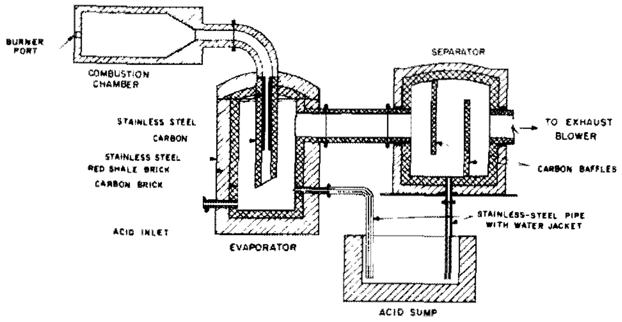

Figure 5. Pilot Plant for Concentration of Wet-Process Phosphoric Acid.

Indirect-heated evaporators usually are heated by steam or in some cases by a heat-transfer medium such as Dowtherm which, in turn, is heated in a fuel-fired heat exchanger. Common types are tubular evaporators, usually with forced circulation, or evaporator-crystallizers. The latter type is intended to convert the precipitating impurities into relatively coarse crystals to decrease scale formation and facilitate removal by settling or centrifuging. Concentration from 30% to 54% P_2O_5 may be carried out in one, two, or three stages, depending on the scale of operation.

Concentration from 30% to 54% P_2O_5 requires about 1.9 tons of steam per ton of P_2O_5 in the acid concentrated. This amount is usually available from the sulfuric acid manufacture if the sulfuric acid is manufactured by burning sulfur. Electric power requirements may range from 11 to 16 kWh/ton of P_2O_5 depending on the scale of operation. About 6 tons of cooling water per ton of P_2O_5 is required for condensing the water evaporated from the acid.

The amount of fluorine removed during concentration from 30% to 54% P_2O_5 may be 70%-80% of that originally present in the acid, most of which is volatilized and recovered in the condensate.

For concentration from 54% to 70% P_2O_5, about 1 ton of high-pressure steam (about 27 atm pressure and 230°C temperature) is required per ton of P_2O_5. Power requirements are about 24 kWh/ton of P_2O_5. When Dowtherm heat transfer medium is used, the fuel requirement is about 640,000 kcal/ton.

In production of superphosphoric acid (69%-72% P_2O_5) by concentrating wet-process acid, most of the fluorine is volatilized so that the acid contains only 0.2%-0.3% F. By addition of reactive silica during evaporation to enhance fluorine volatilization, the fluorine content can be further decreased to about 0.1%. Such acid is suitable for manufacture of animal-feed supplement products, such as dicalcium phosphate or ammonium phosphate, and is used for that purpose. Other advantages of superphosphoric acid are:

1. Savings in freight occur if the acid is shipped.
2. Sludge is eliminated. The polyphosphoric acids sequester most common impurities; however, in some acids, titanium or magnesium pyrophosphates may precipitate.
3. Superphosphoric acid is much less corrosive than lower concentrations.
4. Superphosphoric acid is suitable for production of clear liquid fertilizers (ammonium polyphosphate solutions) since the polyphosphate sequesters impurities that otherwise would precipitate upon ammoniation (see chapter XIX).
5. Superphosphoric acid can be used to produce compound fertilizers by melt processes in which the drying step is eliminated (see chapter XIX).

The main disadvantages of superphosphoric acid are the energy requirement, corrosion in some types of evaporators, and the high viscosity. The viscosity depends on temperature, concentration, and impurity content; some superphosphoric acids must be heated to 60°C or higher to permit pumping with centrifugal-type pumps.

The compositions of superphosphoric acids produced from several types of phosphate rock are shown in table 3.

Utilization of Sludge--As mentioned previously, sludge impurities precipitate in phosphoric acid before, during, and after concentration. If the acid is used onsite for fertilizer production, it may be possible to use the acid without separating the sludge. However, in some cases the amount of sludge may be so great as to lower the grade of fertilizer products below that desired.

Sludge solids that form in filter acid (30% P_2O_5) are mainly gypsum and fluosilicates and may, in some cases, be returned to the phosphoric acid production unit without serious interference with its operation. Sludge forming after concentration is likely to contain a high proportion of iron and aluminum phosphate compounds. One example is $(Al, Fe)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. Lehr has identified 38 distinct crystalline compounds occurring in sludge from wet-process acids (14). The return of iron and aluminum compounds to the acid-production unit is likely to cause some difficulty. When this sludge must be separated, as is usually the case for shipment, it is often used for production of TSP. Most of the P_2O_5 in the sludge solids is citrate soluble but not water soluble; therefore, this solution is not advantageous when the TSP is sold on the basis of water solubility.

The sludge may be used in the production of nongranular monoammonium phosphate (MAP) which, in turn, is used as an intermediate in the production of compound fertilizers. There is no standard grade

TABLE 3. CHEMICAL COMPOSITION OF SUPERPHOSPHORIC ACIDS

Type of Rock:	Florida	Western United States	North Carolina	Morocco	Togo	Taiba
Calcination:	No	Yes	Yes	No	No	No
Composition, % by weight						
Total P_2O_5	72.9	72.5	71.2	72.4	73.0	72.1
Ortho P_2O_5	31.8	34.0	37.6	25.1	35.3	27.1
Fe_2O_3	2.2	1.2	1.4	0.6	1.9	2.4
Al_2O_2	1.8	3.0	1.3	0.4	0.9	0.5
F	0.3	0.3	0.4	0.1	0.1	-
SO_3	2.0	2.1	3.4	2.7	1.7	3.3
MgO	0.3	0.8	0.6	1.1	0.1	0.1
Color	Black	Green	Green	Green	Dark	Dark
Polyphosphate content, % of total P_2O_5	56	53	47	65	52	62.5

for MAP to be used as an intermediate; the user can formulate compound fertilizers on the basis of actual analysis. In this case also, the iron, aluminum, and magnesium compounds are not water soluble. In fact, there is no economical method for utilizing sludge solids in countries where phosphate fertilizer is sold on the basis of water solubility.

Precipitation after concentration to 54% P_2O_5 is slow and never so complete but that more precipitate will form on further storage. However, clarification methods are available that reduce the sludge problem in merchant-grade acids to manageable levels.

Materials of Construction--Although choice of materials of construction is very important, only a brief treatment is possible in this manual. Corrosion rates in phosphoric acid plants are quite variable because of the complex nature of the acid. Factors affecting corrosion rates are not sufficiently well understood to predict accurately how they will be affected by change in rock composition or operating conditions. Therefore, the additional cost of more resistant materials is often economically justifiable, particularly when rock from various sources is likely to be used or when the rock source or operating conditions can be expected to result in highly corrosive conditions. Reaction tanks are often made of rubber-lined steel or concrete with an inner lining of carbon brick. Rubber-lined steel may be used for storage tanks. The use of unlined concrete for reaction tanks has been mentioned previously; its success depends on selection of acid-resistant aggregate and proper installation. Specimens of the concrete should be tested in acidulation slurries before use in plant construction.

The most vital and vulnerable portions of the phosphoric acid plant are agitators, pumps, and filters. Corrosive conditions are the most severe for agitators. However, agitators can be replaced with relative ease and low cost. Filters, on the other hand, are large and expensive and not so easily replaced or repaired. Corrosive conditions are somewhat less severe for the filter than for the agitators because the average temperature is lower and erosion is a lesser factor.

For many years, 316L stainless steel has been a common material of construction for agitators, filters, and other equipment coming in direct contact with wet-process phosphoric acid or reaction slurry. However, there is a growing tendency to use more resistant alloys in new plants, particularly when the rock source may be subject to change or more severe conditions of operation. In order of increasing corrosion resistance, 317L stainless steel, Ferralium, and UB6 alloy are finding increasing use. Many similar alloys are available under other names or designations; these four alloys are mentioned by way of illustration. Their compositions are:

	316L	317L	Ferralium	UB6
Cr	16-18	18-20	25	20
Ni	10-14	11-15	5	15
Mo	2-3	3-4	2	4-5
Cu	-	-	3	1.5
C	<0.03	<0.03	<0.06	<0.02

The cost of 316L stainless steel in U.S. dollars per kilograms is about \$4.4-\$5.2 for castings and \$3.2-\$4.0 for sheet. The cost of the 317L alloy is about 10% higher; ferralium, 25% higher; and UB6, 50% higher. However, this extra cost can easily be justified by longer life, fewer delays for repairs, and greater flexibility in choice of rock and operating conditions.

Hemihydrate and Two-Stage Processes--No attempt will be made to describe the numerous hemihydrate and two-stage processes. However, the simplified flow diagram, figure 6, for the Trepca (Yugoslavia) plant using the Fisons HDH process is more or less typical. A brief description of the process follows (15).

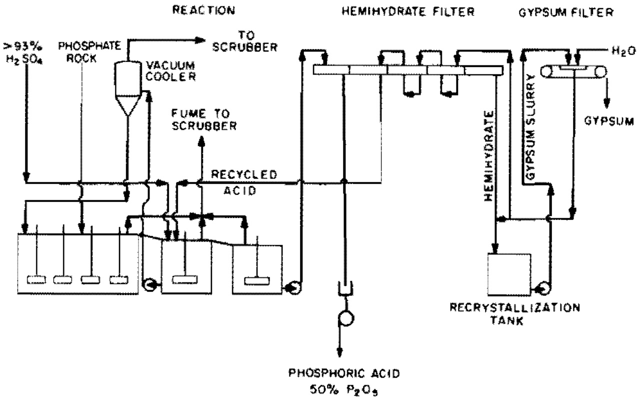

Figure 6. Flow Diagram for Hemihydrate-Dihydrate Phosphoric Acid Process.

The Fisons two-stage hemihydrate or HDH process, as constructed for Trepca, is for the production of 50%-52% P_2O_5 phosphoric acid at high efficiency--generally 98.5%. The process consists of a hemihydrate reaction system, hemihydrate filtration, a recrystallization stage, and dihydrate filtration.

Phosphate rock, 100% less than 1.7 mm, is fed to the first reactor via a weigh belt. The slurry from the first reactor overflows to the second reactor to which premixed sulfuric acid and "return acid" are added. The temperature in both reactors is controlled within 98°-100°C by circulating the slurry through a flash cooler to remove the excess heat of reaction and dilution.

The reaction conditions in both reactors are important since the success of the process depends on the satisfactory growth of uniform crystals with a high filtration and washing rate.

Sulfate control of the acid in reactors is important, and a fixed proportion of the slurry pumped from the second reactor to the flash cooler is recycled to the first reactor to control the precipitation rate of calcium sulfate in this reactor and, thus, the crystal size. Any excess slurry is returned to the second reactor at the 1.5%-2.0% sulfate level, and the slurry then overflows to the filter feed tank.

The first reactor is a fully baffled tank with four six-bladed agitators, two pumping up and two pumping down, to achieve a highly efficient "turnover" flow pattern of the slurry. The second reactor and the filter feed tank are equipped with single six-bladed agitators and are, likewise, fully baffled.

The Fisons process uses two independently controlled filters for the filtration of the slurries. This enables the speed and cake thickness to be optimized on both filters separately.

Slurry from the filter feed tank is pumped to the hemihydrate filter--a standard horizontal tilting-pan vacuum filter with three countercurrent wash stages. "Dihydrate return acid" recycled from the second stage is used for the final cake wash and the pan wash.

The acid from the first wash stage, together with a part of the product acid, is returned to the reaction system. This is the "hemihydrate return acid" which is premixed with 98% sulfuric acid and fed to the second reactor. The remainder of the product acid is pumped to the 50% P_2O_5 acid storage tanks.

The hemihydrate, discharged from the first-stage filter, passes via a chute into an agitated recrystallization tank. In this tank the residence time, solids content, and chemical composition are controlled to ensure complete recrystallization of the hemihydrate to dihydrate. Coprecipitated lattice P_2O_5 is released from the hemihydrate during the process. Sulfuric acid is added to the recrystallization tank to fix the calcium ions so released and to maintain optimum conditions for maximum P_2O_5 recovery and promote the growth of good dihydrate crystals.

The dihydrate slurry is pumped to a continuous belt filter where it is washed with incoming fresh water. The filtrate, the so-called "dihydrate return acid" which contains the recovered lattice P_2O_5, is recycled to the hemihydrate filter as the final cake wash and pan wash. The dihydrate cake is discharged dry from the filter and reslurried in an agitated tank and pumped to disposal. Alternatively, a dry discharge could be used.

Acid spillage is collected in a floor sump and returned to the recrystallization tank. A wash tank is installed to allow a routine closed-circuit wash for the filter equipment with hot water or chemical solutions, if required. No regular washing is required for the reaction slurry equipment.

Some of the fluorine fed with the rock is evolved, and this may be recovered as H_2SiF_6. With standard-grade Morocco rock, 40%-50% of the fluorine, fed in the rock, is evolved in the flash cooler and the reactors.

The vapors from the flash cooler pass to a two-stage vacuum scrubbing tower. In the primary fluorine scrubber, the vapors are scrubbed with recirculating H_2SiF_6. Fresh water is fed into the secondary fluorine scrubber, and a total fluorine recovery in excess of 99% is guaranteed, as a 23% H_2SiF_6 byproduct.

The exhaust gases from the reactors and the hemihydrate filter are passed through a gas scrubber operated under atmospheric pressure, for which the same fluosilicic acid concentration and scrubbing efficiency are obtained.

Advantages of hemihydrate-dihydrate processes in general have been discussed previously. In this particular case there was no surplus steam available from sulfuric acid production; thus, avoidance of the need for steam for acid concentration was an important advantage.

Economics of Phosphoric Acid Production

Raw Material Costs--The cost of producing phosphoric acid is strongly affected by the cost of the raw materials--phosphate rock and sulfuric acid. The quantities of these raw materials, per ton of P_2O_5 recovered, are affected by the grade of the rock and its $CaO:P_2O_5$ ratio, as discussed previously. In further discussion, only the median requirements will be used, but it should be remembered that requirements can vary substantially from the median.

In early 1977, list prices of 72 BPL Morocco rock were \$38.00/ton (Kouribga) and \$35.25/ton (Youssoufia) f.a.s. Moroccan ports; Florida 72 BPL rock was listed at \$28.50/ton, f.o.b. Tampa. Contract prices for large quantities may be substantially lower. Ocean freight rates may range up to \$20/ton (from Morocco to India, for example). In addition, unloading and inland transportation costs could increase the delivered costs up to \$80/ton in some cases.

Delivered costs of sulfur recently ranged from \$50 to \$70/ton. Sulfuric acid made from sulfur costing \$50/ton is likely to cost \$30/ton or more. Assuming rock at \$50 and sulfuric acid at \$30, the sum of the cost of these two raw materials is \$244/ton of P_2O_5 as phosphoric acid.

Phosphate rock	3.22 x \$50 =	\$161
Sulfuric acid	2.78 x 30 =	83
	Total	\$244

Since the current world market price of phosphoric acid is about \$200/ton of P_2O_5, it seems evident that the production of phosphoric acid from imported raw materials is not economically attractive at present (1978). However, the price of phosphate fertilizers and intermediates is currently depressed because of the oversupply. Forecasts indicate that the oversupply will continue at least through 1981.

Most new phosphoric acid plants will be located at or near the source of phosphate rock or sulfuric acid or both. The cost of phosphate rock at the mine may vary widely, but in many cases it is in the range of \$20-\$25/ton. The cost of sulfuric acid (or sulfur) also may vary widely depending on whether it is recovered sulfur, mined sulfur, or byproduct sulfuric acid from smelter acid. In the last case, the cost could conceivably be zero or even negative, since recovery of sulfuric acid from smelter operation is necessary to avoid atmospheric pollution, and the alternative to its use is an expensive disposal operation, such as neutralization with limestone.

Capital Costs--Capital costs for illustrative purposes are taken from TVA Bulletin Y-95 based on December 1974 costs increased by 26% to allow for escalation to 1978 (16). The TVA estimates were further adjusted as follows:

1. Rock unloading facilities were omitted; if the plant is located at the mine, such facilities would not be needed.
2. Acid clarification is omitted; in most cases it will be unnecessary if the acid is used at the plant.
3. Acid storage facilities are decreased to 1 day's production of 30% P_2O_5 acid and 2 days' production of 54% acid. This should be sufficient if the acid is used at the plant. If the acid is to be shipped to other locations, more storage would be needed (discussed under "Shipment of Phosphoric Acid").

The resulting estimated battery-limits cost of a plant in an industrialized location, such as the U.S. Gulf Coast or an equivalent European location, is tabulated below for a plant rated at 600 tons of P_2O_5 per day.

Item	Cost, U.S. \$ Million	% of Total
Phosphate rock storage	0.74	4.4
Phosphate rock grinding	2.96	17.6
Reaction and filtration	7.59	44.9
Acid concentration	2.49	14.7
Gypsum and scrubber ponds	2.59	15.3
Acid storage	0.52	3.1
	16.89	100.0

The plant cost will also vary with capacity. The cost of auxiliary and support facilities will depend on location, and the overall cost will depend on the infrastructure and the remoteness of the location. The following tabulation and figure 7 show illustrative estimates.

Capital Cost of Phosphoric Acid Plants, U.S. \$ Million

Item	Capacity, tons P_2O_5/day			
	200	400	600	900
	- - - - - - tons P_2O_5/day - - - - - -			
Battery limits, industrial location	8.4	13.3	16.9	21.7
Total plant[a], industrial location	12.6	20.0	25.4	32.6
Total plant, developing country[b]	15.8	25.0	31.8	40.8

a. Battery limits x 1.5 allow for auxiliary and support facilities.
b. Total plant cost for industrial location x 1.25.

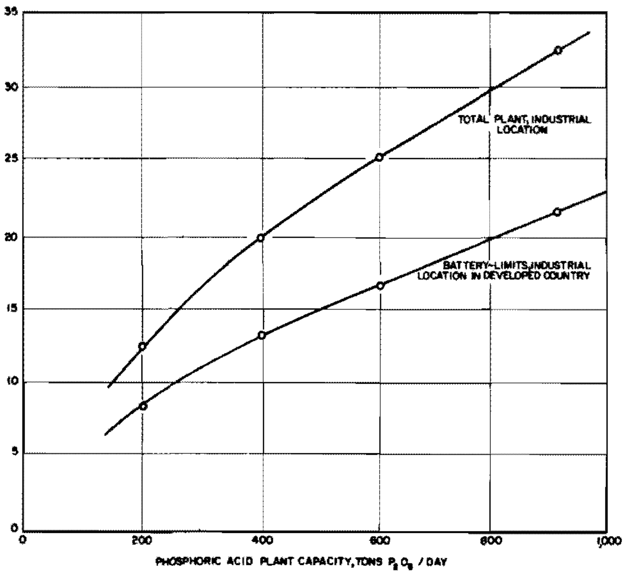

Figure 7. Capital Cost of Wet-Process Phosphoric Acid Plants.

The increased cost in a developing country is arbitrarily assumed to be 25%; actual cost differentials may vary widely depending on accessibility or remoteness of the location and availability of infrastructure.

The estimates do not include infrastructure that may be required such as highways, railroads, port facilities, housing and community developments, guest house, electric generating facilities, etc. Some or all of these may be required in some locations.

If overseas shipment of phosphoric acid is planned, facilities for clarification and storage of 54% P_2O_5 acid will be required which may cost $2-$4 million depending on the amount shipped and size of shipments.

Production Costs--The estimated cost of production of phosphoric acid in a developing country is shown in table 4. The assumed conditions are relatively favorable; phosphate rock was assumed to be available at $20/ton which is possible only when the plant is located at or near a mine where mining and beneficiation costs are moderately low. The sulfuric acid cost at $30/ton is attainable with sulfur at $50/ton. Even with these relatively low raw materials costs, their cost is 71%-78% of the total cost of production when the plant is operated at 100% of rated capacity.

The effect of scale of operation is relatively small as compared with nitrogen fertilizer production; increasing the scale from 200 to 900 tpd would decrease the cost only about $20/ton of P_2O_5 or about 10% of the total. However, if the phosphoric acid unit is part of a complex with sulfuric acid production and phosphatic or compound fertilizer production units sized to matching scale, the effect of scale would be somewhat more important. Also, if the plant requires extensive infrastructure development, the scale of operation should be large enough to justify this expense.

Figure 8 shows the effect of plant size and capacity utilization on production cost. Capacity utilization in the range of 80%-100% does not have a strong effect on cost, but if utilization is as low as 60%, the effect is more serious, especially for small plants. Again, if the phosphoric acid plant is a key unit in a complex, the effect of capacity utilization on the cost of the final product will be more pronounced.

As mentioned previously, the costs of phosphate rock and sulfuric acid comprise a high percentage of

TABLE 4. ESTIMATED COST OF PHOSPHORIC ACID PRODUCTION IN A DEVELOPING COUNTRY

Plant capacity, tons P_2O_5/day	200	400	600	900
Thousands of tons per year, 100% capacity	66	132	198	297
Fixed capital requirement, $ million	15.8	25.0	31.8	40.8
	Production Cost, $ per ton of P_2O_5			
Capital-related costs[a]	42.27	33.48	28.38	24.28
Labor-related costs[b]	8.39	6.42	6.22	5.96
Subtotal	(50.66)	(39.90)	(34.60)	(30.24)
Raw materials costs				
Phosphate rock, 3.22 tons x $20	64.40	64.40	64.40	64.40
Sulfuric acid, 2.78 tons x $30	83.40	83.40	83.40	83.40
Subtotal	(147.80)			
Other costs				
Water and supplies[c]	2.50	2.50	2.50	2.50
Electricity, 150 kWh x $0.02	3.00	3.00	3.00	3.00
Steam,[d] 1.9 tons x $2.50	4.75	4.75	4.75	4.75
Subtotal	(10.25)	(10.25)	(10.25)	(10.25)
Total production costs	208.71	197.95	192.65	188.29

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a. Capital-related costs:

Depreciation, 15 years	6.67% of capital/year
Interest at 8% of 1/2 of capital	4.00% of capital/year
Taxes and insurance	2.00% of capital/year
Maintenance	5.00% of capital/year
Total	17.67% of capital/year

b. Labor-related costs:
Operating labor
Supervision and overhead = 100% of operating labor
Quality control = 20% of operating labor

c. Process water, cooling water, recirculated pond water, antifoam chemicals, and other supplies.

d. If steam is available from a sulfuric acid plant, this cost can be credited to sulfuric acid production.

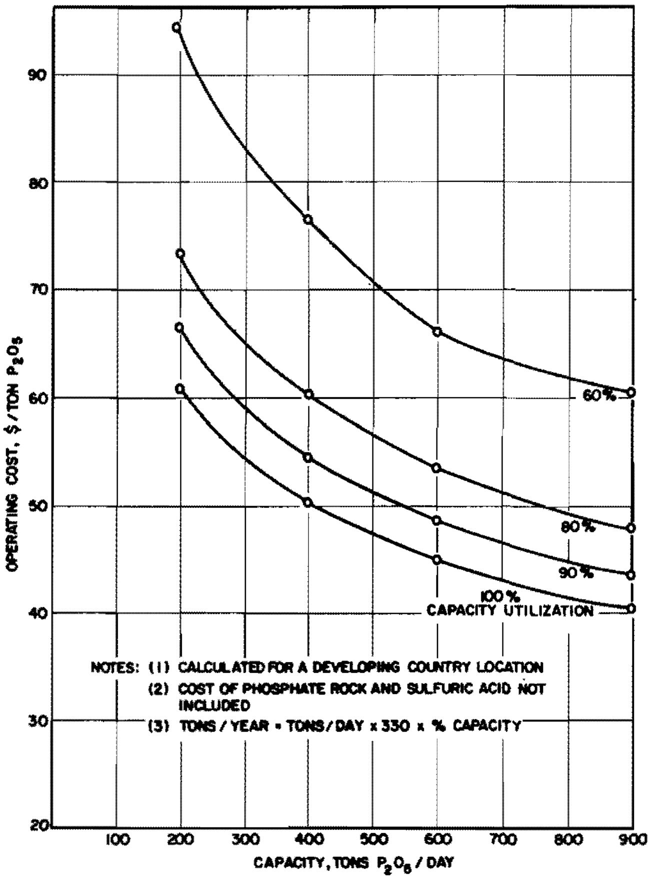

Figure 8. Effect of Scale and Percentage Capacity Utilization on Operating Cost of Phosphoric Acid Plants.

the total production cost of phosphoric acid. As an illustration of what combination of rock and acid costs might result in profitable operation, calculations were made for the following conditions:

Capacity of plant	- 600 tons P_2O_5/day
Capacity utilization	- 90%
Costs other than rock and acid	- \$48.62/ton P_2O_5
Return on investment	- 10% of plant cost/ year (\$17.84/ton P_2O_5)
Sale price of phosphoric acid	- \$200, \$250, and \$300/ton P_2O_5

The results of the calculations are shown in figure 9.

If the sale price of phosphoric acid is \$200/ton of P_2O_5 (about the present world market price), the sum of the rock and sulfuric acid costs should not exceed \$131.54/ton of P_2O_5. This cost could be obtained with rock at \$10/ton and sulfuric acid at \$36/ ton or with rock at \$20/ton and acid at \$25/ton. Thus, an unusually favorable combination would be required to compete on the world market at current (1978) price levels. Additional costs associated with ocean shipment of acid will be discussed later.

However, if the phosphoric acid is to be used to make phosphate fertilizer for domestic use, it should compete with the delivered cost of imported acid which may be as much as \$250/ton in many locations. At this price profitable operation could be obtained with rock and acid at about \$30/ton each or with rock at \$20/ton and acid at \$42/ton.

If the world market price rises (which is likely) or if the plant is in a market area where importation of phosphoric acid would be unusually expensive, a plant price of \$300/ton (or more) may be realistic. In this case combinations, such as rock at \$50/ton and acid at \$26/ton or rock at \$20/ton and acid at \$61/ton, would be potentially profitable.

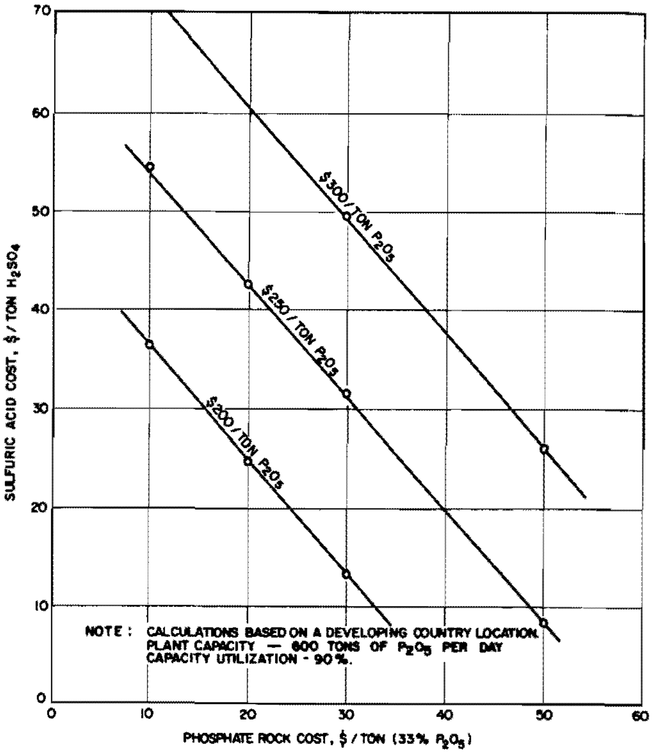

Figure 9. Effect of Sale Price of Phosphoric Acid on Allowable Cost of Phosphate Rock and Sulfuric Acid.

The above calculations are for illustrative purposes only; a thorough technical and economic study should be made for any specific project.

Shipment of Phosphoric Acid

A relatively recent development is the shipment of phosphoric acid from the point of production to other locations where it is converted into finished phosphate or compound fertilizers. Extensive shipment occurs within the United States, mainly by rail, from producers in Florida, North Carolina, and Louisiana to small fertilizer manufacturers located in market areas who produce a variety of compound fertilizers (liquid or solid) for local sale. There are also substantial amounts of phosphoric acid shipped within or between European countries; some of it is shipped by rail, but shipment by coastal vessels or by barge through inland waterways is more common.

Overseas shipment is growing rapidly; several producers have built or are building facilities for producing phosphoric acid intended mainly for export. The principal exporting countries are Mexico, Morocco, United States, Spain, France, Tunisia, South Africa, and Israel. Importing countries include India, Brazil, Colombia, several European countries, and Japan. Overseas shipments exceeded 1 million tons of P_2O_5 in 1976, and a further increase is expected in 1977 because large, new phosphoric acid plants are coming into production in South Africa and Morocco with their output intended for export (17). In 1977 world trade in phosphoric acid was estimated at 1.5 million tons of P_2O_5, a 42% increase over 1976 (18).

Most of the acid shipped overseas thus far has been of 54% P_2O_5 concentration although some "superphosphoric" acid, 69%-72% P_2O_5, has been shipped, and plans are in progress to provide shipment of up to 1 million tpy of superphosphoric acid from the United States (Jacksonville, Florida) to U.S.S.R. ports of Odessa on the Black Sea and Ventspils on the Baltic Sea. Advantages of shipment of phosphoric acid are versatility, rapid loading and unloading of ships, and high concentration. Phosphoric acid may be used to produce any desired phosphate or compound fertilizer to meet local needs; whereas, TSP or ammonium phosphates are less versatile.

As compared to the importing of raw materials, 1.0 ton of P_2O_5 as phosphoric acid requires shipment of 1.85 tons of 54% P_2O_5 or 1.43 tons of 70% P_2O_5 acid as compared with about 4.3 tons of raw materials (3.3 tons of phosphate rock plus about 1 ton of sulfur).

Rapid loading and unloading decrease costs by saving labor, decreasing port time, and decreasing congestion in ports. Also, handling of phosphoric acid (or any liquid) is dust free, thereby avoiding atmospheric contamination by dust and minimizing losses.

Some disadvantages are the requirement for specially equipped ships and special terminals with pumps and storage tanks at both shipping and receiving points. Also, the need for further processing by the importer limits the market to countries which have sufficient demand to warrant such facilities.

Phosphoric acid for shipment should be relatively free of sludge-forming solids, preferably less than 1%. To meet this requirement the acid usually must be clarified, as discussed previously in this chapter. The amount of sludge depends on the composition of the phosphate rock and the phosphoric acid production process and, in some cases, clarification is unnecessary.

Many liquid chemicals other than phosphoric acid are shipped in bulk, and numerous ships are equipped with tanks lined with stainless steel, rubber, or other acid-resistant materials. Such ships may carry phosphoric acid, as well as various other chemicals. In addition several ships have been built specifically for transport of phosphoric acid, and more are under construction. For long distance shipment, large vessels are preferred, and several have been built recently in the range of 20,000- to 24,000-ton capacity. At least one of 38,000-ton capacity is in use (3).

Obviously, the storage capacity at terminals must be at least equal to the size of the largest shipment although ships may load and unload at more than one terminal. A terminal was recently completed at Morehead City, North Carolina, with a storage capacity of 22,000 tons at a cost of $2.6 million (19). Another terminal, in Florida, with a 30,000-ton capacity cost $3 million. A 1973 estimate gave the cost of 30,000-ton acid storage as $1.23 million (20). Construction cost increases since 1973 amount to about 40% (CE plant cost index). A 1976 world survey showed 46 terminals in operation or under construction for shipping and/or receiving phosphoric acid (19). A more recent survey issued by ISMA in August 1978 listed 82 maritime terminals with an aggregate storage capacity of about 1.5 million tons. Another ISMA report lists 128 ships that are suitable for transport of phosphoric acid (and other corrosive liquids), with cargo capacities ranging from 500 to over 30,000 tons. The following tabulation shows the number of ships in various capacity ranges:

Dead Weight Capacity	Number of Ships
950- 2,000	13
2,001- 5,000	38
5,001-10,000	35
10,001-20,000	9
20,001-30,000	25
Over 30,000	8
	128

For construction of storage tanks, rubber-lined steel is commonly used although stainless-steel lining may be used. In some cases, ponds or lagoons are used for storage. The ponds are lined with heavy sheets of rubber or plastic underlaid with gravel with drainage to a sump so that any leakage can be detected and returned to another pond. One such installation near Tampa consists of four ponds with a total capacity of 11,000 tons (19). The ponds have inflatable plastic covers to protect them from rain or other contamination. Most storage tanks have facilities for agitating the acid occasionally to prevent settling of solids.

The operating cost of a terminal depends mainly on the throughput. Assuming that a 30,000-ton storage terminal costs $3 million, annual operating costs are estimated as follows:

Depreciation, 15 years	$200,000
Maintenance, 5%	150,000
Labor and overhead	30,000
Total	$380,000

For an annual throughput of 100,000 tons of P_2O_5 (185,000 tons of 54% P_2O_5 acid), the operating cost would be $3.80/ton of P_2O_5. To this should be added interest and/or return on fixed and working capital. Assuming the storage capacity is half full on the average and the acid is valued at $200/ton, working capital is 15,000 tons x 0.54 x $200 = $1.62 million, and total capital is $4.62 million. If interest and return on investment of 14% is expected, the cost/ton of P_2O_5 would be about $6.45, giving a total cost of $10.25. For superphosphoric acid the cost/ton of P_2O_5 would be 54/70 x $10.25 = $7.91/ton of P_2O_5. A similar cost would be involved for a receiving terminal.

It is difficult to compare the terminal cost for phosphoric acid with that for solid products such as triple superphosphate (TSP) or monoammonium phosphate (MAP). The cost of storage facilities for the same number of tons of solids (30,000 tons) has been estimated to be about 40% of the cost for phosphoric acid (20). However, a substantial investment in mechanical equipment would be required to reclaim bulk solids from storage and convey them to a ship. In addition, a substantial amount of labor would be required for operating the equipment; whereas, loading and unloading costs are negligible for phosphoric acid. For a receiving terminal in a developing country which may not be well equipped with mechanical devices, the total of unloading and port storage costs might well be higher for solids. On balance, it seems likely that overall terminal storage and handling costs may be about the same for acids as for bulk solids.

Freight rates for ocean shipment of phosphoric acid are not published; the larger cargoes are moved under long-term contracts in custom-designed vessels. Bulk solids are often shipped in tramp vessels; the freight rates fluctuate widely with supply and demand for shipping space. It is reasonable to assume that the freight costs would be higher for phosphoric acid because of the special construction required. A study in 1973 assumed that the cost would be 40% higher for a short haul (north Africa to northern Europe) and 25% higher for a long haul (United States to India). However, at that time, only a few ships were equipped to transport acid. Now that there are a much larger number of ships the differential may well be lower.

Utilization of Byproduct Gypsum

In production of wet-process phosphoric acid, 4.5-5.0 tons (dry basis) of byproduct gypsum is produced per ton of P_2O_5 recovered as phosphoric acid. The phosphogypsum retains at least 20% of free water by weight. The disposal of this material as a waste product is discussed in chapter XXIII. The present chapter will briefly review ways for utilizing the by-product. The principal means for utilizing phosphogypsum are to:

1. Make ammonium sulfate by reaction of the gypsum with ammonia and carbon dioxide (discussed in chapter VIII).
2. Make cement and sulfuric acid by calcining the gypsum with coke and clay or shale (discussed in chapter XII).
3. Make plaster or plasterboard for building materials or make pressed or cast blocks for construction purposes.
4. Use in cement as a set retardant.
5. Use as a fertilizer filler.
6. Use for direct application to farmland when the soil requires it.

Use for Building Materials--Plaster consists mainly of gypsum that has been dehydrated to hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) under carefully controlled conditions so that it will rehydrate rapidly when mixed with water. The dehydrated gypsum usually is finely ground and sometimes mixed with a filler before use. Phosphogypsum must be purified for this use; the extent of purification depends on the amount and character of the impurities and how the plaster is to be used.

When plaster is used as a coating on interior walls, a bright white color is often desired. Organic impurities originating from some phosphate rocks may cause an undesirable dark color. Some phosphogypsum may be purified sufficiently by slurrying in water and passing the slurry through a hydroclone to recover the coarser fraction; the undersize which has a high impurity content is discarded.

When the gypsum is sufficiently pure, simple washing to remove residual acid may be sufficient. The last trace of acid may be neutralized with lime and wash water separated by filtration.

For wallboard production, rapid setting is especially necessary and phosphogypsum with a high P_2O_5 content is unsuitable. Gypsum produced by a hemihydrate-dihydrate process usually has a sufficiently low insoluble P_2O_5 content for this purpose.

Phosphogypsum may contain radionucleides originating from the phosphate rock; in some cases these radioactive impurities may cause a radiation level high enough for some concern in dwellings using phosphogypsum-derived building materials.

Aside from impurities, the main disadvantage of phosphogypsum for use as plaster is the high moisture content which results in a high fuel cost for drying. For this reason there has been comparatively little use of phosphogypsum for building materials in countries where natural gypsum is abundant. In Japan where there are no domestic supplies of natural gypsum, phosphogypsum has long been used for plaster and cement additive. More recently the rising cost of environmentally acceptable disposal methods has caused some European countries to undertake utilization.

The literature on the subject of production of plaster products from phosphogypsum is voluminous; only a very brief review of the many processes that are in use or under development is possible in this manual. A more detailed review has been published in Phosphorus and Potassium in a four-part series, titled "Getting Rid of Phosphogypsum"; parts III and IV describe processes for making plaster products (21). In general, the processes consist of (1) purification of phosphogypsum including, in some cases, the addition of chemicals such as lime to neutralize acidity, (2) thermal treatment to convert gypsum to hemihydrate or anhydrite or some combination of the two, and (3) preparation for the market, which may include grinding or agglomeration and, in some cases, drying.

Hemihydrate exists in two crystalline forms. The alpha form is produced when wet phosphogypsum is heated under pressure in an autoclave to about 130°-160°C. The beta form is prepared by drying and calcining at about 140°C under controlled conditions. Either form can be used for making plaster products, but the alpha form produces denser and harder plaster. Most calcination processes are likely to produce a mixture of beta hemihydrate and anhydrite, but such mixtures are acceptable for most plaster uses and may be preferred for some.

The C&F Chemie process has been described by Neveu (22) and is used in France in a plant of 130,000-tpy capacity mainly to make plasterboard. Phosphogypsum is wet screened to remove large particles such as quartz, washed to remove soluble impurities and organic impurities, neutralized with lime water, and dewatered by filtration. It is then dried and calcined in a series of three cyclones with hot air and ground to a fine powder.

The Rhone-Poulenc process is used in two plants in France with a total capacity of about 300,000 tpy. Other plants are under construction in Romania and Brazil. Purification procedures depend on the character of the phosphogypsum; a minimum treatment involves separation of larger particles, washing to remove soluble impurities, neutralization with lime, and dewatering by filtration or centrifuging. For phosphogypsum with more impurities, repeated washing with slime removal or flotation may be used. The purified material is dried and calcined in one step or two. An advantage of the two-step process is that some of the dried phosphogypsum can be removed after the first (drying) step for use as cement additive. Either a direct-fired calciner or a fluidized-bed calciner heated with hot air may be used.

The Knauf processes are offered by the West German company, Gebrueder Knauf Westdeutche Gipswerke. Three different processes are used in two plants in Germany and one in Belgium with a total capacity of nearly 1 million tons of various plaster products including gypsum partition blocks. The three processes differ mainly in the degree of purification. For example, one of the processes receives hemihydrate from the Central Prayon process, which is already quite pure. The extent of purification is minimized by additives that precipitate phosphates in an inert form. This reaction is slow and is carried out in a reaction silo after partial dehydration of the dihydrate. One unusual feature is that products intended for construction plaster are pelletized in a pan granulator to a particle size of at least 20% plus 0.2 mm after partial dehydration by adding a small amount of water to rehydrate some of the hemihydrate. This coarse particle size is preferred for construction plaster.

The CERPHOS[4] process is used in a plant of 30,000-tpy capacity in Senegal. It appears to be very similar to the C&F Chemie process except that more extensive purification of the phosphogypsum is used, and this involves wet screening, flotation, two washes, and calcium carbonate addition. The product is dried with heated air in a flash dryer and calcined in an indirect-fired kiln.

The ICI process was used in two large plants in England, but both were shut down because of difficulties resulting from changes in composition of the phosphate rock. The process used standard methods

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[4] Centre d' Etudes et de Recherches des Phosphates Mineraux.

of washing and neutralization to purify the phosphogypsum followed by calcination to beta hemihydrate. The company has developed a wet-phase dehydration process to produce alpha hemihydrate, but it is not yet in use.

Other processes, not known to be in commercial use, have been developed by FCI (India) and Allied Chemical (United States). The latter process, which is intended specifically for plasterboard manufacture, includes the unusual feature of ammonia neutralization of acidic components of the phosphogypsum. Processes used in Japan for making plaster products are influenced by the prevalence of hemihydrate-dihydrate phosphoric acid processes which produce an unusually pure gypsum; therefore, the purification step can be simplified.

From the above brief summary, it is apparent that processes to make plaster products by the dry (beta hemihydrate) route may vary widely depending on the impurity content of the phosphogypsum which, in turn, depends on the composition of the phosphate rock and the process used to convert it to phosphoric acid. The general tendency toward utilization of lower grade rocks is likely to result in more complicated phosphogypsum purification processes. A substantial portion of the phosphogypsum may be lost in the purification process; the recovery may be as low as 70%.

For the above reasons process requirements vary widely, but the following average requirements for the Rhone-Poulenc process may be illustrative (21).

Item	Requirement per Ton of Plaster
Phosphogypsum	1,500 kg
Water	3 m^3
Lime	5-10 kg
Fuel oil	45 kg
Power	50 kWh

The only known commercial process for producing alpha hemihydrate from phosphogypsum is the Giulini process which was developed in West Germany (23) and is used in two plants in that country, one in Ireland, and one under construction in Russia. As mentioned previously, alpha hemihydrate is formed by dehydration of gypsum in an aqueous suspension in an autoclave.

The purification step of the Giulini process, as with other processes, depends on the impurity level of the incoming phosphogypsum and the type of plaster product to be made. It may consist of washing or flotation or both. After purification, the gypsum is pumped to an autoclave as a slurry which is operated at 120°C and a pH of 1-3. The temperature is maintained by injection of steam. Dehydration and recrystallization occur in the autoclave, releasing cocrystallized impurities (mainly phosphates) which dissolve in the liquid phase. The size and shape of the alpha hemihydrate crystals that are formed in the autoclave are important and are controlled by additives. The slurry is withdrawn from the autoclave continuously and sent to a filter where the crystals are washed and dewatered to 10%-20% moisture. The filtrate contains an appreciable amount of P_2O_5 and may be returned to the phosphoric acid plant. The treatment of the wet crystals from the filter depends on the desired end product. Cast building blocks are produced by adding a controlled amount of water to the filter cake and pouring the slurry into molds where it solidifies as the hemihydrate rehydrates to dihydrate. For production of dry plaster powder, the crystals must be dried and ground after which the powder can be stored for use as plasterboard or various other plaster products.

The main process requirements per ton of alpha hemihydrate are:

Low-pressure steam	0.4-0.6 tons
Hot water (90°C)	0.5 m^3
Raw water	2.0 m^3
Electricity	25 kWh

If a dry product is required, an additional 10 kWh of electric power and 200,000 kcal of fuel are needed per ton of product.

The new ICI process, which has not yet been used on a commercial scale, is generally similar to the Giulini process. However, it uses two autoclaves in a series which are operated at 150°C, and the product crystals are separated from the liquid phase by centrifuging. As does the Giulini process, it makes use of crystal modifiers to control the size and shape of the crystals.

Use as Cement Additive--Portland cement usually contains about 5% gypsum which is added to control (retard) the setting time. For this purpose P_2O_5 cocrystallized with gypsum is undesirable and fluorine compounds are also undesirable. However, the byproduct from a hemihydrate-dihydrate process is said to be suitable (24). Also a process for treating phosphogypsum from dihydrate processes to make it suitable for use as cement additive (and other purposes) has been described (25). It consists of calcining the phosphogypsum to hemihydrate and then rehydrating it with addition of limewater, $Ca(OH)_2$. Recrystallization during dehydration releases the cocrystallized P_2O_5, and the lime converts the P_2O_5 to inert forms. The lime also converts fluorine compounds to inactive forms. Requirements for the process per ton of treated gypsum are:

Quick lime (CaO)	55 kg
Fuel oil	45 liter
Electricity	15 kWh

As a variation in the process, the lime may be added to the gypsum before calcining which eliminates fluorine evolution during calcining. The product may be granulated during rehydration for convenience in handling. In general, any of the above-described processes for making plaster products can be used to make gypsum for cement additive by adding a rehydration step.

Use in Compound Fertilizers--Small amounts of phosphogypsum are used as a filler or additive to compound fertilizers. Calcined gypsum is sometimes added to assist in granulation or to increase granule strength. In other cases the purpose may be to supply sulfur for agronomic reasons. Granular gypsum is available in some countries for use in bulk blends.

Direct Application to Farmland--Gypsum is used in fairly large amounts on some soils to combat the effects of salinity or alkalinity or to reclaim soil that has been inundated by seawater. Clayey soils tend to retain sodium from salt water; use of gypsum replaces sodium with calcium. Gypsum is also a good source of sulfur for use on sulfur-deficient soils.

Some crops, such as groundnuts, benefit from soluble calcium in gypsum. Wet phosphogypsum is difficult to handle and apply; the cost of drying is an economic disadvantage that often leads to a preference for natural gypsum. In dry climates the phosphogypsum can be air-dried in the sun. Drying to about 6% moisture is sufficient to make it free flowing.

Despite the numerous uses mentioned above, only a small percentage of the phosphogypsum is actually used on a worldwide basis; in most cases it seems to be economically preferable to dispose of the byproduct in ponds, in other land disposal areas, or in the sea by dissolving it in seawater.

Utilization of Fluorine

In the dihydrate process, only a small percentage of the fluorine in the phosphate rock is volatilized during digestion and filtration; 15%-75% of the fluorine is retained in the gypsum (depending mainly on the rock composition), and most of the remainder is in the filter acid (26). About two-thirds of the fluorine in the filter acid is volatilized when the acid is concentrated to 50%-54% P_2O_5. In a typical case, about 50 kg of F is volatilized per ton of P_2O_5, usually as SiF_4 or HF, or some mixture of the two. Collection of this fluorine to prevent atmospheric pollution is discussed in chapter XXIII.

Numerous processes have been proposed and developed experimentally for recovering salable fluorine compounds; some of these processes are in use on an industrial scale. A description of all of these processes is beyond the scope of this manual.

Fluorine usually is recovered in the form of an aqueous solution of fluosilicic acid, H_2SiF_6. The concentration may be as high as 20%-25%. The fluosilicic acid is used directly for "fluoridation" of municipal water supplies in some countries to prevent decay of teeth. The acid is shipped to various municipalities in rubber-lined railcars. Salts of fluosilicic acid, such as sodium, potassium, and ammonium fluosilicates, have various uses and can be produced readily from the acid. Sodium fluosilicate is used for fluoridation of municipal water supplies, but fluosilicic acid is generally preferred.

Processes have been developed for making aluminum fluoride (AlF_3) and cryolite (Na_3AlF_6) from fluosilicic acid. These materials are used by the aluminum industry in substantial quantity. However, they must be quite pure for this use; in particular, the silicon and phosphorus must be very low. This requirement complicates production from byproducts of the phosphate industry. Calcium fluoride may be produced and used instead of natural fluorspar for production of hydrogen fluoride (HF) which is the basic material for producing numerous organic and inorganic fluorine compounds or for metallurgical purposes (27).

In general, the economics of producing chemical-grade fluorine compounds from byproduct fluosilicic acid is marginal to unfavorable for small phosphoric acid plants. However, large plants may find recovery profitable. Where several phosphoric plants are operating within economical shipping distance, the crude fluosilicic acid may be shipped to a central point for production of refined fluorine compounds. For more details on fluorine utilization, see reference (26).

Purification of Phosphoric Acid

For most fertilizer production processes, purification of wet-process phosphoric acid is not necessary. However, there are two common fertilizer uses that may call for partial purification:

1. "Merchant-grade" acid which is shipped by rail, barge, or ocean vessels and is often stored at shipping and receiving terminals should be purified sufficiently so that formation of insoluble precipitates (sludge) during shipping and storage is minimized.
2. Phosphoric acid to be used for production of liquid fertilizers, such as ammonium polyphosphate solution, sometimes requires partial purification to prevent formation of precipitates upon ammoniation or during storage of the ammoniated solution.

Although ammonium polyphosphate sequesters most of the common impurities, excessive amounts of some impurities (especially magnesium and organic matter) cause precipitate formation. Superphosphoric acids usually do not form sludge, but magnesium or titanium have been known to cause sludge-forming precipitates.

A major fraction of sludge in most merchant sludge acids is the compound $(Fe,Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$. It precipitates slowly over a period of several weeks; therefore, long storage periods are needed to ensure reasonably near completion of the precipitation reaction. Methods for clarification of merchant-grade acid have been discussed in a previous section of this chapter. A recently developed method of "stabilizing" the acid is to concentrate it to 40% P_2O_5 (a point of minimum impurity solubility), treat the acid by undisclosed means, and then concentrate the acid further to 60% P_2O_5. This method is said to be successful in preventing further sludge formation.

Several solvent extraction methods have been developed, and some are in commercial use. These processes have been reviewed in recent publications (28, 29). Such processes usually separate the phosphoric acid into two fractions, a cleaner fraction and a dirtier fraction containing most of the impurities. The cleaner fraction can be used for production of liquid fertilizers and the less pure fraction for TSP or monoammonium phosphate. One exception is a process developed by Garrett Research that selectively extracts magnesium and calcium by extraction with sulfonic acid dissolved in kerosene (28). The objective is to upgrade acid made from low-grade rock; 94% to 97% of the P_2O_5 is recovered as partially purified acid.

Methods have been developed for removing organic matter by flocculation or copolymerization during digestion (29). The agglomerated carbonaceous matter is removed along with the gypsum filter cake. Many other methods are under study; for further details see the following references: (28,29, 30). Possibly further development of acid purification methods will permit utilization of low-grade rocks that cannot be utilized because of their high impurity content.

Production of Phosphoric Acid Using Acids Other than Sulfuric

Phosphate rock can be dissolved by several organic and inorganic acids to produce phosphoric acid. The use of nitric acid for this purpose is described in chapter XV, Nitrophosphates. Commercially used nitrophosphate processes produce phosphoric acid containing nitrates and, hence, are used to produce compound NP or NPK fertilizers. It is technically feasible to produce phosphoric acid substantially free from calcium or nitrates by separation methods involving solvent extraction. One such process using tertiary amyl alcohol as the solvent has been developed in Finland and described by Lounamaa (31). However, no commercial use has been reported.

Several processes using hydrochloric acid have been developed or patented, but only that developed by the Israel Mining Industry (IMI) has been used commercially. The IMI process has been described in a UNIDO publication (32). The following description is a condensation from that publication. The main stages of the process are:

1. Dissolution of phosphate rock by hydrochloric acid, resulting in an aqueous solution of calcium chloride and phosphoric acid;
2. Liquid-liquid contacting in a number of solvent extraction steps to obtain a solution of substantially pure phosphoric acid; and
3. Acid concentration to obtain 95% H_3PO_4(69% P_2O_5).

The raw materials and reagents used are as follows:

1. Phosphate rock (any commercial grade). The P_2O_5 recovery is over 98%.
2. Hydrochloric acid for acidulation can be used as a solution of 20% HCl or higher or in gaseous form by combining absorption with reaction. For reasons of economy, concentrated acid is preferred because most of the water accompanying the acid must be evaporated in a later stage of the process. HCl consumption is dependent on the composition of the rock. Acid consumption for Florida rock of 34% P_2O_5 is about 2 tons HCl (calculated as 100%) per ton P_2O_5.
3. Solvent. Several solvents can be used for extraction. Those preferred are technical isoamyl alcohol or n-butanol or a mixture of both. Solvent makeup is 4 kg/ton P_2O_5.
4. Process water.
5. Auxiliary reagents. Depending on the type of rock and the method of separation of insoluble residue from dissolution liquor, minor quantities of filter aids of flocculating agents may be required.

Dissolution and Mechanical Separation of Insoluble Residue

The dissolution of phosphate rock is essentially decomposition of fluorapatite by HCl according to the equation:

$$Ca_{10}F_2(PO_4)_6 + 20HCl \rightarrow 2HF + 6H_3PO_4 + 10CaCl_2$$

Other acid-soluble components of the rock, such as $CaCO_3$, decompose simultaneously.

The rock is dissolved by hydrochloric acid. The insoluble residue amounts to a small percentage of the rock feed and consists mainly of silica, silicates, insoluble organic matter, etc. The insoluble matter can be separated from the dissolution liquor by filtration, followed by washing of the cake or by sedimentation in a thickener, followed by countercurrent decantation washing of the sediment. The choice of the proper method of separating solids depends on the character of the insoluble residue and on economic considerations. The dissolution liquor is fed to the subsequent section.

Figure 10 shows a typical flowsheet of the process.

Liquid-Liquid Contacting

This stage consists of a number of operations: extraction, purification, washing, and stripping.

Extraction--This is performed by a countercurrent contact of dissolution liquor with the selected solvent. Phosphoric acid transfers selectively from the aqueous dissolution liquor to the organic solvent

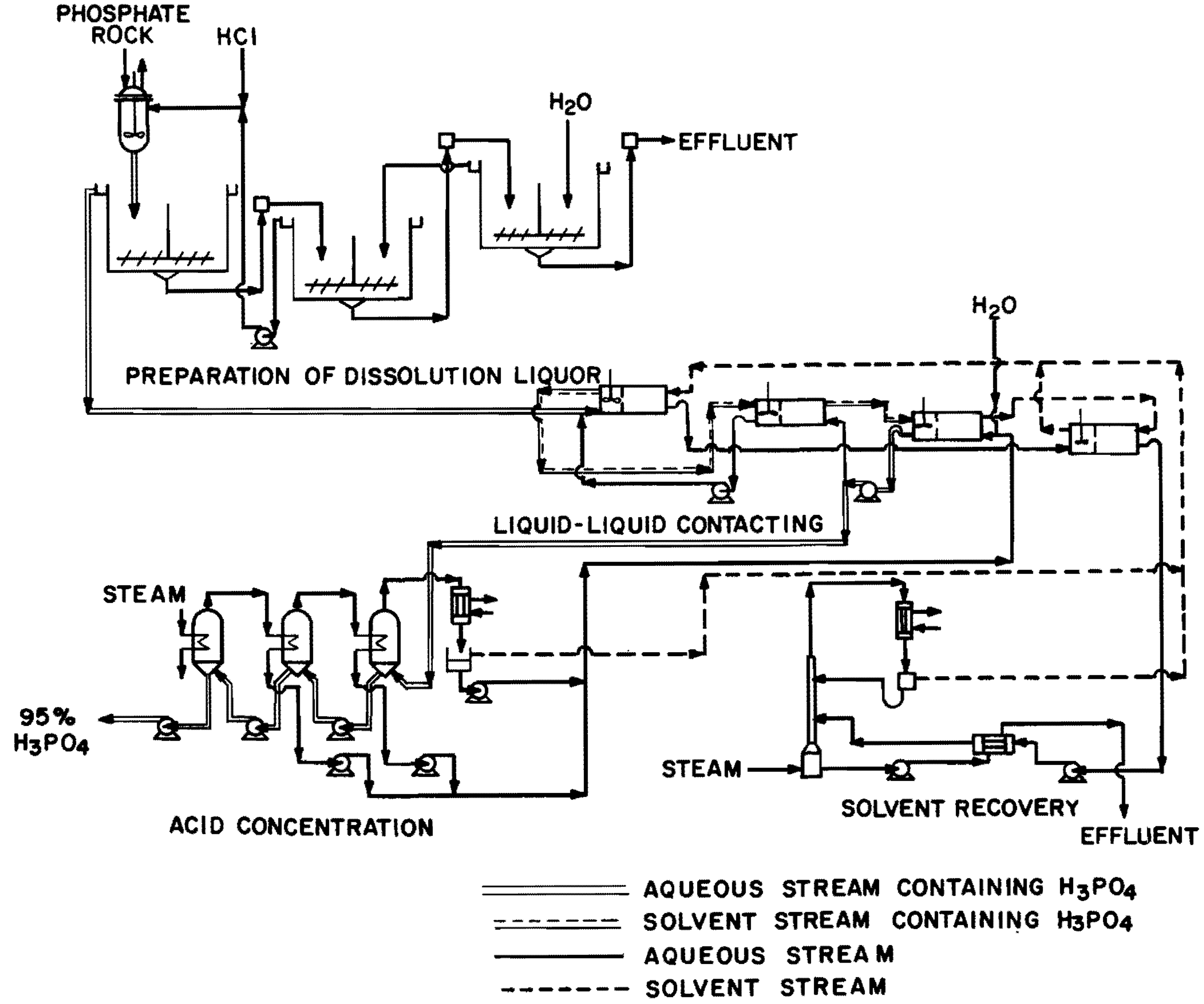

Figure 10. Typical Flowsheet of the IMI Phosphoric Acid Process (HCl-route).

phase, giving the extract and a calcium-chloride brine (raffinate) containing substantially all the impurities, such as fluorine and iron.

Purification--The solvent extract, which contains small amounts of Ca^{++} and some other impurities, is purified further by countercurrent contact with an aqueous phase.

Washing--The acid of the purified extract is transferred into water. The solvent leaving this stage is virtually free of acid.

Stripping--The acid-free solvent stream extracts the residual acids present in the raffinate and is recycled to extraction. The spent calcium-chloride brine is stripped by steam to recover any dissolved solvent.

Acid Concentration

The dilute aqueous acids emerging from washing consist of an aqueous solution of H_3PO_4, HCl, and some dissolved solvent. This solution is concentrated to 95% H_3PO_4, which is the end product. The separation of H_3PO_4 from other components of the solution is essentially a distillation operation; this permits a full recovery of the minor quantity of solvent that is dissolved in the aqueous phase on washing and of the HCl, both maintained in closed cycle in the process.

The main requirement of this operation is heat economy, and a multiple-effect evaporator is used to achieve this. The amount of steam used is less than 0.5 ton/ton of water evaporated. The complete absence of dissolved solids in the solution being concentrated permits maintenance of high heat-transfer coefficients. All of the volatile streams from the system are recycled to the previous steps of the process.

Solvent Recovery from Spent Calcium Chloride Brine

The residual brine leaving the stripping stage contains a small amount of dissolved solvent, which has to be recovered for economic reasons. The solvents used form an azeotrope with water on rectification so that the simplest system to be applied is steam stripping. The costs of this operation are reduced by the recovery of heat from the brine leaving the system. The recovered solvent is recycled to the liquid-liquid contacting section, and the brine is discarded.

Construction Materials

The process requires the use of acid-resistant construction materials that are solvent resistant, as well, in those parts of the process where solvent is present (i.e., the liquid-liquid contacting section and a part of the sections where acid is concentrated and where solvent is recovered from the brine).

For the dissolution and mechanical separation of insoluble residue, rubber-lined steel is the least expensive material. In the liquid-liquid contacting section, rigid polyvinyl chloride (PVC) is very satisfactory. In the parts of the system operating at elevated temperatures, impervious graphite can be used for the heat exchangers. Other construction materials include thermosetting resins and lined steel.

Quality of HCl-Route Phosphoric Acid

HCl-route phosphoric acid is much purer than wet-process acid, and its analysis is similar to that of thermal acid (table 5). By slight adjustments in the process, food-grade acid can be obtained. The composition of wet-process acid is dependent on the rock as raw material; whereas, almost the opposite is true for HCl-route phosphoric acid.

TABLE 5. COMPARISON OF ANALYSIS OF HCl-ROUTE PHOSPHORIC ACID AND WET-PROCESS ACID

Component	HCl-Route Phosphoric Acid (%)	Wet-Process Acid (%)
H_3PO_4	95	69-77
P_2O_5	69	50-56
Heavy metals[a]	0.002-0.01	0.5-1.5
CaO	0.008-0.04	0.014-0.35
Fe_2O_3	0.003-0.05	0.86-2.30
Al_2O_3	Traces	0.3-2.45
Mg	Traces	0.0-0.8
H_2SO_4	Traces	1.0-5.6
SiO_2	Traces	0.04-0.10
F	Traces	0.25-1.10

a. Calculated as Pb.

Capital Investment

The capital investment required for a plant may vary from location to location. In this report cost estimates for battery-limits plants assume a location in western Europe, a feed of phosphate rock containing 33%-34% P_2O_5, and the use of a 30% aqueous solution of HCl.

The estimated total fixed capital investment (battery limits) as dependent upon capacity for HCl-route phosphoric acid plants is shown by one of the curves in figure 11.

Present capital costs (1978) would be at least double those shown in figure 11. However, for comparative purposes, it will be noted that the capital cost for the HCl process is about 35% higher than for the standard (H_2SO_4) wet process when production of the acid (HCl or H_2SO_4) is excluded.

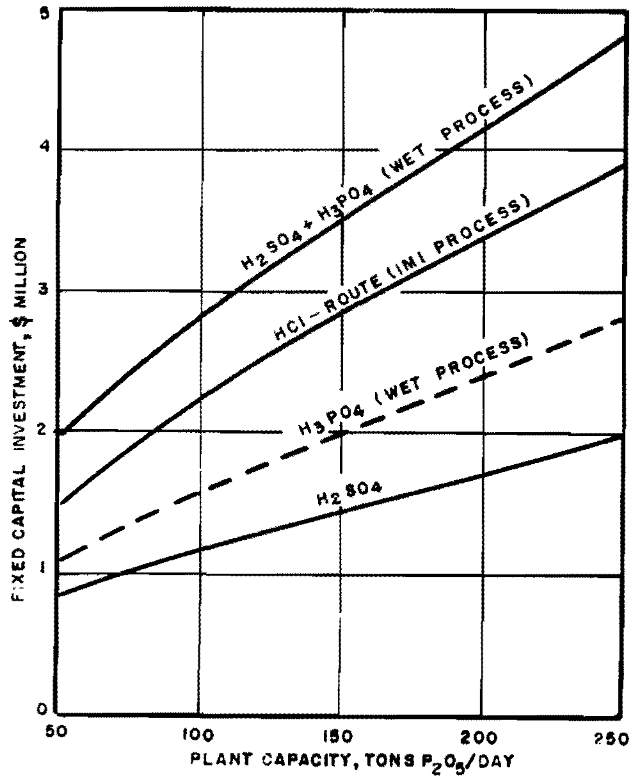

Figure 11. Fixed Capital Investment in Battery-Limits Phosphoric Acid Plants, HCl-Route and Wet Process (1969).

If HCl were available as a byproduct from another process, the capital cost would be lower than for a wet-process plant including H_2SO_4 production facilities. However, when using byproduct HCl, the scale of the operation would be limited by the amount of byproduct HCl available.

Process Requirements

Operating costs may be estimated from the process requirements which are given in table 6 for a plant of 100-tpd capacity.

TABLE 6. PRODUCTION COSTS PER TON P_2O_5 IN A PLANT WITH A CAPACITY OF 100 TONS PER DAY (1969 BASIS)[a]

Item	Amount	Cost, $	
Raw materials			
Phosphate rock 34% P_2O_5	3 tons	Price not considered	
HCl (calculated as 100%)	2 tons	Price not considered	
Variable costs			
Solvent (isoamyl alcohol) makeup	4 kg	1.60	
Steam	4.3 tons	7.17	
Power	100 kWh	0.87	
Cooling water (25°C)	165 m^3	1.10	
Process water	3 m^3	0.45	
Total variable costs			11.19
Fixed costs			
Labor: 4 men/shift (including shift supervisor), 4 shifts/day		2.56	
Overhead: 100% of labor		2.56	
Maintenance: 5% of fixed capital investment (FCI)		3.36	
Depreciation: 6.7% of FCI		4.51	
Insurance and taxes: 1.3% of FCI		0.87	
Total fixed costs			13.86
Total operating costs			25.05

a. Excluding raw materials and interest on capital.

In addition to the process requirements given in table 6, the expense of disposal of the byproduct calcium chloride brine must be considered. If the plant is located adjacent to the sea, disposal in the sea may be acceptable and economical; for an inland location disposal may be difficult and expensive.

HCl-route phosphoric acid has certain disadvantages as compared with wet-process acid. Its production is economic only in places where HCl is available or where it can be produced at a moderate price. Transport of HCl in the form of an aqueous solution of perhaps 33% HCl is possible only in pipes or railcars lined with rubber, PVC, or similar materials.

However, HCl-route phosphoric acid has some advantages over wet-process acid. Unlike wet-process acid, it contains no scale-forming components, and its composition and quality are practically independent of the type of phosphate rock used. Superphosphoric acid (70%-72% P_2O_5) can easily be produced from HCl-route phosphoric acid.

Wet-process acid would be suitable for the manufacture of triple superphosphate of about 44%-46% P_2O_5 and of diammonium phosphate with a grade of 18-46-0. Diammonium phosphate (21-53-0) can be manufactured directly from HCl-route phosphoric acid owing to its high concentration and purity.

HCl can be used where it is available as a byproduct. This is important for developing countries producing NaOH, where there is no captive market for the chlorine that is produced simultaneously. Byproduct hydrochloric acid is sometimes available from other sources and may even create disposal problems. In such cases the production of phosphoric acid by the acidulation of phosphate rock with hydrochloric acid can be advantageous if the quantity of the byproduct is adequate for an economical scale of operation and disposal of or utilization of the calcium chloride brine is economically feasible.

An interesting possible source of hydrochloric acid is through calcination and hydrolysis of magnesium chloride according to the equation:

$$MgCl_2 + H_2O \rightarrow 2HCl + MgO$$

This possibility is under study in Israel using magnesium chloride from the Dead Sea. The magnesium oxide could be useful for production of refractories.

Another possible source of hydrochloric acid is from the production of potassium phosphate from phosphoric acid and potassium chloride (see chapter XVI).

At present the only plants using the HCl process are relatively small ones, and most of the product is used to make industrial phosphates rather than fertilizers.

Phosphoric Acid Production by the Electric Furnace Process

The first step in the production of furnace acid is to produce elemental phosphorus in an electric furnace (see figure 12). Phosphate nodules or other lump phosphate material, silica pebble, and coke are mixed and fed to the furnace. The electric current which enters the furnace through carbon or graphite electrodes fuses the rock and silica, and the carbon in the coke reduces the phosphate. A mixture of phosphorus vapor and carbon monoxide gas is withdrawn continuously from the furnace. The phosphorus is condensed to a liquid which is converted into phosphoric acid in a separate plant, often located far from the phosphorus plant. Molten calcium silicate slag and an iron-phosphorus compound known as ferrophosphorus are tapped from the furnace periodically. The following equation represents the principal reaction in the furnace:

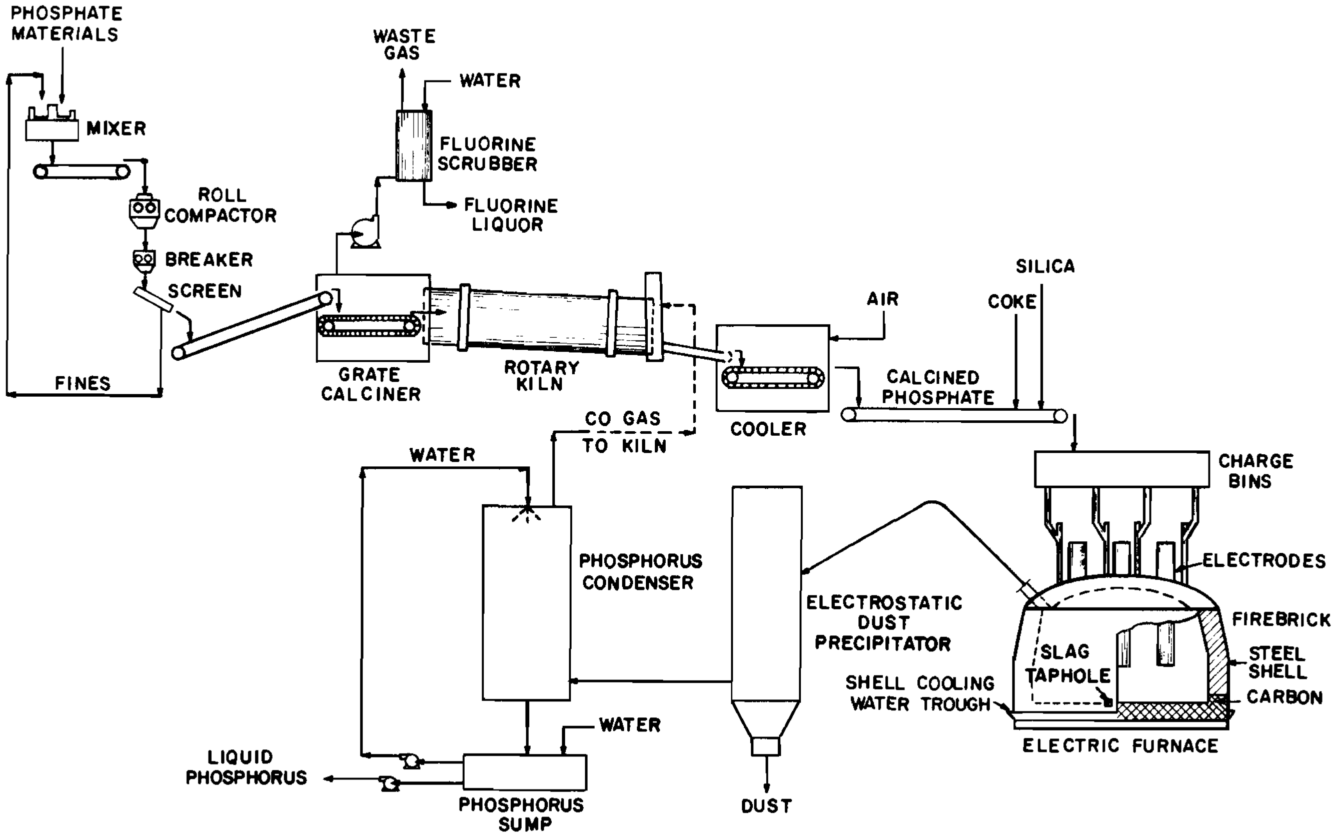

Figure 12. Manufacture of Elemental Phosphorus.

$$Ca_{10}F_2(PO_4)_6 + 15C + 6SiO_2 \rightarrow \underbrace{1.5P_4 + 15CO}_{\text{gas}} + \underbrace{3(3CaO\cdot 2SiO_2) + CaF_2}_{\text{slag}}$$

One advantage of the furnace process is its ability to use low-grade phosphate rock provided that the principal impurity is silica. Iron oxide and alumina are much less objectionable in the furnace process than in the wet process. Siliceous phosphate rock containing about 24% P_2O_5 is used in several plants. Such rock may be obtained at a very low cost in some locations. Rock containing as much as 7% Al_2O_3 is acceptable.

If lump or pebble rock of suitable size (about 0.6-4.0 cm) that is resistant to decrepitation on heating is available, the cost of agglomerating the charge may be avoided. However, such rock is seldom available; therefore, the rock usually is agglomerated and calcined or sintered before charging it to the furnace. Carbon monoxide gas which is a byproduct from the furnace is the usual fuel for the calcination. Even so, this step is expensive.

The recovery of P_2O_5 as elemental phosphorus usually is in the range of 86%-92% of that charged to the furnace. The loss of P_2O_5 in the slag is about 3%. From 2% to 8% of the P_2O_5 charged is recovered as ferrophosphorus which contains about 23% phosphorus, 70% iron, and small amounts of manganese, silicon, and other metallic elements, depending on the charge composition. The amount of ferrophosphorus formed depends on the iron oxide content of the charge. The ferrophosphorus is sold to the steel industry, but the income only partially compensates for the loss of phosphorus production.

Of the phosphorus recovered as elemental phosphorus, about 5% is in the form of sludge, even after a series of settling steps to separate sludge from clean phosphorus. This sludge phosphorus may be recovered by burning it separately to produce impure phosphoric acid, by distillation, or by dewatering and returning it to the furnace.

One advantage of the furnace process is that the production of elemental phosphorus provides opportunity for saving on transportation cost. One ton of elemental phosphorus is equivalent to 2.29 tons of P_2O_5. When the market area is remote from the phosphate mine, a very substantial saving may be realized by shipping elemental phosphorus rather than phosphate rock or finished fertilizer. For instance, 1 ton of elemental phosphorus is equivalent to the phosphorus content of 5 tons of TSP or DAP or 7 tons of high-grade phosphate rock. Since shipping costs may amount to as much as \$15/ton, a saving of \$26-\$39/ton of P_2O_5 is possible.

Another advantage of the furnace process is its ability to produce high-grade products. Superphosphoric acid (76%-80% P_2O_5) may be made without extra cost and, from it, ammonium polyphosphate (15-60-0), high-analysis superphosphate (54% P_2O_5), or high-analysis liquid fertilizer (11-37-0). Diammonium phosphate made from furnace acid has an analysis of 21-53-0 compared with 18-46-0 for the wet-process product.

The main drawbacks of the furnace process are the relatively high capital cost of the plant and the scarcity of locations where low-cost electricity is available. For this reason the electric furnace process is used almost exclusively to produce phosphorus and phosphoric acid for industrial chemicals, insecticides, detergents, and food or animal feed additives.

Production of phosphoric acid from elemental phosphorus is relatively simple. It is carried out by burning liquid elemental phosphorus in air and hydrating the resulting P_2O_5 to H_3PO_4. A diagram of a typical plant is shown in figure 13. All process equipment is made of stainless steel, usually type 316. The overall reaction is:

$$P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4$$

Typical process requirements per ton of P_2O_5 recovered as phosphoric acid assuming 86% overall re-

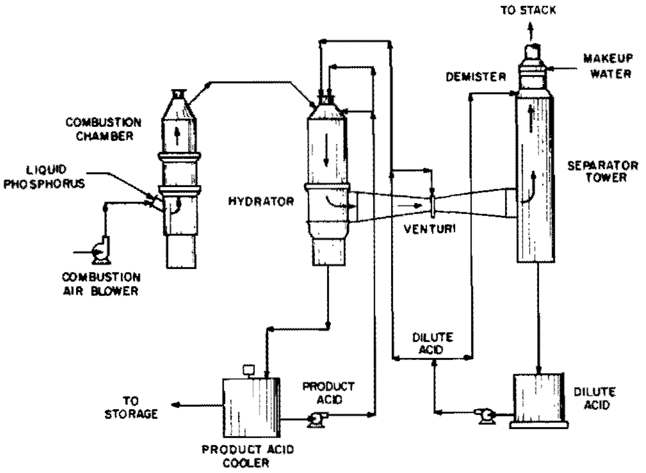

Figure 13. Manufacture of Phosphoric Acid from Elemental Phosphorus.

covery for a plant of about 100,000 tons P_2O_5/year capacity are:

1.	Phosphate rock, 31.2% P_2O_5 (or equivalent amounts of rock of other grade)	3.73	tons
2.	Silica rock or pebble, 95% SiO_2, dry (Less silica is needed if the phosphate rock is high in silica)	1.1	tons
3.	Coke, screened and dried, 86% fixed carbon	0.6	ton
4.	Carbon or graphite electrodes	25	kg
5.	Electricity	6,700	kWh
6.	Cooling water (once-through basis)	110	tons
7.	Steam	1	ton
8.	Operating labor	4	man-hours
9.	Maintenance (labor and materials)	10%	of plant cost per year
10.	Fuel, negligible to 1.2 million kcal depending on efficiency of use of byproduct carbon monoxide gas		

Estimated capital costs for an electric furnace plant in the range of 25,000-100,000 tpy of elemental phosphorus (57,000-229,000 tons of P_2O_5) are shown in figure 14. These costs are for a U.S. industrialized location, including ancillary facilities and offsites, adjusted from 1969 estimates to December 1976 costs by means of the Chemical Engineering Plant Construction Cost Index.

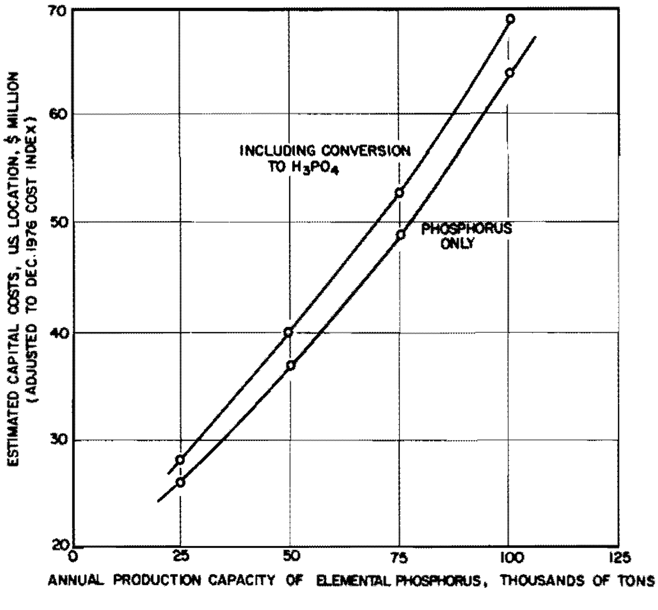

Figure 14. Estimated Capital Costs for an Electric-Furnace Elemental Phosphorus Plant.

If phosphate rock is available that is satisfactory for use without agglomeration and calcining, the plant capital cost would be 25%-30% lower, maintenance and labor costs would also be 25%-30% lower, and fuel requirements would be virtually eliminated. The byproduct carbon monoxide gas from the furnace would be more than sufficient for drying coke, silica, and rock. Some rocks that have been used successfully in electric furnaces without agglomeration, calcining, or sintering are screened Florida pebble (plus 6 mm), Florida hard rock, and Montana hard rock (crushed and screened). Use of uncalcined rock may increase the electric power consumption in the furnace by as much as 10%, depending on the CO_2 and combined water content.

The Tennessee Valley Authority (TVA) began development of the electric-furnace process for producing phosphate fertilizers in 1933 and produced phosphorus and phosphoric acid from 1934 to 1977. At one time five furnaces were in operation. In 1977 operation of all furnaces was discontinued by TVA since the process could no longer compete with the wet process for fertilizer production. Numerous publications are available from TVA on production of elemental phosphorus and phosphoric acid by the electric-furnace process; selected references are included at the end of this chapter (33, 34, 35, 36, 37, 38, 39).

Phosphoric Acid Production by the Blast-Furnace Process

A flow diagram of a TVA pilot plant for producing phosphoric acid by the blast-furnace process is shown in figure 15. The scale of the pilot plant was about 1 ton of P_2O_5/24 hours (40).

In general, the blast-furnace process differs from the electric furnace in the following respects:

1. Coke is used for both fuel and phosphorus reduction. The estimated coke requirement for a large-scale unit is 2.5 tons/ton of P_2O_5 recovered as phosphoric acid (allowing for ferrophosphorus losses). About 0.6 ton of coke is consumed in reduction of P_2O_5 to phosphorus, and the remainder generates heat by combustion with preheated air to form carbon monoxide.
2. As with the electric furnace, the charge--phosphate rock, coke and silica--must be in lump or agglomerated form, but it is not necessary to calcine or dry the charge since there is sufficient heat in the ascending gases in the furnace shaft for this purpose.
3. The gas from the furnace contains about 37% CO and 1.0%-1.5% P_4 by volume. The remainder is mainly nitrogen. Although recovery of elemental phosphorus by cooling and condensation is feasible, it would be difficult to recover a high percentage because of the low concentration in the gas. In the TVA pilot plant, phosphoric acid was recovered after preferential oxidation of the phosphorus in the gas with air.
4. The gas remaining after phosphoric acid recovery contains about 34% CO, 1%-2% O_2, and the remainder N_2 (dry basis). About 40% of this gas can be used advantageously for preheating the air to the blast furnace. The remainder would be available for other uses.

The blast-furnace process was used commercially to produce phosphoric acid for industrial and chemical products from 1929 to 1938 by the Victor Chemical Works, now Stauffer Chemical Company. The plant was located at Nashville, Tennessee (United States).

The use of the blast furnace to produce phosphoric acid for fertilizer purposes seems unpromising

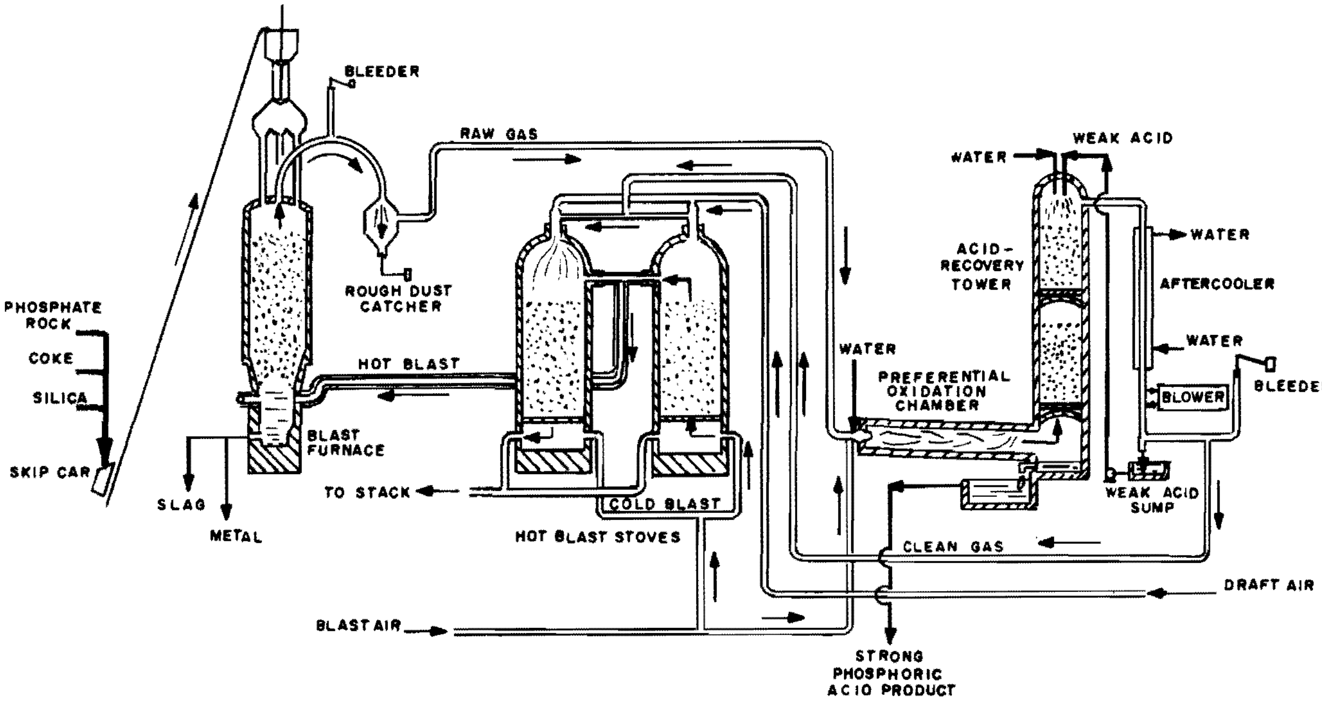

Figure 15. TVA Experimental Phosphate Blast-Furnace Plant.

at present due to the high cost of coke. However, with some improvements it might be considered in certain circumstances (41). As does the electric furnace it can utilize low-grade siliceous ore with moderately high alumina and iron oxide content.

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XIV Fertilizers Derived from Phosphoric Acid

Phosphoric acid may be used as a fertilizer, and a relatively small amount is so used (about 50,000 tpy in the United States). It is particularly useful on alkaline soil. However, expensive corrosion-resistant application equipment is needed.

Theoretically, any phosphate can be made from phosphoric acid. With minor exceptions, the commercial fertilizer products are triple superphosphate, ammonium phosphates, and other compound fertilizers. (Some of the minor exceptions are potassium phosphates and magnesium ammonium phosphate--$MgNH_4PO_4$.) Use of phosphoric acid in compound fertilizers will be described under subject headings, "Compound Fertilizers," "Liquid Fertilizers," and "Nitrophosphates (Mixed-Acid Processes)" (chapters XV and XIX). The present chapter will deal mainly with triple superphosphate and solid ammonium phosphates.

Triple Superphosphate (TSP)

Since 1965 TSP has supplied approximately 15%-20% of the world's fertilizer phosphate. No definite trend toward increased or decreased popularity is evident. As phosphate fertilizer consumption has increased, TSP production has increased at about the same rate.

One of the advantages of TSP is that it is the most highly concentrated straight phosphate fertilizer available. Another advantage is that part of its P_2O_5 content is derived directly from phosphate rock, a relatively low-cost source. From another viewpoint, with a given amount of phosphoric acid, a greater amount of fertilizer P_2O_5 can be produced as TSP than as ammonium phosphate.

The percentage of P_2O_5 in TSP that is derived directly from rock varies from about 25% to 30%, depending on the $CaO:P_2O_5$ ratio in the rock, the impurity content of the rock and acid, and other factors.

The main disadvantages of TSP are: (1) the total nutrient content is lower than that of ammonium phosphates, (2) its acidic character may cause deterioration of some types of bags (paper or hemp), and (3) it is not well suited for blending with urea because of reactions that cause deterioration of physical condition.

TSP may be prepared in either granular or nongranular form. The nongranular form is preferred for use as an intermediate for production of compound fertilizer by granulation processes, whereas the granular form is preferred for direct application or for blending.

The basic chemical reaction involved in production of TSP is:

$$\underset{\text{(Fluorapatite)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(Phosphoric acid)}}{14H_3PO_4} + 10H_2O \rightarrow \underset{\text{(Monocalcium phosphate)}}{10Ca(H_2PO_4)_2\cdot H_2O} + \underset{\text{(Hydrofluoric acid)}}{2HF}$$

In most processes, a large percentage of the fluorine remains in the product, probably as fluosilicates and possibly as calcium fluoride. If some of the calcium is converted to calcium fluoride or fluosilicate, somewhat less phosphoric acid is required than indicated by the equation. However, phosphate rock usually contains a higher ratio of $CaO:P_2O_5$ than fluorapatite. The proportion of acid to rock often is calculated to yield a $P_2O_5:CaO$ mole ratio of 0.95 to 1.0 (weight ratio = 2.41 to 2.54) according to the formula:

$$\frac{\text{Acid } P_2O_5 + \text{ rock } P_2O_5}{\text{Rock CaO}} = 2.41 \text{ to } 2.54 \text{ (weight ratio)}$$

However, various impurities in the acid and rock cause variations in the optimum acid:rock ratio. The product will contain--in addition to monocalcium phosphate--iron, aluminum, and magnesium phosphates; probably a small amount of dicalcium phosphate; unreacted rock; calcium sulfate originating from free sulfuric acid in the phosphoric acid and sometimes from rock impurities; and various other impurity compounds.

The economic optimum acid:rock ratio is best determined by test methods and will depend on whether the commercial value is based on solubility in water, ammonium citrate, or other solvents. When water solubility is the criterion, both the rock and acid should be as low in iron and aluminum as is economically feasible.

The effects of $CaO:P_2O_5$ ratio of the rock and grade of rock on the proportions of rock and phosphoric acid and on the grade of the TSP product are shown in table 1. As the $CaO:P_2O_5$ weight ratio increases from 1.35 to 1.70, the percentage of P_2O_5 derived from rock decreases from 30% to 24% while the percentage derived from acid increases from 70% to 76%; the grade of the product TSP increases from 45% to 47% P_2O_5. As the grade of the rock increases from 28% to 38% P_2O_5 (with the $CaO:P_2O_5$ ratio constant at 1.5), the grade of the product increases from 43.0% to 48.5% P_2O_5. These calculations are based on phosphoric acid of average impurity content and rock with the usual amounts and types of impurities. The calculations are intended only for illustration of general trends; accurate values can be obtained only from experimental data derived during tests with the specific phosphate rock and phosphoric acid in question.

The reactivity of phosphate rock is of more importance in TSP production than in phosphoric acid production. Unreactive rocks may require unusually fine grinding or long reaction times or both. Even so, it may be difficult to attain an acceptable degree of completion of reaction with some igneous apatites.

Rock containing carbonates or carbonate substitutions in apatite releases CO_2 during reaction. The released gases result in a porous structure of the superphosphate made by den processes. This is considered desirable when the superphosphate is to be used in making compound fertilizers. When the rock contains very little carbonate, the superphosphate may be hard and dense, leading to granulation difficulties and poor ammoniation characteristics.

TABLE 1. EFFECT OF GRADE AND $CaO:P_2O_5$ RATIO OF ROCK ON PROPORTIONS OF ROCK AND PHOSPHORIC ACID AND ON GRADE OF TSP

Weight Ratio CaO/P_2O_5 in Rock	% Total P_2O_5 in Product from		Grade of Rock, % P_2O_5	Tons/Ton of Product P_2O_5 [a]		Grade of Product, % Total P_2O_5 [b]
	Rock	Acid		Rock	Acid	
1.70	24.0	76.0	33	0.73	1.40	47.0
1.50	27.0	73.0	33	0.82	1.35	46.1
1.35	30.2	69.8	33	0.92	1.29	45.2
1.50	27.0	73.0	28	0.965	1.35	43.0
1.50	27.0	73.0	38	0.71	1.35	48.5

a. Phosphoric acid containing 54% P_2O_5. Acidulation mole ratio $P_2O_5:CaO = 0.97$.

b. The grade will be increased by loss of volatile ingredients in the rock and by loss of free moisture; the grade in terms of "available" P_2O_5 will be decreased by citrate-insoluble P_2O_5 in the product. These two factors may approximately offset each other depending on the composition of the phosphate rock and acid.

Production of Nongranular Triple Superphosphate

Nongranular superphosphate is commonly produced by continuous den processes followed by a storage curing period of up to 1 month during which chemical reactions are completed. Dens that are suitable for single superphosphate (SSP) are often also suitable for TSP and will be described in connection with SSP. The main difference is that TSP sets (hardens) more rapidly than SSP, thus the den retention time can be much shorter. If the retention time is too long, the TSP may become so hard that disintegration is difficult. Depending on the reactivity of the rock and other factors, denning times of 5-20 minutes are suitable for TSP as compared with 30 minutes to 2 hours for SSP.

Special belt conveyors are often used for TSP rather than conventional dens. In any case, the belt or den must be enclosed and connected to a fume exhaust system to remove fluorine-containing gases to a scrubber. Small amounts of fluorine compounds continue to be evolved during storage curing, and good ventilation is needed to remove the fluorine from the working area. Scrubbing of the exhaust gas may be necessary to prevent atmospheric pollution.

After storage curing, the TSP usually is reclaimed with a power shovel and disintegrated in a cage mill to pass a 6-mesh screen (3.3 mm). Sometimes blasting is necessary to loosen the pile of TSP before reclaiming. The disintegrated TSP (sometimes called run-of-pile TSP) may be used for making compound fertilizer by granulation processes, or it may be granulated for direct application. In some cases it is used for direct application without granulation, but in most countries, farmers do not favor such a product. Also the nongranular product tends to cake in bags; caking can be prevented or alleviated by the addition of about 5% of ground limestone.

Many plants use the cone-mixer process that was originated by TVA (1, 2). Figure 1 shows a flow diagram of the process. A somewhat similar process is known as the Kuhlmann process; the mixer is a small cylindrical vessel equipped with a high-speed stirrer. The mixed product discharges to a belt conveyor where its retention time is in the range of 5-10 minutes.

Both batch and continuous dens have been used; a Broadfield-type continuous den (described later) is suitable with a retention time of about 20 minutes.

Granulation of Cured TSP--TSP is granulated in some plants by the procedure shown in figure 2. Cured run-of-pile TSP, 3-6 weeks old, is removed from storage and fed to a screen. The oversize is milled and recycled; the fine material is conveyed to a rotary-drum granulator. Water is sprayed onto the bed of material, and steam is sparged underneath the bed to provide wet granular material. The wet granules are discharged to a rotary dryer. The dried granules are screened. The oversize is milled and returned with the fines to the granulator. Dust and fumes from the dryer are scrubbed in a water scrubber.

A few plants feed phosphate rock and acid to the granulator to supply a portion of the phosphates; production cost is lowered and granulation is improved, but greater investment is required.

The requirements per ton of product are summarized in the following tabulation:

Requirements per Metric Ton of Product
for the Production of
Granular Triple Superphosphate

Cured TSP, tons	1.02
Steam, kg	75
Water, kg	250
Fuel, kcal	160,000
Electricity, kWh	29
Operating labor, man-hour	0.3

Direct Granulation of Triple Superphosphate

When granular TSP is the desired end product, it is usually preferable to produce it directly rather than by granulation of cured TSP. Some advantages of direct granulation processes are:

1. Cost is usually lower.
2. Granules are denser and stronger.
3. Granulation equipment can be used interchangeably for producing TSP and ammonium phosphates.
4. Storage curing is eliminated, thereby reducing working capital and eliminating the difficulty of dealing with fluorine emissions from storage curing.
5. In some processes, compound fertilizers containing potash or other plant nutrients may be produced optionally during granulation. (This is also true of granulation of cured superphosphate, but that is somewhat more difficult.)

The main disadvantages of direct granulation are:

1. Because the reaction time is limited, unreactive rocks are poorly suited for use in direct granulation processes.
2. Somewhat greater loss of soluble P_2O_5 may occur because of incomplete reaction or, alternatively, a higher acid:rock ratio may be needed to prevent this loss.

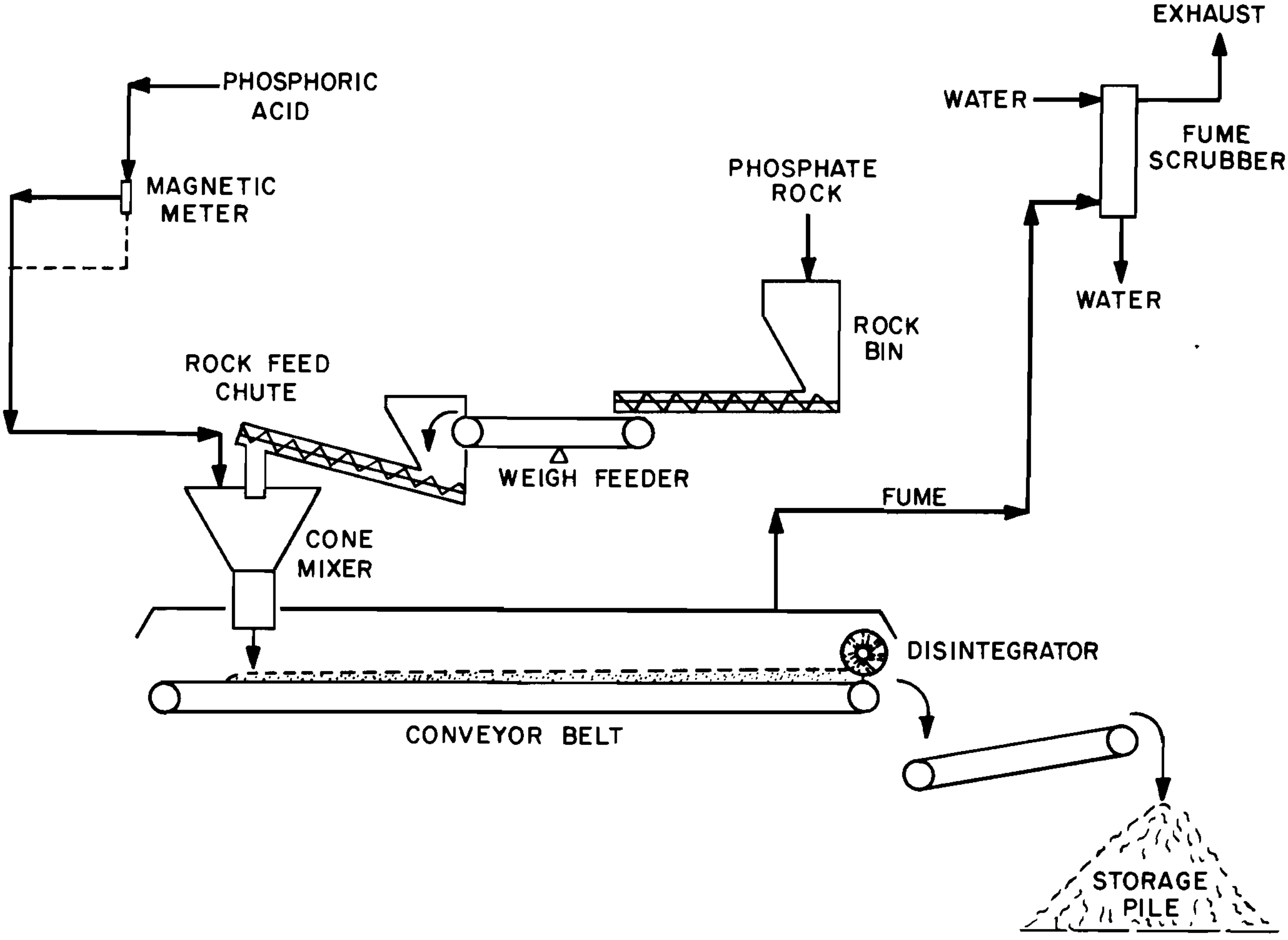

Figure 1. Manufacture of Run-of-Pile Triple Superphosphate.

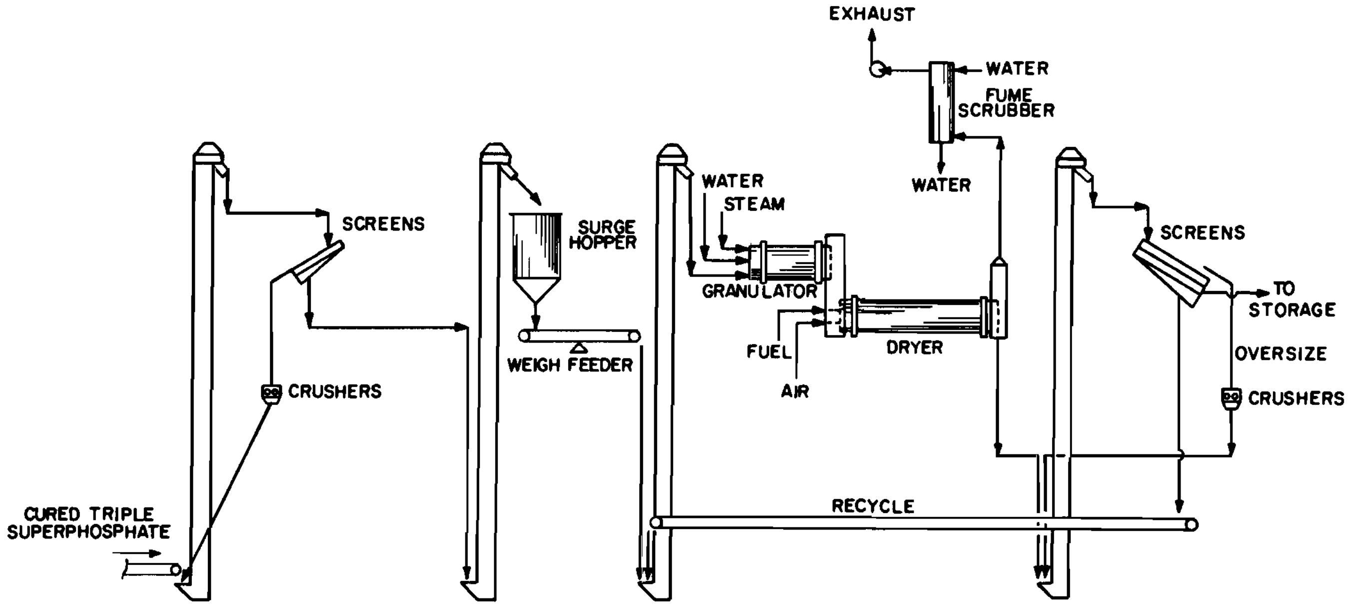

Figure 2. Granulation of Cured Run-of-Pile Triple Superphosphate.

Two general types of direct granulation processes are in use: slurry granulation and ex-den granulation. In ex-den granulation the acidulation and denning steps are similar to those described above for producing nongranular TSP except that the rock may be somewhat more finely ground and the den retention time is longer (25-45 minutes vs. 10-20 minutes). Also, the product from the den goes directly to a granulator rather than to storage. After granulation, the product is dried, screened, and conveyed to storage. Drying is controlled to yield a product of 4%-6% moisture. Under these conditions some further reaction takes place in storage.

Sinte Maartensdijk has described a plant of this type which is capable of producing 20-35 tph of TSP, SSP, or mixtures of the two (3). It can also make PK compound fertilizers by the addition of potash at the granulator. A simplified flow diagram of a typical direct ex-den granulation system is shown in figure 3.

Typical data for the production of TSP given by Sinte Maartensdijk follow:

Phosphoric acid concentration	50% P_2O_5
Ratio of recycle to product	1.25:1.0
Moisture content, ex-den	10%-12%
Moisture content after granulation and drying	5%-6%
Water-soluble P_2O_5 content of product	46%
Water solubility of P_2O_5:	
ex-plant	94%
after curing	98%
Steam consumption, kg/ton	50-60
Water consumption, kg/ton	60-65
Power consumption, kWh/ton[a]	38
Labor required, man-hours/ton	0.25
Particle size of granules	1.6-4 mm

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a. Presumably includes rock grinding which was given as 25 kWh/ton of rock or about 10 kWh/ton of TSP.

The plasticity and heat content of fresh TSP (or SSP) make it much easier to granulate than cured TSP; less recycle, water, and steam are required. Presumably, less fuel is required for drying. Total electric power consumption is somewhat lower, and labor requirements are only 36% of that required for the "conventional" two-step process. The product quality is said to be superior in hardness, shape, uniformity, and smoothness.

The most popular slurry-type granulation process is the Jacobs-Dorrco process, formerly known as the Dorr-Oliver process. A simplified flow diagram is shown in figure 4. Ground phosphate rock and phosphoric acid, 38%-40% P_2O_5, are fed to the first of a series of two or three steam-heated, stirred reaction vessels. The overall retention time is about 30 minutes, and the temperature is about 90°C. The thick slurry is fed to a blunger or rotary drum granulator together with a high proportion of recycle. The moist granules are dried and screened, and the product size is cooled and sent to storage.

Leyshon has described some recent improvements in the process (4). An "aging conveyor" is used to transport the granules from the granulator to the cooler. A small amount of moisture is evaporated on the conveyor, and moisture is absorbed into the interior of the granule. The result is that the granules are less sticky when they reach the dryer and, hence, less likely to clog feed chutes or cake on the walls of the dryer. Single-deck screens are used; the oversize is separated on one screen, crushed in a chain mill, and recycled. The stream of undersize, including the product size, is split into two streams; one portion is withdrawn for recycle to the granulator, and the other is screened to separate fines which are recycled and product size which is cooled. A final "polishing screen" is used following the cooler for more complete removal of fines and oversize. As with all granulation systems, the dust and fume removal system has been improved to increase efficiency. The slurry process for granulating TSP is essentially the same as for granulating ammonium phosphates and will be described further under that topic.

Recycle ratios (ratio of recycle:product) are between 10 and 12:1 for blunger granulation and about 8:1 for rotary-drum granulation. The lower ratio for

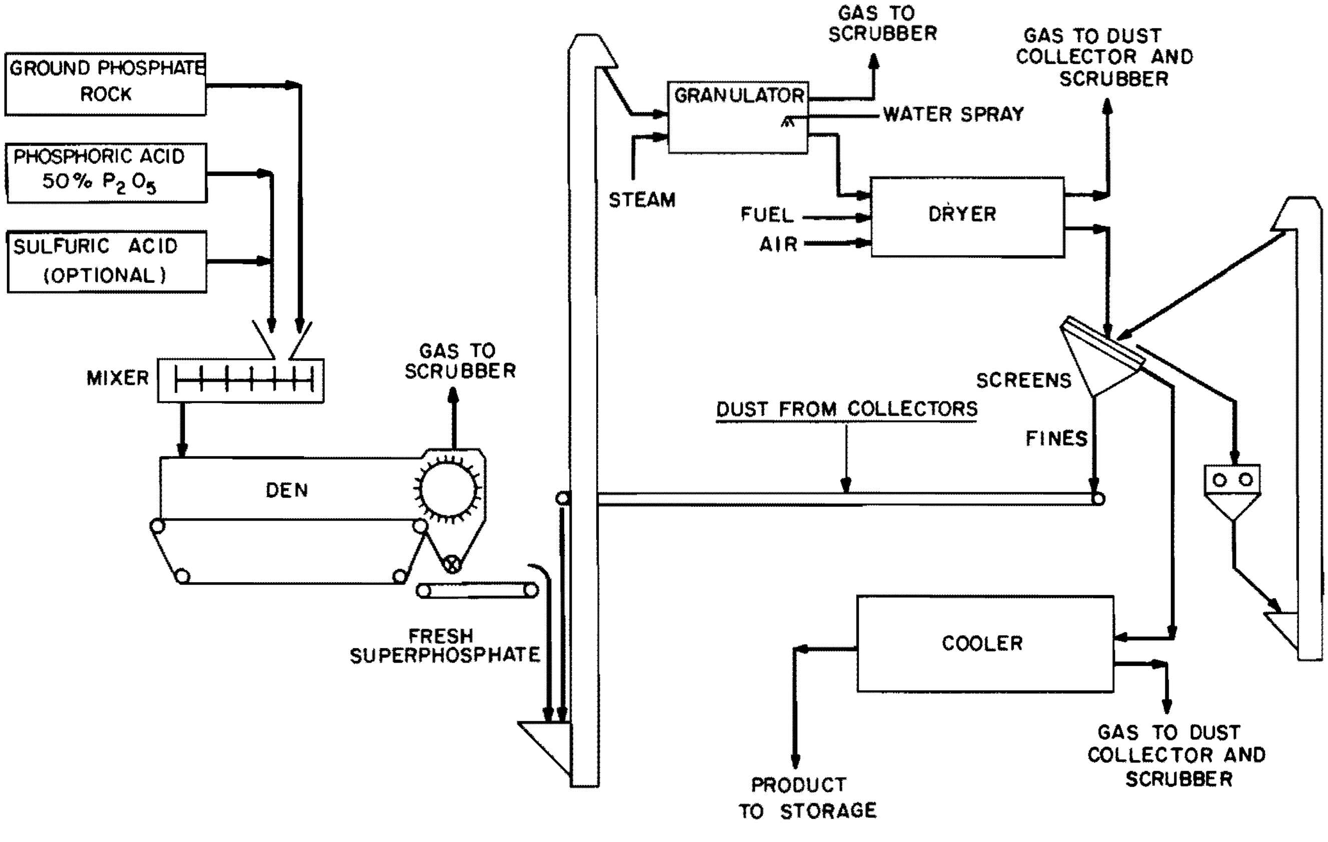


Figure 3. Direct Granulation of Triple Superphosphate (Also Adaptable to Production of Granular Single or Enriched Superphosphate).

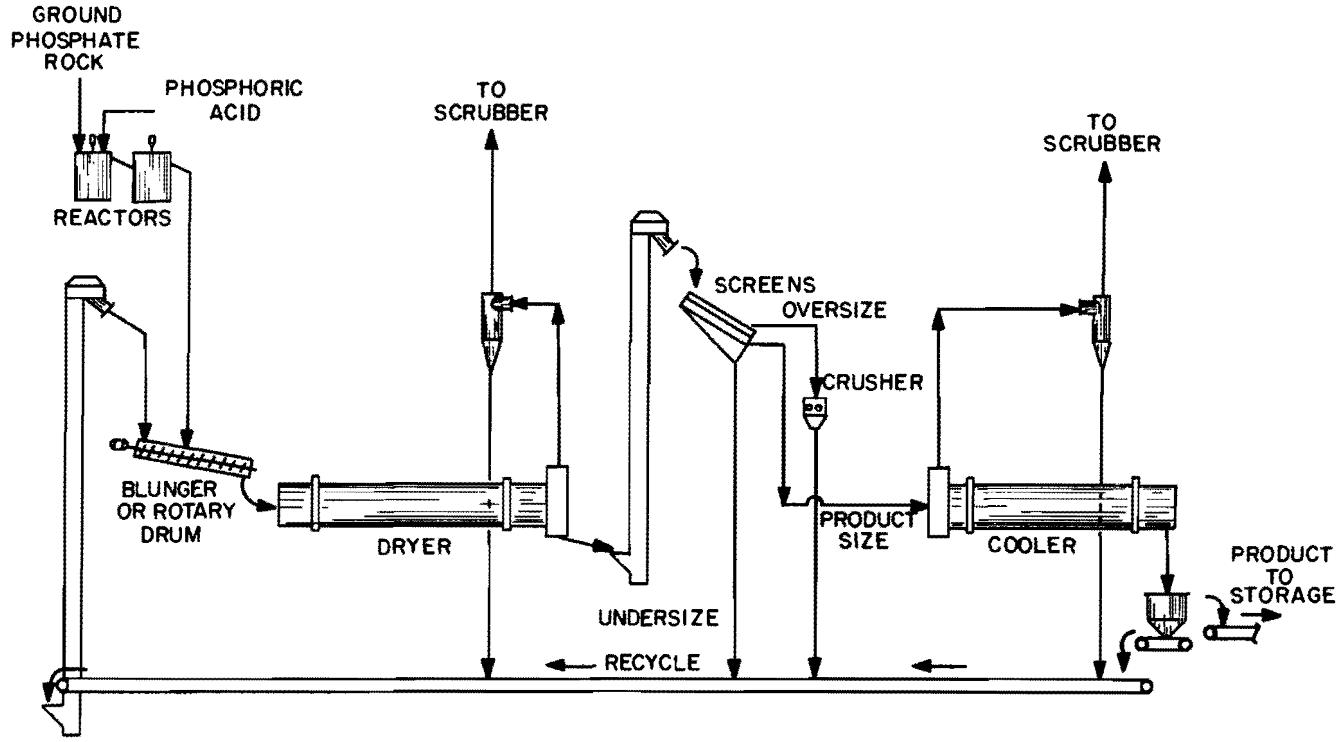


Figure 4. Slurry Process for the Manufacture of Granular Triple Superphosphate.

rotary-drum granulation is ascribed to moisture evaporation in the drum granulator enhanced by a countercurrent sweep of air.

The estimated utility requirements per ton of product are about 40 kWh for electric power (including phosphate rock grinding), about 125,000 kcal of fuel oil for drying, and about 20 kg of steam, mainly for heating the reactors.

Another slurry process reported to have been developed in Europe is similar to the Jacobs-Dorrco process (5). However, granulation and drying are combined by spraying the slurry onto a cascading curtain of granules at the feed end of a cocurrent rotary dryer.

Ammonium Phosphates

Ammonium phosphates, particularly diammonium phosphate (DAP), are the most popular phosphate fertilizers on a worldwide basis because of their high analysis and good physical properties.

The compositions of the pure salts--monoammonium phosphate (MAP) and diammonium phosphate (DAP) are:

	Monoammonium Phosphate (MAP)	Diammonium Phosphate (DAP)
N, %	12.17	21.19
P_2O_5, %	61.71	53.76

Grades made from wet-process acid of average impurity content are 18-46-0 for DAP and 11-55-0 for MAP. A lower grade MAP product, 11-48-0, has been produced since 1933; the lower grade is due to the addition of small proportions of phosphate rock and sulfuric acid. Grades containing both MAP and DAP also are produced; examples are 13-52-0 and 16-48-0. Recently, ammonium polyphosphate has been produced by TVA. When produced from furnace acid the grade was 15-62-0; at present a similar product made from wet-process acid is 11-55-0. Ammonium polyphosphate consists mainly of monoammonium orthophosphate and diammonium pyrophosphate, $(NH_4)_2H_2P_2O_7$).

Relatively small amounts of pure DAP and MAP are made by crystallization processes using phosphoric acid made by the electric-furnace process. Also, a nearly pure crystalline product (20-52-0) is produced in Europe from wet-process acid made from Kola apatite; most of the impurities from the apatite are eliminated by bleeding off a portion of the mother liquor in the crystallization process. The sidestream of mother liquor is utilized in other fertilizer products. The pure, fully soluble DAP is used mainly for liquid fertilizers.

Granular DAP is commonly produced by a slurry process; the process developed by TVA and illustrated in figure 5 is typical. The average concentration of the wet-process acid is about 40% P_2O_5; however, most plants use part of the acid at 54% P_2O_5 and part at 30% P_2O_5. The acid reacts with ammonia in a preneutralizer where the mole ratio of $NH_3:PO_4$ is controlled at about 1.4. This ratio corresponds to a point of high solubility (figure 6). The heat of reaction raises the slurry temperature to the boiling point (about 115°C) and evaporates some moisture. The hot slurry containing about 16%-20% water is pumped to the granulator where more ammonia is added to increase the mole ratio approximately to 2.0. Additional heat is generated, evaporating more moisture. The decreased solubility in going from 1.4 to 2.0 mole ratio assists granulation. The moist granules from the granulator are dried and screened, the product size is cooled, and the undersize and crushed oversize are recycled. Some of the product size may also have to be recycled to control granulation. The usual ratio of recycle to product is about 5:1. Ammonia escaping from the granulator, dryer, and preneutralizer is recovered by scrubbing with weak acid (30% P_2O_5), and the scrubber solution is added to the preneutralizer.

The same equipment can be used to make MAP by one of two procedures.

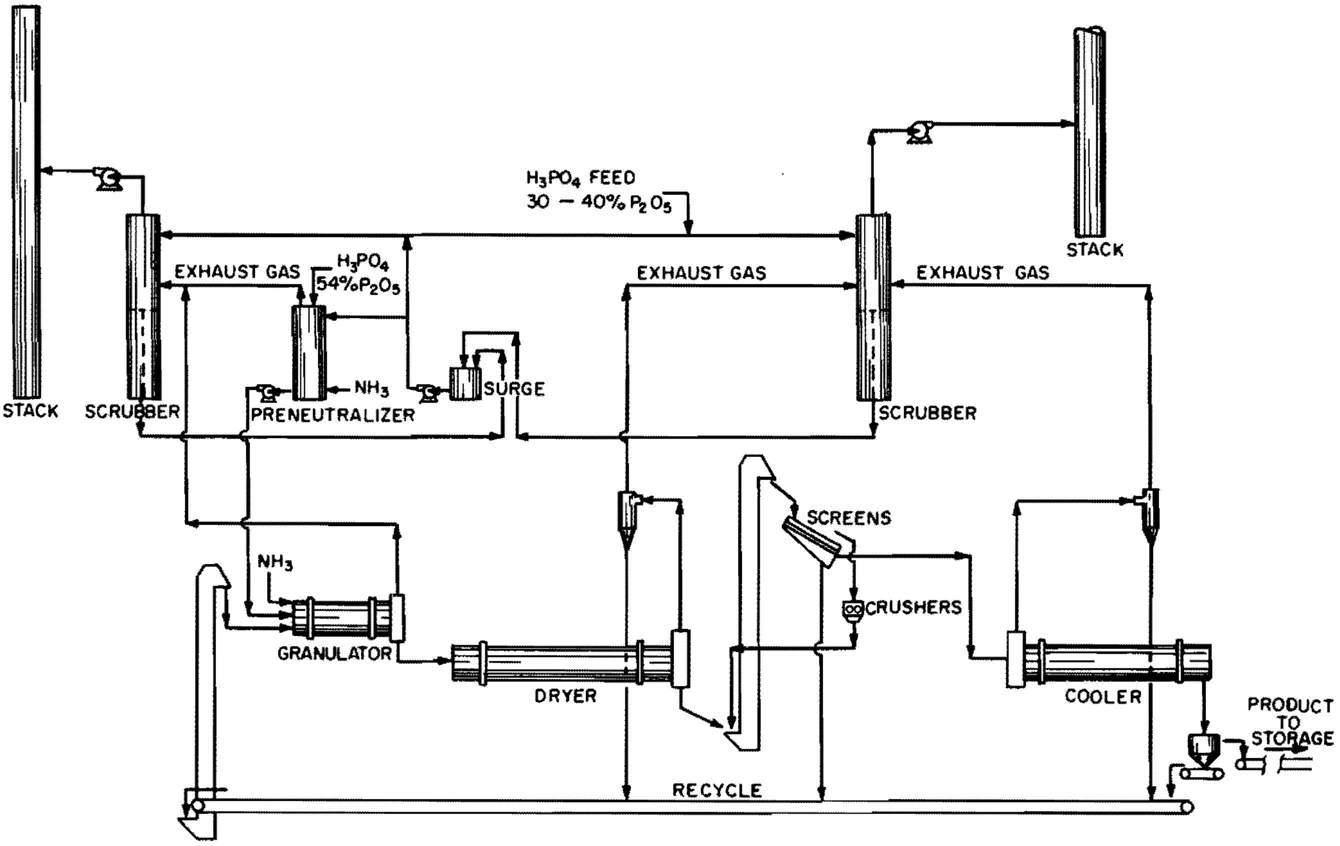


Figure 5. TVA Diammonium Phosphate Process.

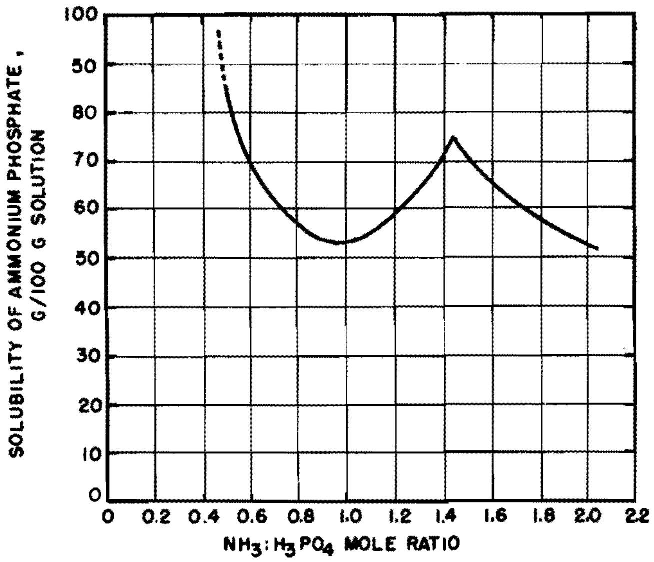


Figure 6. Effect of NH_3:H_3PO_4 Mole Ratio on Solubility of Ammonium Phosphate at 75°C.

1. The preneutralizer is operated at a mole ratio of 0.6 (a point of high solubility), and more ammonia is added in the granulator to increase the mole ratio to 1.0.
2. The preneutralizer is operated at a mole ratio of about 1.4, and phosphoric acid is added in the granulator to decrease the ratio to 1.0.

In producing MAP, ammonia recovery by acid scrubbing is not necessary, but all gaseous effluents are scrubbed to recover dust and fumes.

A recent improvement in the TVA-type process for making DAP is to substitute a pipe reactor for the preneutralizer. Ammonia and phosphoric acid react in a pipe which discharges directly into the granulator. Steam generated by the reaction is released in the granulator and swept out with a current of air. This arrangement is simpler and less expensive than the tank preneutralizer. An additional advantage is that, by using more concentrated phosphoric acid, the slurry discharged into the granulator contains less water and, hence, the recycle ratio is decreased. Torney reports that a plant in Australia using the pipe reactor has a recycle ratio of 3:1 (as compared with a 5:1 ratio for tank preneutralization) (6). A somewhat similar system is used in Spain by the firm of S. A. Cros to produce DAP and other grades of compound fertilizers (7). The use of pipe reactors in granulation processes will be described further in a later section of this chapter and in chapter XIX ("Compound Fertilizers").

Recently, Danos of Jacobs Engineering Group, Inc., has described a process for DAP production which involves use of a pipe reactor and eliminates the need for drying (8). About 65% of the ammonia used in the process is fed to the pipe reactor where it reacts with a mixture of phosphoric acid (52% P_2O_5), scrubber liquor containing partially neutralized phosphoric acid, and a small proportion of sulfuric acid. The pipe reactor discharges a viscous, frothy mixture of steam and slurry directly into a rotary-drum granulator through multiple spray nozzles onto a bed of dry recycled material. The remaining 35% of the ammonia is added through a sparger in the granulator bringing the N:P atomic ratio up to 1.8. The granules leaving the granulator contain about 2% moisture, and after cooling from 98°C to 52°C, the moisture content is reduced to 1.2%. No drying is required, and the recycle ratio (2.5:1) is only about half that of most slurry processes. Danos estimates a saving of $1.1 million in capital costs for a 60-tph plant and an annual saving of $583,000 in operating costs because of eliminating fuel for drying and decreasing electric power consumption (8).

The process described above is the same in principle as that demonstrated in a pilot plant at TVA's 12th Demonstration of Fertilizer Technology on October 18-19, 1978 (9). The equipment is similar to that described in chapter XIX under "Melt Granulation" (see figures 10 and 11, chapter XIX). Part of the phosphoric acid is used in a scrubber to recover ammonia and dust from the exhaust gas from the ammoniator and cooler. The pipe-cross reactor receives phosphoric acid at a concentration in the range of 40%-54% P_2O_5 (including partially neutralized acid from the scrubber), ammonia in liquid or gaseous form, water (if necessary to control the reaction), and sulfuric acid if necessary to adjust the grade to 18-46-0. The pipe-cross reactor discharges a mixture of low-moisture melt and steam through spray nozzles into the ammoniator granulator at a temperature ranging from 116°C to 137°C. The N:P atomic ratio of the melt is about 1.4:1. Additional ammonia in gaseous form is added through a sparger under the bed to increase the N:P ratio to about 1.95:1. This ratio does not include the ammonia that combines with sulfuric acid when that acid is used in the formulation. The granular product leaves the ammoniator at 86°-92°C with a moisture content of 2.5%-4.0%. It is cooled to about 38°C in a cooler; the moisture content is reduced during cooling to a range of 2%-3%. The product is said to have satisfactory noncaking properties when the moisture content is 3.0% or less. When sulfuric acid was used the amount was about 50 kg/ton, and the purpose was to adjust the grade to 18-46-0. Without sulfuric acid the analysis was 18.4%-18.8% N and 47.2%-47.5% available P_2O_5 using clarified phosphoric acid. However, when unclarified acid from some low-grade rocks is used, it may be difficult to attain a grade as high as 18-46-0 (10).

In the TVA pilot-plant tests, from 12%-20% of the ammonia input was evolved in the exhaust gases from the ammoniator-granulator and collected by scrubbing with part of the incoming phosphoric acid. The recycle ratio ranged from 2.6 to 4.1:1.

It should be noted that if a plant is designed to make MAP or DAP by the pipe-reactor process and a dryer is not provided, the plant cannot be used to make TSP. Also control of the moisture content of the product may be more difficult. Therefore, some engineers suggest that a dryer should be provided, at least for the final product, to provide more versatility even though it may not be necessary to use it most of the time.

The original Dorr-Oliver (now Jacobs-Dorrco) slurry granulation process for DAP production resembled the TVA process with the following exceptions:

1. All ammoniation was done in reaction vessels; for DAP production, three vessels in series were operated at 0.6, 1.4, and 1.85 NH_3:PO_4 mole ratios.
2. Granulation of the slurry with recycle was carried out in a blunger.

The recycle ratio was about 8:1. As in the TVA process, ammonia losses were recovered by acid scrubbing. MAP and grades in between MAP and DAP could be produced by adjusting the mole ratio in the reaction vessels. In subsequent modifications, ammonia was added in the blunger, or an ammoniator-granulator drum was substituted for the blunger. Other improvements have been mentioned under TSP and in the description of the Jacobs Engineering pipe-reactor process.

Both the original TVA process and the original Dorr-Oliver process have been modified and improved, and in addition other organizations have developed similar slurry granulation systems using similar basic principles. A basic flowsheet for the improved Jacobs-Dorrco slurry granulation process is shown in figure 7. This and other slurry granulation processes are adaptable to production of a variety of compound fertilizers by the addition of potash salts and urea, ammonium nitrate, or ammonium sulfate.

Both MAP and DAP usually have very good physical properties when made from wet-process acid. Both their storage properties and ease of granulation depend on the impurity content; a gel-like structure of impurities, mainly aluminum and iron phosphates, promotes granulation and serves as a conditioner to prevent caking, even at a moderately high moisture content (about 3%). On the other hand pure ammonium phosphates are difficult to granulate and tend to cake badly in storage, even with a very low moisture content unless coated with a conditioner. It has been demonstrated that the addition of impurities, particularly compounds containing aluminum, can improve granulation and product quality when there are insufficient impurities in the acid for this purpose. Also, the addition of a small proportion of phosphate rock to the phosphoric acid before ammoniation can improve granulation.

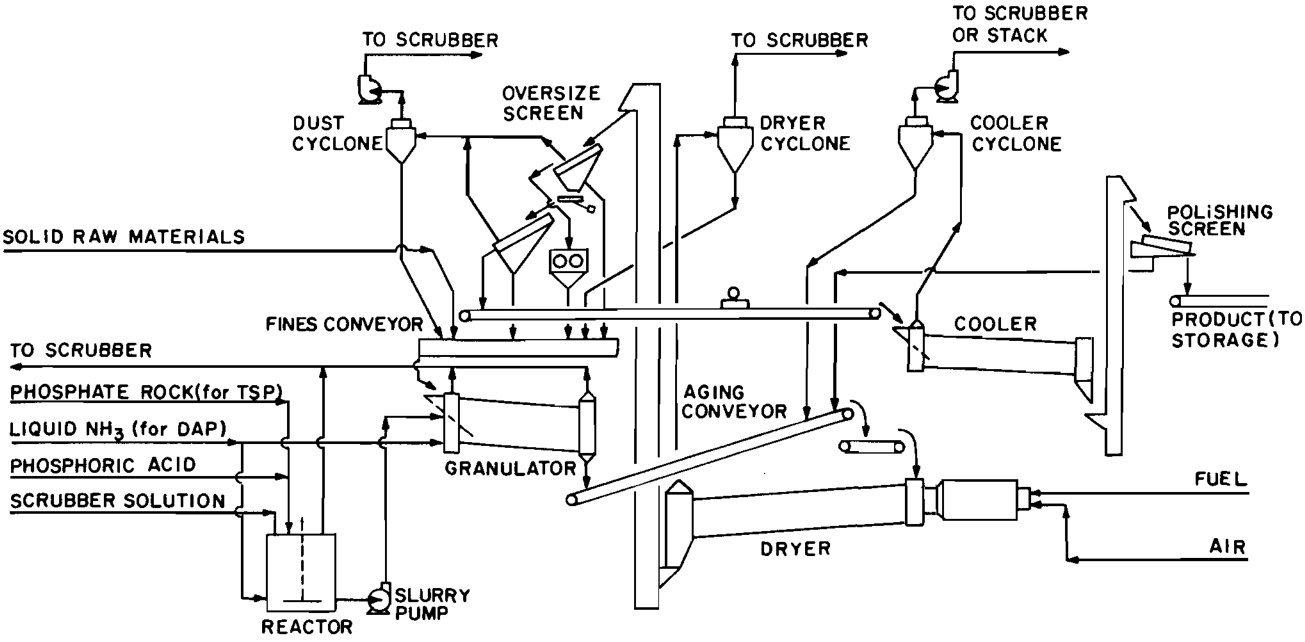


Figure 7. Jacobs-Dorrco Slurry Granulation Process.

A recent development is the growth in production of nongranular MAP for use as an intermediate in producing compound fertilizers. World capacity was estimated at 3.4 million tpy in December 1973, including plants under construction. In most cases the product is made in large plants located adjacent to phosphoric acid plants. Often the product is shipped to smaller granulation plants for use in making compound fertilizers.

Processes for making nongranular MAP have been developed by Scottish Agricultural Industries (SAI), Fison's Ltd., Swift Agricultural Chemicals (now Estech), and Nissan. In general, all processes aim at a simple, low-cost method by eliminating granulation, recycling, and drying. However, the product should have sufficiently good physical properties to permit storage, handling, and transportation without excessive caking or dust problems.

In the Fisons process (figure 8), phosphoric acid of about 50% P_2O_5 concentration is reacted with gaseous ammonia under 2.1 kg/cm^2 gauge pressure. The heat of reaction drives off part of the water as superheated steam. The remaining slurry contains 9%-10% water; the temperature is 170°C, and the pH is 3.5-4.0. This hot slurry is released into a spray tower through a special spray nozzle. More water is flashed off and evaporates as the droplets cool and solidify by falling through an ascending airstream. The product (trade name--Minifos) contains about 6% moisture; the grade ranges from 10-50-0 to 12-56-0, depending on the impurity content of the acid. The product is in the form of small round particles (microprills) ranging from 0.1 to 1.5 mm.

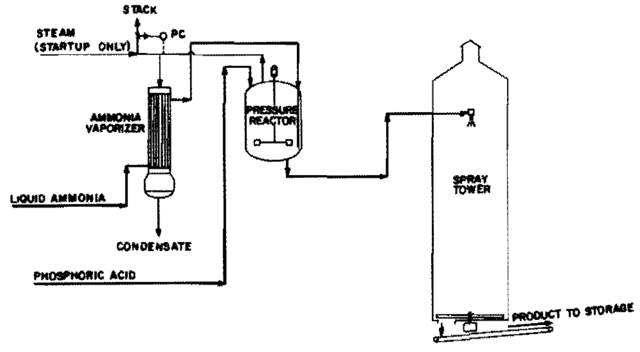


Figure 8. Fisons "Minifos" Process.

In the Swift process (figure 9) phosphoric acid (50% P_2O_5) and liquid ammonia react in a two-fluid nozzle which discharges into a reactor pipe. The mixture of finely divided MAP and steam is ejected into a cooling tower where a countercurrent airstream carries away the water vapor formed by the heat of reaction and cools the product. The product moisture content is 3%-5%.

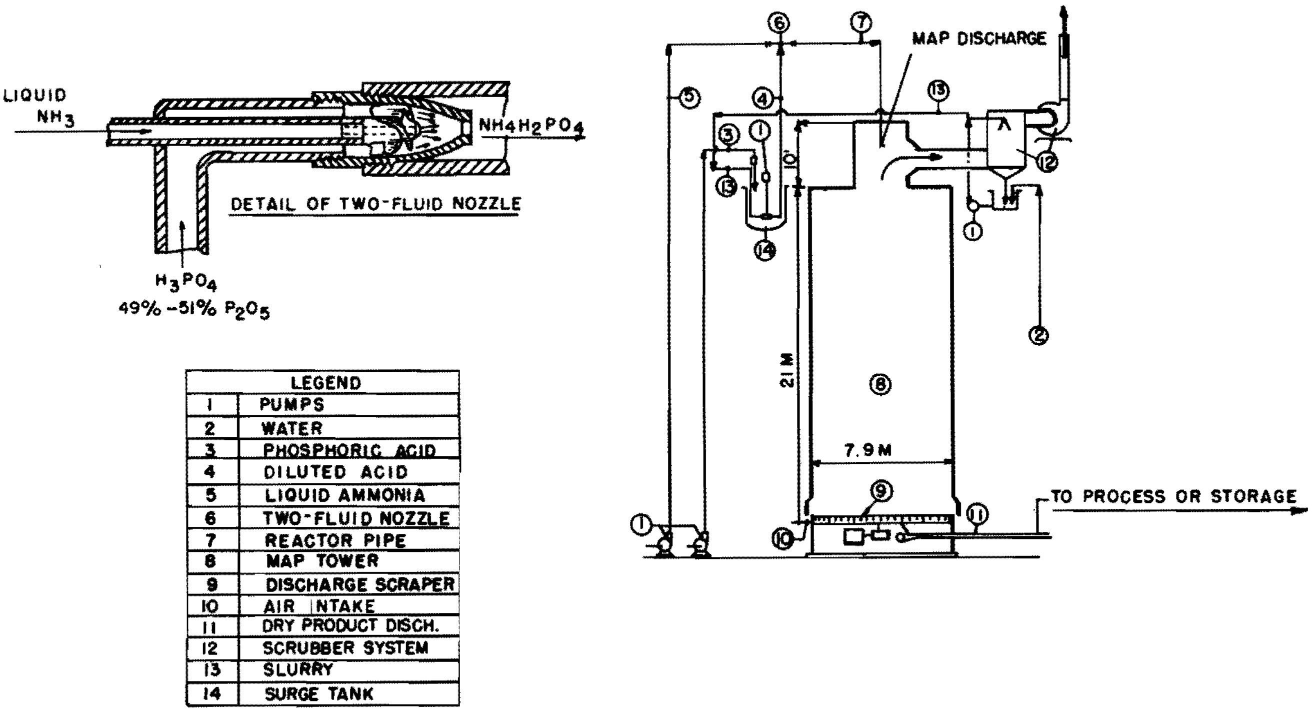
The Nissan process is also a spray tower process, in which droplets of phosphoric acid react with ammonia in an ascending airstream.

The Scottish Agricultural Industries (SAI) process (figure 10) consists of a reaction vessel in which phosphoric acid (about 50% P_2O_5) is neutralized with ammonia to a mole ratio of about 1.35, and the resulting hot slurry is mixed with more phosphoric acid in a specially designed twin-shafted mixer somewhat like a pugmill, which disintegrates the mass into small particles releasing water vapor. Water is evaporated in both steps. The product (trade name "PhoSAI") typically contains 6% moisture, 11% N, and 50% water-soluble P_2O_5 (11). The process can be modified to produce a nongranular diammonium phosphate called "Di-PhoSAI" or an ammonium phosphate-sulfate.

Recent articles discuss the storage and granulating properties of MAP made by different processes (12, 13). Better properties of the product made by the lower temperature process (SAI process) were attributed to precipitation of impurities in a gelatinous form that coated the MAP crystals.

Ammonium Polyphosphate

TVA has developed a process for producing ammonium polyphosphate, and in late 1973 the process



LEGEND	
1	PUMPS
2	WATER
3	PHOSPHORIC ACID
4	DILUTED ACID
5	LIQUID AMMONIA
6	TWO-FLUID NOZZLE
7	REACTOR PIPE
8	MAP TOWER
9	DISCHARGE SCRAPER
10	AIR INTAKE
11	DRY PRODUCT DISCH.
12	SCRUBBER SYSTEM
13	SLURRY
14	SURGE TANK

Figure 9. Swift Powder MAP Process.

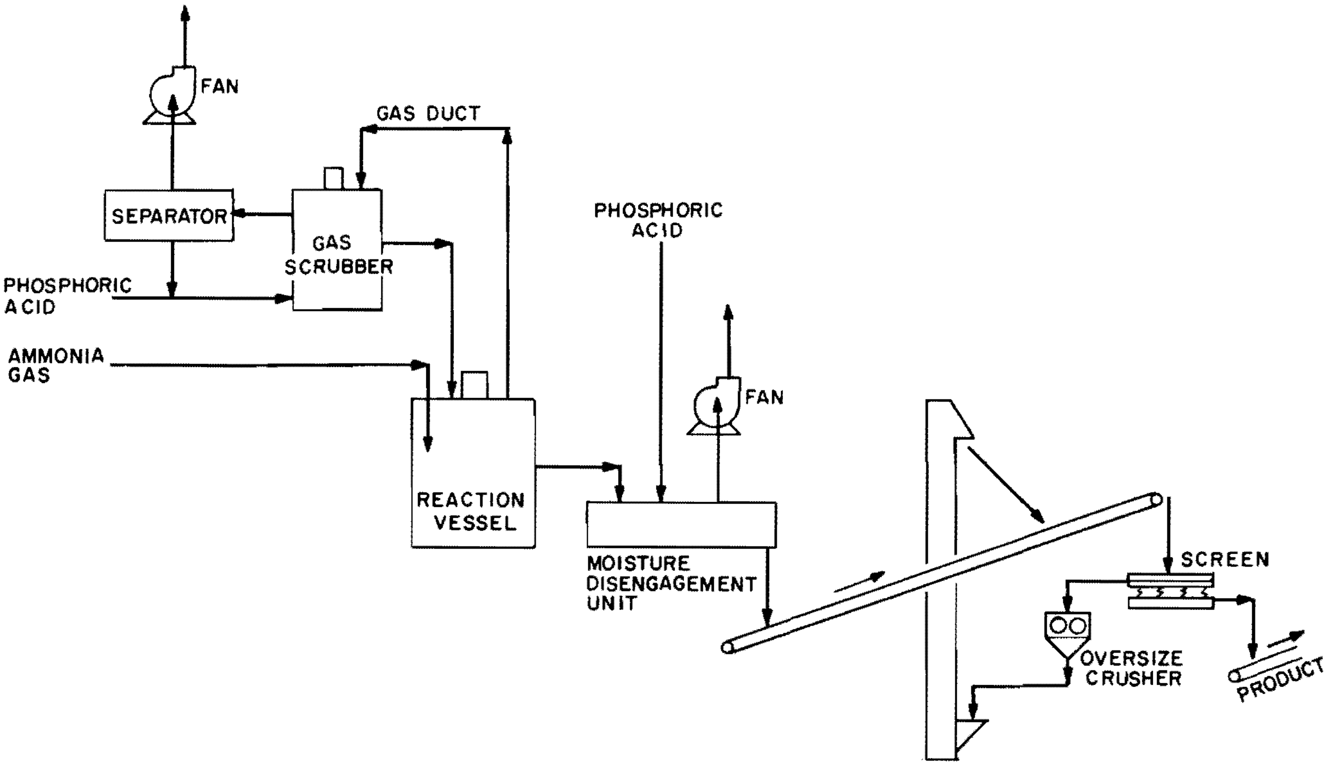


Figure 10. SAI Process for Producing Nongranular MAP.

was put into operation in a demonstration-scale plant with a capacity of 13-17 tph. The plant produces straight ammonium polyphosphate and urea-ammonium phosphate alternately. A flow diagram is shown in figure 11.

The process is based on utilization of the heat of reaction of phosphoric acid (54% P_2O_5) with gaseous ammonia to evaporate water and dehydrate the ammonium phosphate, thereby forming a melt which can be granulated with or without urea or other additives.

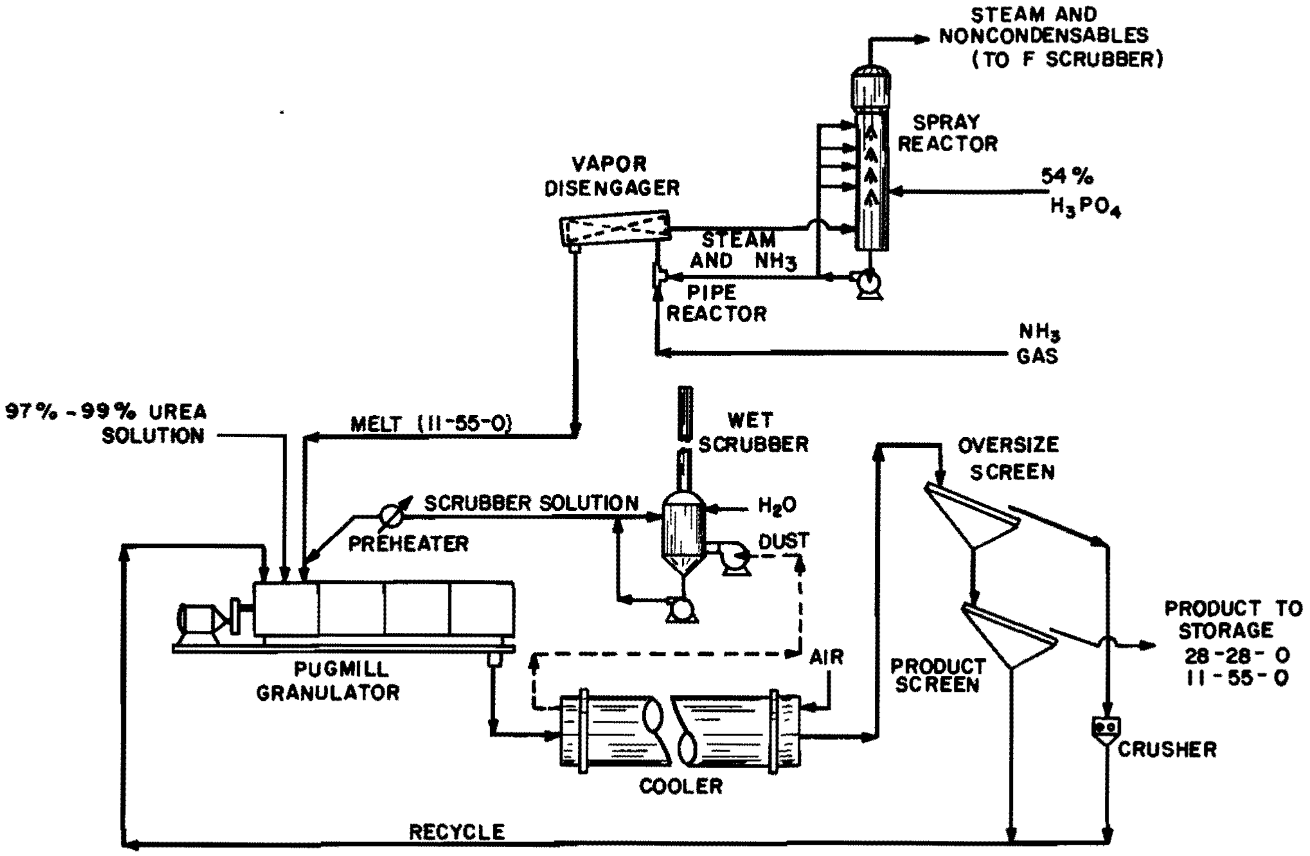


Figure 11. TVA Pipe Reactor-Pugmill Process for Production of Granular Urea-Ammonium Polyphosphate.

The main reaction takes place in a pipe reactor where the temperature reaches 210°-230°C. The melt usually contains 15%-25% of the P_2O_5 as polyphosphate, but the polyphosphate content can be increased to 50% or more by preheating the acid and ammonia or by using a more highly concentrated phosphoric acid. The melt is granulated in a pugmill in the demonstration-scale plant, but a rotary granulator has been used in the pilot plant. The usual grade produced in the demonstration-scale plant is 11-55-0; higher grades (such as 12-57-0) which were made in the pilot plant using phosphoric acid contain less impurities. By the addition of urea, 28-28-0 and 36-17-0 are produced.

The principal advantage of the process is that very low-moisture products are made without drying. Elimination of the rotary dryer and its appurtenances substantially decreases the investment cost and the energy requirement (fuel and electrical energy). Another advantage of the process is that the product has exceptionally good storage properties which are attributed to the low-moisture content and the polyphosphate content of the product.

TVA estimates the saving in capital cost as compared with a slurry process would be $740,000 for a 30-tph plant or $1,120,000 for a 50-tph plant. This is equivalent to 20%-25% of the battery-limits cost of a granulation plant. The saving in energy cost was estimated at 7 kWh of electrical energy and 140,000 kcal of fuel/ton of product (11-55-0). The fuel saving would be partially offset by an increased steam requirement for concentrating the phosphoric acid to about 54% P_2O_5 as compared with an average of about 40% for the slurry process.

Norsk Hydro has developed a method for air-prilling MAP melt containing some polyphosphates (14). The melt is produced in a pipe reactor. The grade is 11%-12% N and 57%-58% P_2O_5, depending on the acid composition.

Other Fertilizers Made from Phosphoric Acid

Ammonium Phosphate-Sulfates

A group of fertilizers known as ammonium phosphate-sulfates has been popular for many years and still is popular in many areas. The best known grade is 16-20-0, which essentially consists of MAP and AS. One reason for its popularity is that it is relatively nonhygroscopic. Hygroscopicity, as measured by the critical relative humidity (CRH) of some phosphate and nitrogen fertilizers and combinations, is tabulated below and discussed further in chapter XXII. The values given are for pure chemical compounds; impurities present in fertilizers may lower the CRH somewhat.

Material(s)	Critical Relative Humidity at 30°C
Monoammonium phosphate (MAP)	91.6
Diammonium phosphate (DAP)	82.8
Ammonium sulfate (AS)	79.2
Urea (U)	72.5
Ammonium nitrate (AN)	59.4
Combinations	
MAP + DAP	78
MAP + AS	76
MAP + U	65
MAP + AN	58
DAP + U	62
DAP + AN	59

It is evident that MAP is the least hygroscopic (has the highest CRH) of the materials listed and that ammonium sulfate (AS) is the least hygroscopic of the straight nitrogen materials. When a fertilizer with a higher $N:P_2O_5$ ratio than that of DAP (0.4:1.0) is needed, the MAP plus AS combination is the least hygroscopic.

Another advantage of ammonium phosphate-sulfate is the sulfur content, which is agronomically useful for many crops and soils.

Ammonium phosphate-sulfates have been produced by the Dorr-Oliver slurry process (previously discussed) since 1933 and more recently by other slurry granulation processes. The usual method involves reaction of sulfuric and phosphoric acid with ammonia, although ammonium sulfate from byproduct sources can be used. In addition to 16-20-0 and 11-48-0, several NPK grades are produced such as 14-28-14, 12-36-12, and 13-13-13.

Still more recently, TVA has developed the pipe-cross reactor system which is illustrated in figure 12. In this process, most of the reaction of phosphoric and sulfuric acids with ammonia is carried out in a pipe which discharges a melt into the drum granulator. Steam generated by the heat of reaction is swept out of the granulator by an airstream. One advantage of the process is that the heat of reaction is utilized to dry the product, thus no dryer is necessary. Another advantage over slurry processes is the comparatively low recycle ratio, in the range of 2-3:1 for 12-48-0 or 1-2:1 for 13-13-13 or 6-24-24. A somewhat similar process has been developed by S.A. Cros in Spain (7). In both processes, part of the acid is sprayed on the bed of material in the rotary granulator and reacts with ammonia which is injected under the bed, thereby promoting granulation and supplying more chemical reaction heat for drying.

Ammonium Phosphate-Chloride

Ammonium chloride is used in Japan and some other countries, both as a straight nitrogen fertilizer and as an ingredient of compound NP, NPK, and PK fertilizers. Ando described the operation briefly (15). He mentioned that, as compared with ammonium sulfate, ammonium chloride was 10% cheaper per unit of nitrogen (in Japan in 1970) and more concentrated (25% vs. 21% N). Filter-grade, wet-process phosphoric acid is ammoniated to form a MAP slurry which is fed to a pugmill along with ammonium chloride, recycle, (optionally) potassium chloride, and other fertilizer materials. Ando mentions that granulation in the pugmill was not as easy as with ammonium sulfate but that the difficulty had been overcome. The recycle ratio ranged from 2-4:1. The moisture content of the granulator product ranged from 5%-6% before drying and 0.5%-0.8% after drying. The main NP grade was 18-22-0; NPK grades included 14-14-14 and 12-18-14 (16).

Ammonium Phosphate-Nitrate (APN)

There are several processes that produce fertilizers containing ammonium phosphate and ammonium nitrate, but most of them are used to produce NPK grades and will be described further under "Compound Fertilizers."

Leyshon, in describing slurry granulation in the blunger in 1967, mentioned a plant in Romania that produced 23-23-0 and several others that produced various NPK grades (17). The slurry was produced by ammoniation of phosphoric and nitric acids. Detunc has described a Pechiney-Saint Gobain process in which concentrated ammonium nitrate solution (97%) and ammonium phosphate slurry were fed to a rotary-drum granulator (18). The ammonium phosphate slurry was produced by ammoniating phosphoric acid to an $NH_3:PO_4$ mole ratio of 0.6 in a preneutralizer;

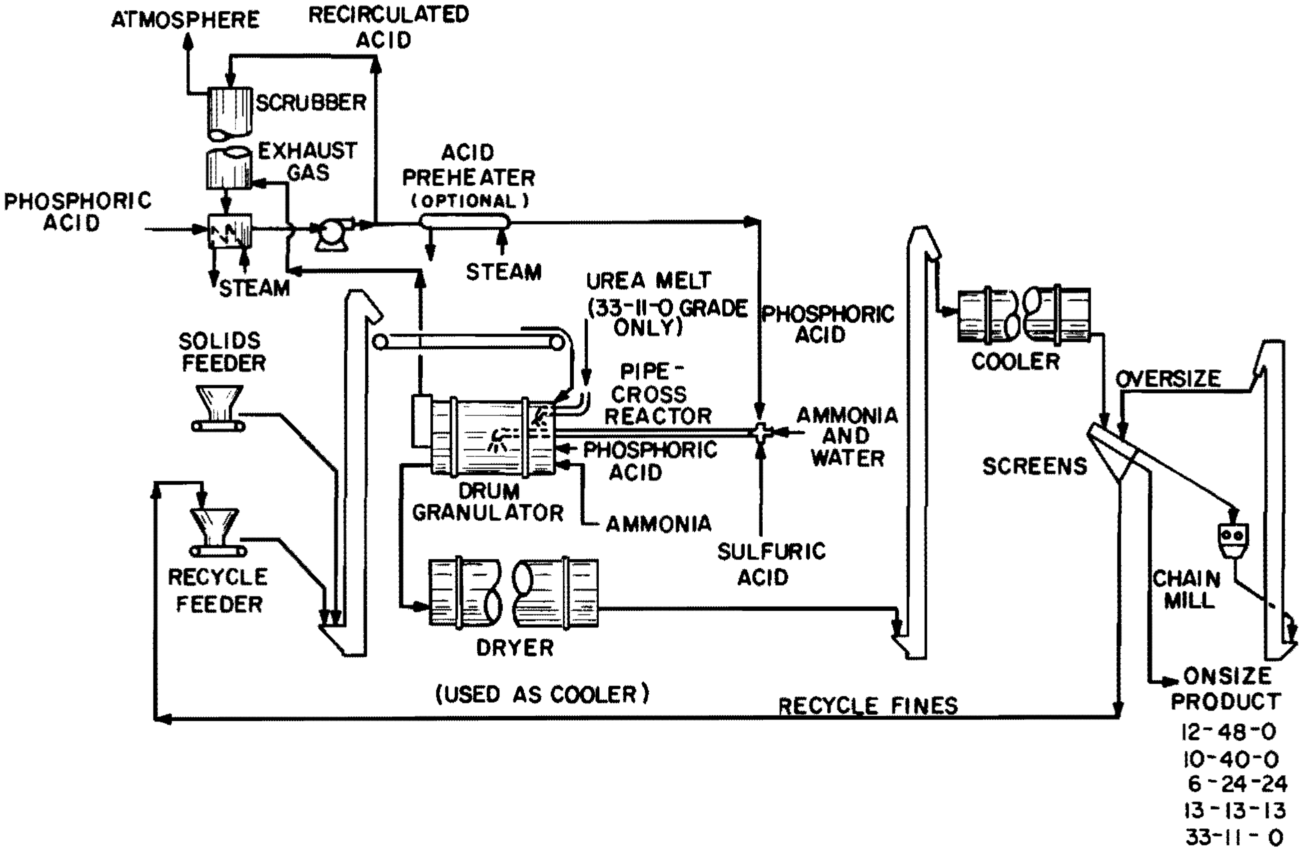


Figure 12. Flow Diagram of Pilot Plant for Production of Granular Fertilizer Using TVA Pipe-Cross Reactor.

more ammonia was added in the granulator to raise the mole ratio to 1.05. The principal product was 17-17-17. TVA operated a demonstration-scale plant for several years producing 25-25-0 and 30-10-0 APN grades. The slurry or concentrated solution was prepared by reaction of ammonia with nitric and phosphoric acid, concentrating the solution to about 5% water by evaporation, and granulating the resulting slurry in a pan granulator. The production rate was about 20 tph. Mixed phosphoric and nitric acids were neutralized with ammonia in a first stage to a pH of 1.6, then concentrated, and then neutralized in a second stage to a pH of about 5.6 to prepare the hot (170°C) concentrated solution for granulation (19).

SAI has also developed a system for coneutralization of phosphoric and nitric acids to produce a concentrated APN solution which was granulated with potash in a combination granulator dryer consisting of two concentric drums with internal recycle (20).

APN solutions are readily produced by neutralizing phosphoric acid with ammonia-ammonium nitrate solutions (chapter X). This method is used in many small granulation plants in the United States, but the solution is used as supplemental feed for compound fertilizer production.

Sheldrick has described Fisons' melt granulation process for producing APN such as 24-24-0 (21). Prilling of APN melts has been carried out by Monsanto Chemical Co. Processes for prilling APN melts, with the addition of potash, have been developed by Stamicarbon and Albright and Wilson (see chapter XIX). APN melts usually contain some polyphosphate, which lowers the melting point.

Urea-Ammonium Phosphates (UAP)

Combinations of urea with ammonium phosphate represent the last step, with available materials, in progress toward higher analysis fertilizers. Although many compound fertilizer manufacturers use some urea and ammonium phosphate in their formulations, relatively few use only these materials.

Fertilizers based primarily on urea and ammonium phosphate have been produced in Japan for many years. Ando has described a variety of processes that were in use in 1970 (15). Ammonium phosphate was supplied either as a slurry produced in the plant by ammoniation of phosphoric acid or in solid form as MAP or DAP. Urea was supplied as a solid (crushed prills or crystals), as a melt, or as a concentrated solution. Several types of granulators were in use; rotary drums were the most common, but pan granulators, pugmills, and other types were used in some plants.

A more recent paper gives a detailed description of a granulation plant which produces UAP grades, such as 28-28-0, 22-22-11, 18-18-18, etc. (22). The main raw materials are crushed urea prills, spray-dried ammonium phosphate (12-50-0), and potash salts.

One unusual feature of the plant is a methylene-urea reactor, which is used for production of some NPK grades. Part of the urea is fed into the steam-heated reactor with formaldehyde solution to produce a methylene-urea slurry containing unreacted urea, monomethylene diurea, dimethylene triurea, and trimethylene-tetraurea. The purpose of this step is to facilitate drying, improve the physical properties of the products, and provide some slow-release nitrogen.

Another unusual feature of the plant is a rotary ammoniator-mixer containing roller shafts. Its function is to receive the solid raw materials, the recycled fines, and the methylene-urea slurry (if used) and mix them thoroughly by a kneading action. Ammonia is added in the mixer although, in the example given, the amount of ammonia is small (6 kg/ton of 18-18-18). From the mixer, the product goes to a rotary granulator and then to a dryer, screening facilities, a cooler, and a coating drum. A typical moisture content of the granules leaving the granulator is about 3%, and this is controlled by the addition of steam and/or water in the granulator or mixer and by the moisture content of the methylene-urea slurry. The temperature in the granulator is about 63°C, and the recycle ratio is 2.0-2.5:1. Formulations given in the paper indicate that the methylene-urea reactor is not used for 28-28-0; it is used for several NPK grades in which the mole ratio of urea:formaldehyde is 3-7:1. The paper also mentions that gypsum may be added as a granulation aid; magnesium or manganese is added to some grades; and nitrification inhibitors are added in some products (chapter XXI).

TVA has pursued the development of UAP processes for several years. The first approach was to incorporate urea into the TVA DAP slurry granulation process. In pilot-plant tests of this method, UAP grades ranging from 38-13-0 to 21-42-0 were produced. Urea was added in the granulator either as concentrated solution or solids (crystals or prills). This general method has been used in at least two plants in India to make 28-28-0 and other grades using solid urea.

TVA's present production of UAP by a melt granulation process has been mentioned previously; ammonium polyphosphate melt and molten urea are cogranulated in a pugmill. The principal grade is 28-28-0 which is produced at a rate of 16 tph; 35-17-0 has also been produced. The production rate is limited by the capacity of the urea synthesis unit. TVA has also prilled a molten mixture of UAP in a pilot-plant oil-prilling unit. Norsk Hydro has developed a process on a pilot-plant scale for prilling UAP in air with or without potash addition (23). In the TVA work, ammonium polyphosphate melt was premixed with urea melt immediately before prilling. In one variation of the Norsk Hydro process, preheated solid MAP is premixed with urea melt before prilling; alternatively preheated solid urea is premixed with MAP melt. The prills are relatively large (1.8 mm, average), hard, and dense. Grades of 29-29-0 and 38-16-0 were produced. A diagram of the Norsk Hydro process is shown in figure 13.

Use of Phosphoric Acid in Granulation Processes

Phosphoric acid often is used in granulating compound fertilizers to supply part of the P_2O_5 in formulations in which the remainder of the P_2O_5 is supplied by single or triple superphosphate or ammonium phosphates. The acid usually is sprayed into the granulator, and ammonia or ammoniating solution is added during granulation to neutralize it. The heat of reaction promotes granulation and moisture evaporation. Both merchant-grade (54% P_2O_5) and superphosphoric acid (69%-72% P_2O_5) have been used in this way (chapter XIX).

Miscellaneous Fertilizer Uses for Phosphoric Acid

A potentially promising use for phosphoric acid is in the production of potassium phosphates (chapter XVI).

Substantial amounts but relatively small percentages of phosphoric acid are used for direct application to the soil, especially alkaline soils.

Slow-release fertilizers, $MgNH_4PO_4$ and $MgKPO_4$ (or mixtures of the two salts), represent another use. Compounds of the general formula MNH_4PO_4, where M may be a divalent metal ion, such as Fe, Mn, Cu, or Zn, have been tested as slow-release sources of micronutrients.

Urea phosphate $CO(NH_2)_2{\cdot}H_3PO_4$ is an interesting compound that has been considered for use as a fertilizer. However, a more promising use is an in-

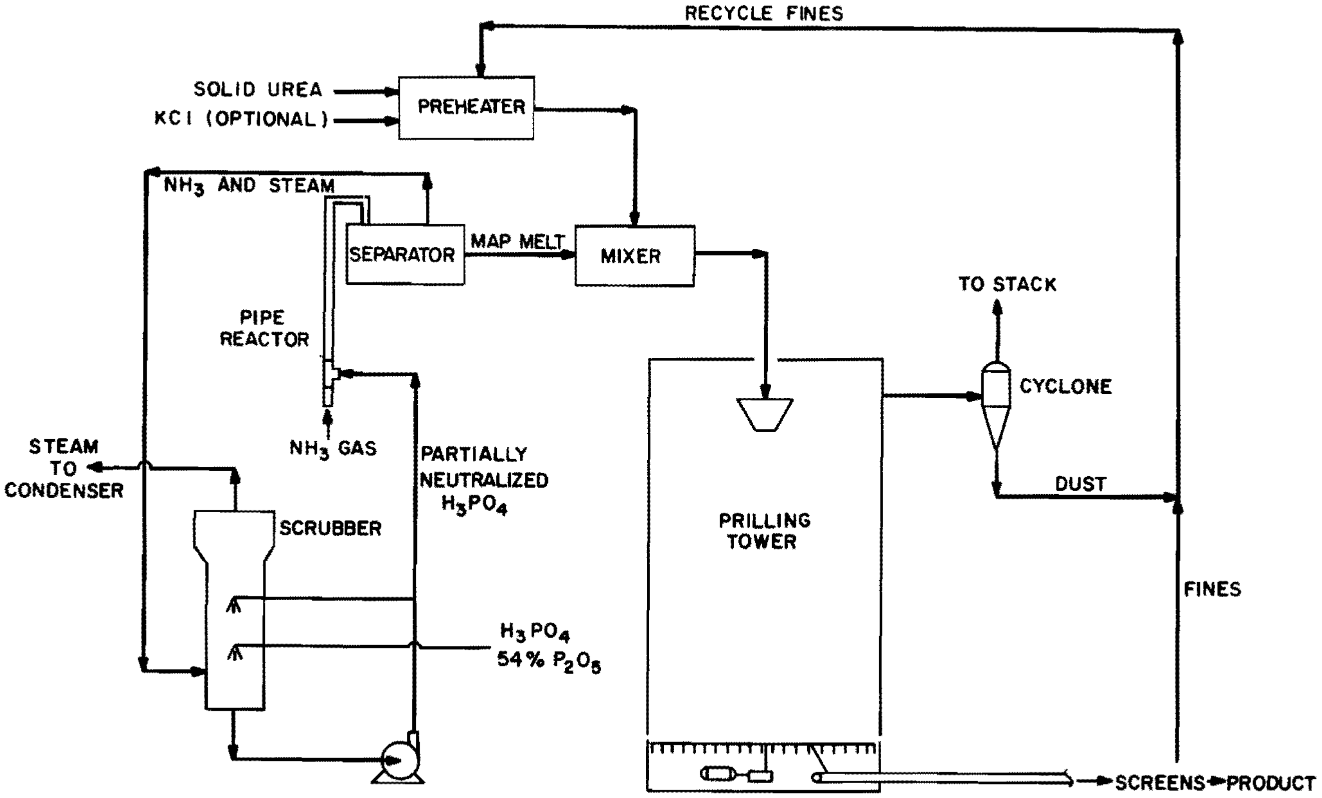


Figure 13. Norsk Hydro UAP Process.

termediate for production of high-analysis solid and liquid fertilizers. These possibilities are under study by TVA and others (9, 24).

Important uses for phosphoric acid which are covered in other chapters are for production of liquid fertilizers (chapter XIX) and mixed-acid nitrophosphates (chapter XV).

Comparative Economics of TSP, DAP, and MAP

The question of the choice of a phosphate product to be produced from phosphoric acid often arises. With established technology the choice often lies with MAP, DAP, TSP, or compound fertilizers based on these products. All of these products can be made in a slurry-type granulation plant; therefore, it is possible to build a single plant that can make the three products alternately although the plant cost would be somewhat higher than that of one designed for a single product. When there is likely to be a market for two or three products, it is probably desirable to have this flexibility, and many plants are so equipped. In large plants there may be two or three granulation lines, but even so it is well to be able to use each line interchangeably for different products so that the product mix can be altered to suit the market demand.

A given granulation plant will have different capacities for different products. For instance, the production rate may be only 65%-70% as much for TSP as for DAP because of the higher recycle ratio for TSP. Alternatively, a granulation plant for production of TSP by the slurry process should be larger than for DAP if the same output is required.

Since TSP requires finely ground rock, the cost of equipment to grind the rock should be added. If the TSP unit is associated with a wet-process phosphoric acid plant, it is sometimes possible to prepare ground rock for both units in the same equipment. However, phosphoric acid plants often use wet grinding, coarse grinding, or even no grinding; whereas, TSP requires dry, finely ground rock. Also, in many plants a higher grade of rock is used for TSP than for acid production. Therefore, separate rock-grinding facilities often are required.

In addition to the factors outlined above, any economic comparison will be influenced by the overall plan, whether there are coexisting phosphoric acid or ammonia production facilities and whether the plant is located adjacent to a phosphate rock mine.

In order to make a comparison of the relative economics of production of TSP (three processes), DAP (two processes), and MAP (two processes), the following assumptions are made:

1. The production unit is assumed to be part of a complex, hence no storage of raw or intermediate products was assumed beyond that required by the process. If phosphoric acid or ammonia is not produced on site, storage will be necessary.
2. Storage facilities for the final product are not included in the capital cost but are considered separately.
3. Prices of raw materials and intermediates are approximate current (1978) world market prices. However, since no specific location is assumed, no transportation cost has been added. Assumed prices are:

Phosphoric acid (54% P_2O_5)	\$200/ton of P_2O_5
Ammonia	\$120/ton
Phosphate rock (33% P_2O_5)	\$25/ton
Urea (bulk)	\$120/ton

4. The capacity of the plant is 800 tpd, 264,000 tpy.
5. The cost of the granulation plant is related to the throughput rate according to figure 14. The throughput rate is the production rate plus the recycle rate. Thus, for an 800-tpd product rate with a recycle ratio of 5:1, the throughput rate is (5 x 800) + 800 = 4,800 tpd.

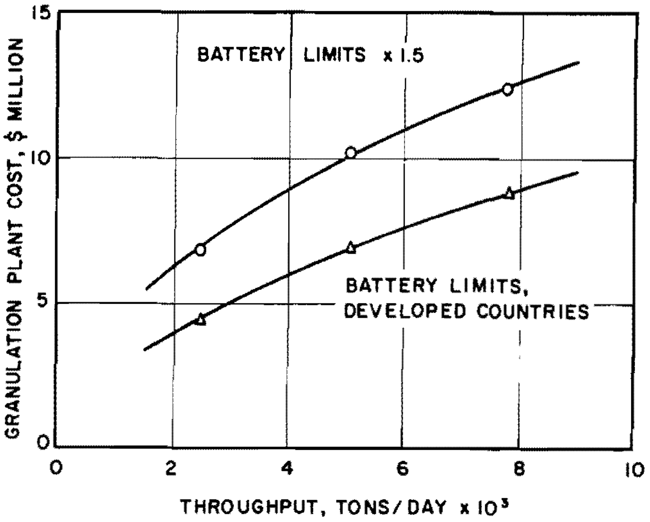


Figure 14. Capital Cost of Granulation Plants as Related to Throughput (Throughput = Output + Recycle).

6. For present purposes, total plant cost is considered equal to 1.5 times battery-limits cost for an industrialized location in a developed country.

The process requirements based on these assumptions are shown in tables 2 and 3, and the estimated production cost entering storage is shown in tables 4 and 5.

Of the three TSP processes considered, the exden granulation process shows the lowest investment and operating cost. However, there has been little experience with the process. Of the two more popular processes, the slurry granulation process has a higher investment cost but a lower operating cost. The operating cost of the two-step process is higher because the process actually consists of three steps: (1) preparation of nongranular TSP, (2) 30 days' storage curing, and (3) granulation of cured superphosphate. The capital cost of storage curing, including fluorine elimination and mechanical handling equipment, was assumed to be \$50/ton of storage capacity. If the value of the material in storage curing (about \$2 million) were added to the capital cost, the process would have the highest capital cost.

Comparing the net cost of P_2O_5 in ammonium phosphates with that of TSP by crediting the nitrogen cost at the cost of an equivalent amount of urea, it is evident that DAP is the most economical source of P_2O_5. MAP by the melt process is slightly less than the lowest cost TSP process in net cost of P_2O_5.

Because of its high concentration of total plant nutrients, DAP provides further savings in storage, bagging, and transportation. These savings are illustrated by table 6 which indicates costs after leaving the plant production unit for 1 ton of DAP as compared with 1 ton of TSP plus 0.39 ton of urea. The latter combination provides the same amount of N and P_2O_5 as DAP.

Naturally, the cost of transport will depend on the method and distance, and the cost of bags will depend on the type and size of bags required by the

TABLE 2. ESTIMATED REQUIREMENTS FOR PRODUCTION OF GRANULAR TSP (800 tpd)

Product:	TSP (0-46-0)		
Process:	Two-Step	Ex-Den Granulation	Slurry Granulation
Plant Investment, \$ Million			
Rock grinding	1.0	1.0	1.0
Acidulation	0.8	0.8	-
Storage curing[a]	1.2	1.2	-
Granulation	4.5	4.0	7.5
Total, battery limits	7.5	7.0	8.5
Total plant (BL x 1.5)[b]	11.25	10.5	12.75
Process Requirements per Ton of Product			
Rock, 33% P_2O_5, tons	0.39	0.39	0.40
Acid, tons P_2O_5	0.345	0.345	0.345
Electricity, kWh	40	38	40
Steam, kg	75	55	20
Fuel, kcal x 10^3	160	100	125
Labor, man-hour	0.55	0.25	0.25
Recycle ratio	2.5	1.6	8

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a. Cost of storage curing facilities, including removal of evolved fluorine, estimated on basis of 24,000 tons' capacity (30 days' production) and \$50 capital cost per ton of capacity.

b. Estimated plant investment for an industrial location in a developed country (e.g., U.S. Gulf Coast).

TABLE 3. ESTIMATED REQUIREMENTS FOR PRODUCTION OF GRANULAR DAP AND MAP (800 tpd)

Product:	DAP (18-46-0)		MAP (11-55-0)	
Process:	Slurry Granulation	Pipe Reactor Granulation	Slurry Granulation	Melt Granulation[a]
Plant Investment, \$ Million[b]				
Battery limits	6.8	5.8	6.8	5.1
Total plant (BL x 1.5)[c]	10.2	8.7	10.2	7.65[d]
Process Requirements per Ton of Product				
Phosphoric acid, tons P_2O_5	0.47	0.47	0.56	0.56
NH_3, tons	0.224	0.224	0.137	0.137
Electricity, kWh	30	20	30	20
Fuel, kcal x 10^3	125	-	125	-
Labor, man-hours	0.25	0.20	0.25	0.20
Recycle ratio	5.0	2.5	5.0	4.5[d]

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a. This product contains 15%-30% ammonium polyphosphate.

b. Estimated capital investment for an industrial location in a developed country (e.g., U.S. Gulf Coast).

c. Product storage not included.

d. Plant cost estimated by TVA to be 7.5% less than for the slurry granulation process. The recycle ratio was not used for estimating plant investment.

TABLE 4. ESTIMATED PRODUCTION COST OF TSP (\$/TON OF PRODUCT, 264,000 TONS OF PRODUCT PER YEAR)

Product:	TSP (0-46-0)		
Process:	Two-Step	Ex-Den Granulation	Slurry Granulation
Rock, \$25/ton	9.75	9.75	10.00
Acid, \$200/ton of P_2O_5	69.00	69.00	69.00
Electricity, \$0.027/kWh	1.08	1.03	1.08
Steam, \$0.04/kg	3.00	2.20	0.80
Fuel, \$0.01/thousand kcal	1.60	1.00	1.25
Labor-related costs[a]	9.68	4.40	4.40
Capital-related costs[b]	7.50	7.00	8.50
Subtotal	101.61	94.38	95.03
Adm. and misc. costs, 5% of subtotal	5.06	4.72	4.75
Total production cost	106.67	99.10	99.78
Cost/ton of P_2O_5	230.91	215.43	216.91

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a. Labor-related costs include labor, overhead, supplies, and chemical control--\$17.60/man-hour.

b. Capital costs = 17.67% of capital cost per year. Includes depreciation--6.67%; maintenance--5.0%; interest--4.0%; and taxes and insurance--2%.

TABLE 5. ESTIMATED PRODUCTION COST OF DAP AND MAP ($/TON OF PRODUCT, 264,000 TONS OF PRODUCT PER YEAR)

Product:	DAP (18-46-0)		MAP (11-55-0)	
Process:	Slurry Granulation	Pipe Reactor Granulation	Slurry Granulation	Melt Granulation
Phosphoric acid, $200/ton P_2O_5	94.00	94.00	112.00	112.00
Ammonia, $120/ton	26.88	26.88	16.44	16.44
Electricity, $0.027/kWh	0.81	0.54	0.81	0.54
Fuel, $0.01/thousand kcal	1.25	-	1.25	-
Labor-related costs[a]	4.40	3.52	4.40	3.52
Capital-related costs[b]	6.80	5.82	6.80	5.10
Subtotal	134.14	130.76	141.70	137.60
Adm. and misc. costs, 5% of subtotal	6.71	6.54	7.08	6.88
Production cost	140.85	137.30	148.78	144.48
Nitrogen credit[c]	46.96	46.96	28.70	28.70
Net P_2O_5 cost				
Per ton of product	93.89	90.34	120.08	115.78
Per ton of P_2O_5	204.11	196.39	218.33	210.51

a. Labor-related costs include labor, supplies, overhead, and chemical control--$17.60/man-hour.

b. Capital-related costs = 17.67% of total plant cost per year. Includes depreciation--6.67%, maintenance--5%, taxes and insurance--2%, and interest--4%.

c. Based on cost of equivalent amount of bulk urea at $120/ton = $260.87/ton of N.

TABLE 6. COST OF STORAGE, HANDLING, BAGGING, AND SHIPPING OF DAP VERSUS TSP PLUS UREA

	$/Ton of DAP (18-46-0)	$/Ton of TSP Plus 0.39 Ton of Urea
Cost of bulk material, ex-plant	137.30	99.10 (TSP) 46.80 (Urea) 145.90 Total
Storage cost, $2.10/ton[a]	2.10	2.92
Reclaiming from storage, bagging, and shipping	15.00	20.85
Transportation cost	20.00	27.80
Total delivered cost (bagged)	174.40	197.47
Savings for DAP	$23.05 = about 12%	

a. Based on 45 days' storage in bulk and 10 days' storage in bags.

market conditions. However, table 6 shows that a total saving in delivered cost of $23 or about 12% would result under the assumed conditions by producing and marketing 0.18 tons of N and 0.46 tons of P_2O_5 in the form of DAP as compared with TSP and urea.

The illustration does not assume that TSP and urea are mixed. The mixture (blend) would have poor physical properties because the two materials are incompatible.

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XV Nitrophosphates

"Nitrophosphate" is a generally accepted term for any fertilizer that is produced by a process involving treatment of phosphate rock with nitric acid. The term "nitric phosphate" has been used to some extent, particularly by TVA, but on a worldwide basis "nitrophosphate" seems to be more generally accepted.

Production of nitrophosphate has increased rapidly, especially in Europe, since 1945; world capacity in 1975 was estimated at 3.46 million tons of P_2O_5 of which 57% was in western Europe and 33% in eastern Europe (1). Assuming an average P_2O_5 content of 15%, world capacity is equivalent to about 23 million tons (gross weight) of fertilizer.

The principal advantage of nitrophosphate processes is that nitric acid is used for the dual purpose of converting phosphate rock to a more soluble form and furnishing fertilizer nitrogen in the product. Since the cost of the nitric acid may properly be charged to fertilizer nitrogen production, the nitrophosphate processes enjoy an economic advantage over processes that use sulfuric acid or other nonnutrient reagents to solubilize phosphate rock.

Chemistry of Nitrophosphate Processes

The simplest process is the reaction of nitric acid with phosphate rock to produce monocalcium phosphate and calcium nitrate:

$$Ca_{10}F_2(PO_4)_6 + 14HNO_3 \rightarrow 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF \quad \text{(Equation 1)}$$

The reaction may be considered analogous to that occurring in SSP production except that nitric acid replaces sulfuric acid. The Lonza process, which was used commercially for several years in Switzerland, utilized this method. Nitric acid of 65%-70% concentration was mixed with ground phosphate rock in equipment resembling a superphosphate mixer and den. The product contained about 8% N and 16% P_2O_5. A technical difficulty was loss of nitrogen as NO_2 by decomposition of nitric acid (or calcium nitrate) due to the heat of reaction. The calcium nitrate content caused the product to be quite hygroscopic; this and the low analysis of the product were serious disadvantages.

TVA has produced superphosphates on a pilot-plant scale in which up to 50% of the sulfuric acid was replaced with nitric acid (2). The products contained 3%-5% N and 18% P_2O_5. Nitrogen losses in the range of 1%-8% were minimized when the water content of the mixed acid was 29% or more and when the phosphate rock was calcined.

Most nitrophosphate processes involve dissolution of phosphate rock in nitric acid (50%-60% HNO_3) to form phosphoric acid and calcium nitrate:

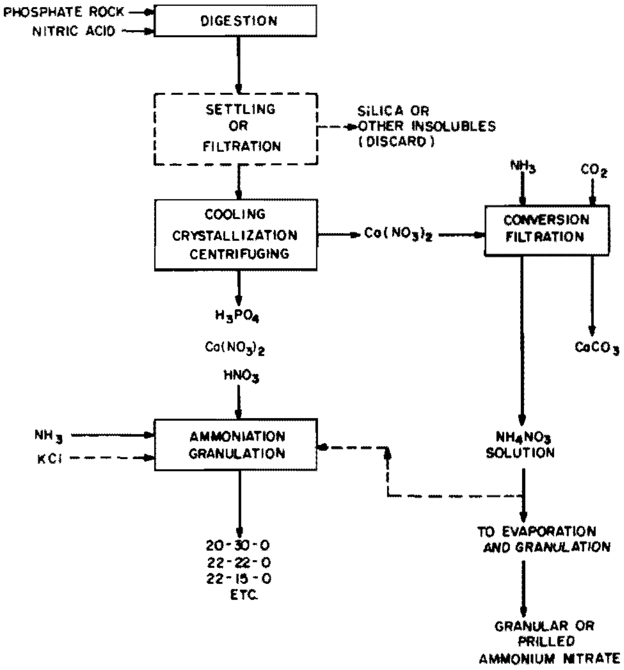
$$Ca_{10}F_2(PO_4)_6 + 20HNO_3 \rightarrow 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF \quad \text{(Equation 2)}$$

Although the equation shows formation of HF, only a small percentage (usually less than 10%) of the fluorine content of the rock is volatilized. In most cases, the proportion of nitric acid used is at least stoichiometrically sufficient to convert all of the calcium in the rock to calcium nitrate; often a slight excess is used.

Nitrophosphate processes differ mainly in their treatment of the phosphoric acid-calcium nitrate solution that is formed in the first step of the process (equation 2). The general objective is to remove calcium or at least precipitate it in an insoluble form so that it will not interfere with the desired course of subsequent ammoniation reactions.

Calcium Nitrate Removal

The most common second step is calcium nitrate removal by crystallization. Calcium nitrate removal processes are based on the Odda process which was invented by Erling Johnson in Norway in 1928. Variations and improvements have been developed by several European firms. The basic flow diagram of the process is shown in figure 1. The heat of reaction of



NOTE: DASHED LINES INDICATE OPTIONAL STEPS

Figure 1. Typical Odda Nitrophosphate Flow Diagram.

phosphate rock with nitric acid raises the temperature of the solution to 50°-60°C. When the solution is cooled to 15°-20°C, about 60% of the calcium nitrate crystallizes as tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$. The crystals are separated from the solution by centrifuging or filtration. The remaining solution, now containing only 40% of the original calcium nitrate, is ammoniated according to the following reaction:

$$6H_3PO_4 + 4Ca(NO_3)_2 + 2HF + 11NH_3 \rightarrow 3CaHPO_4 + 3NH_4H_2PO_4 + 8NH_4NO_3 + CaF_2 \quad \text{(Equation 3)}$$

According to the equation, half of the P_2O_5 would be present as ammonium phosphate which is water soluble, and the other half would be present as dicalcium phosphate, which is citrate soluble. However, since the Ca:P ratio in most phosphate rocks is higher than in pure fluorapatite, the usual range of water solubility is 30%-40%. For the same reason, more ammonium nitrate occurs in the final product than that indicated by equation 3.

One variation in the Odda process is to crystallize calcium nitrate as the double salt, $5Ca(NO_3)_2 \cdot NH_4NO_3 \cdot 10H_2O$, by the addition of ammonia or ammonium nitrate before cooling.

Another variation is to control the pH during ammoniation to form monocalcium phosphate rather than ammonium phosphate according to the equation:

$$6H_3PO_4 + 4Ca(NO_3)_2 + 2HF + 8NH_3 \rightarrow 2Ca(H_2PO_4)_2 + CaHPO_4 + 8NH_4NO_3 + CaF_2 \quad \text{(Equation 4)}$$

The percentage of calcium nitrate removed by crystallization depends on the temperature. By cooling to about -5°C about 85% of the calcium nitrate can be removed by crystallization, and the resulting product, after ammoniation, has a water solubility of 80%-85% (3).

The calcium nitrate can be melted either as such or as the double salt, $5Ca(NO_3)_2 \cdot NH_4NO_3 \cdot 10H_2O$, and granulated or prilled. However, there is relatively little demand for this low-grade (about 15% N)hygroscopic product. Therefore, the usual procedure is to convert it to ammonium nitrate according to the following equation:

$$Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O \rightarrow 2NH_4NO_3 + CaCO_3 \quad \text{(Equation 5)}$$

The ammonium nitrate solution can be separated from the calcium carbonate solution by filtration. Part or all of the ammonium nitrate solution can be combined with the ammoniated product from equation 3 to adjust the $N{:}P_2O_5$ ratio. The remainder can be granulated or prilled with or without the addition of some of the calcium carbonate to provide a straight nitrogen coproduct. As an alternative, the ammonium nitrate-calcium carbonate slurry can be evaporated and granulated without separation; the product, usually called calcium-ammonium nitrate (CAN), contains about 20% N. A higher grade CAN product is preferred (26% N is now the usual grade); therefore, most plants separate the calcium carbonate and use only part of it for CAN production. In countries where marketing of straight ammonium nitrate is permitted, the solution may be prilled or granulated without calcium carbonate. By varying the amount of ammonium nitrate solution returned to the nitrophosphate product, the ratio of $N{:}P_2O_5$ in the nitrophosphate product can be varied within certain limits. The minimum ratio is about 0.6 with no ammonium nitrate return and maximum calcium nitrate removal. The maximum ratio is about 2 if all of the ammonium nitrate is returned. Most plants produce nitrophosphate products with 1:1 $N{:}P_2O_5$ ratio (20-20-0, 15-15-15, or 13-13-20). In this case, for each ton of nitrogen produced as nitrophosphate, there is approximately 1 ton of additional nitrogen as CAN coproduct. The grade of the nitrophosphate product depends on the extent of calcium removal and impurities in the phosphate rock; for a 1:1 ratio the usual grade ranges from 20-20-0 to 23-23-0.

Removal of Calcium by Ion Exchange

The firm Superfos (Denmark) has developed an ion-exchange process for calcium removal (4). The phosphoric acid-calcium nitrate solution resulting from equation 2 is passed through a potassium-loaded resin which absorbs calcium and releases potassium. The resin is regenerated by a potassium chloride solution, discharging calcium chloride to waste. A simplified flow diagram of the process is shown in figure 2.

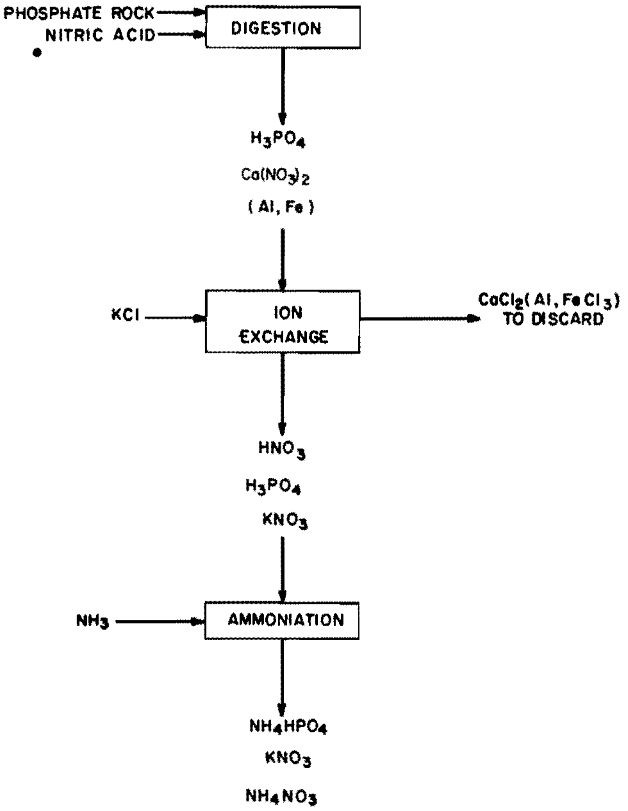


Figure 2. Superfos Ion Exchange Nitrophosphate Process Used in Demark.

The net reaction is:

$$Ca(NO_3)_2 + 2KCl \rightarrow CaCl_2 + 2KNO_3 \quad \text{(Equation 6)}$$

If the rock contains cationic impurities other than calcium, such as iron and aluminum, these elements may also be removed by the ion-exchange process. After ion exchange the solution which contains phosphoric acid, potassium nitrate, some excess nitric acid, and perhaps some residual calcium nitrate is ammoniated, dried, and granulated. Grades ranging from 21-9-12 to 17-17-17 are produced.

The solution leaving the ion-exchange unit has a $K_2O{:}P_2O_5$ weight ratio of about 1.8:1.0. When lower ratios are desired in the final product, the current practice is to add phosphoric acid from another plant unit before ammoniating. An alternative, which is under study, is to remove part of the potassium nitrate by cooling the solution to crystallize KNO_3 which can be marketed as a separate product.

One advantage of the process is the production of low-chlorine fertilizers (less than 0.6% Cl). Such products are agronomically desirable for some crops and soils. Another potential advantage is the ability to use phosphate rocks of high iron and aluminum content, even aluminum phosphate ores. This possibility is under study.

Removal of Calcium by Sulfate Addition

The solution obtained by reaction of nitric acid with phosphate rock (equation 2) can be treated by the addition of a soluble sulfate to precipitate part or nearly all of the calcium as calcium sulfate (gypsum or hemihydrate). In commercial processes, ammonium sulfate, potassium sulfate, and sulfuric acid have been used. Langbeinite ($K_2SO_4 \cdot 2MgSO_4$) has been used experimentally. The calcium sulfate may be separated by filtration or left in the product. In most plants, the calcium sulfate is removed in order to produce a higher grade product. Chemical reactions are:

$$(NH_4)_2SO_4 + Ca(NO_3)_2 \rightarrow 2NH_4NO_3 + CaSO_4 \quad \text{(Equation 7)}$$

$$K_2SO_4 + Ca(NO_3)_2 \rightarrow 2KNO_3 + CaSO_4 \quad \text{(Equation 8)}$$

$$H_2SO_4 + Ca(NO_3)_2 \rightarrow 2HNO_3 + CaSO_4 \quad \text{(Equation 9)}$$

Ammonium sulfate solution obtained as a byproduct from caprolactam production is used in at least two plants. Two other plants are known to use potassium sulfate. In the Veba phosphoric acid process (figure 3), phosphate rock is reacted with a mixture of sulfuric and nitric acids under conditions that form calcium sulfate in the hemihydrate form, which is removed by filtration (5). In this process, part of the sulfuric acid may be replaced by ammonium sulfate.

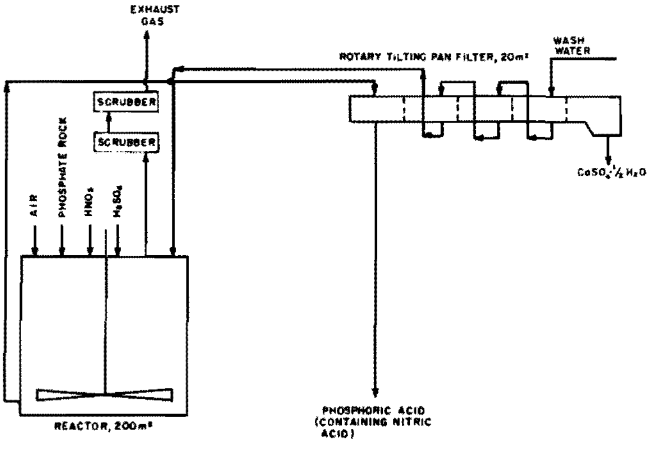


Figure 3. The Veba Phosphoric Acid Process (200 tpd P_2O_5).

When ammonium sulfate is used to precipitate calcium as gypsum, the gypsum can be treated with ammonia and carbon dioxide to regenerate ammonium sulfate which is recycled and to convert the calcium to calcium carbonate:

$$CaSO_4 \cdot 2H_2O + 2NH_3 + CO_2 \rightarrow CaCO_3 + (NH_4)_2SO_4 + H_2O \quad \text{(Equation 10)}$$

This is the basis of the "sulfate recycle process" which was developed by TVA on a pilot-plant scale (6). One disadvantage of this process is that the $N:P_2O_5$ ratio in the product is fixed at about 2:1 (28-14-0). However, various methods were developed experimentally to separate ammonium nitrate from ammonium phosphate by crystallizing ammonium nitrate, monoammonium phosphate, or triammonium phosphate at various stages in the process (7, 8, 9). Complete (99+%) separation of phosphate from nitrate was obtained only by the triammonium phosphate method. Triammonium phosphate crystals were precipitated by ammoniating the solution to a pH in the range of 9-10. The crystals were separated from the ammonium nitrate solution by filtration and washing with water containing ammonia. Heating the triammonium phosphate converted it to diammonium phosphate and ammonia which was recycled.

Use of potassium sulfate for calcium precipitation has the disadvantage that the $K_2O:P_2O_5$ ratio in the product can be varied only within narrow limits and only by varying the percentage of calcium precipitated. For precipitation of 90% or more of the calcium, a weight ratio of $K_2O:P_2O_5$ of 2 or more may be required; this ratio is seldom optimum for compound fertilizers. Since the potassium is present as KNO_3 (see equation 8), most of it can be separated by crystallization by cooling the solution. Sale of potassium nitrate as a separate product could be profitable, but the demand is relatively small.

Addition of Phosphoric Acid or Soluble Phosphates

Instead of removing calcium, the $CaO:P_2O_5$ ratio may be adjusted to a desired level by adding phosphoric acid or a soluble phosphate such as ammonium phosphate. This is the basis of the "phospho-nitric" or "mixed-acid" process. Several firms have developed or use mixed-acid processes. After adjustment of the $CaO:P_2O_5$ ratio, the solution is ammoniated as indicated in equation 3 or 4. Mixed acid processes have been developed and used by Kemira Oy (Finland), PEC (Societe Potasse et Engrais Chemiques) (France), TVA (United States), and FCI (India). The FCI process used DAP rather than phosphoric acid for adjustment.

The advantages of mixed-acid processes are:

1. The process is relatively simple.
2. There is no coproduct.
3. The $N:P_2O_5$ weight ratio can be varied in the range of 1:2 to 2:1.

The main disadvantage is that phosphoric acid (or ammonium phosphate) is required and, hence, part of the advantage of nitric phosphate processes--the elimination of the need for sulfuric acid that is needed to manufacture phosphoric acid--is lost. However, a mixed-acid process can be a good choice for small plants which use imported phosphoric acid or imported ammonia or are associated with an ammonia plant.

The proportion of the product P_2O_5 that is derived from phosphoric acid is related to the water solubility of the P_2O_5 in the final product. Table 1 shows this relationship as determined experimentally by TVA (10). To obtain a product in which 40% of the P_2O_5 is water soluble, for example, 62% of the P_2O_5 is derived from phosphoric acid and 38% directly from phosphate rock. These proportions will vary slightly depending on the composition of the rock and acid and on the extent of ammoniation. The water-insoluble P_2O_5 is soluble in neutral ammonium citrate and consists mainly of dicalcium phosphate. Under certain conditions of ammoniation, some of the phosphate can be precipitated as citrate-soluble apatite as shown below in equation 11 (11):

$$6H_3PO_4 + 4Ca(NO_3)_2 + 2HF + 16NH_3 \rightarrow 4(NH_4)_2HPO_4 + 0.33Ca_{10}F_2(PO_4)_6 + 8NH_4NO_3 + 0.67CaF_2 \quad \text{(Equation 11)}$$

The effect of this type of reaction is to increase the proportion of water-soluble P_2O_5 with a given Ca:P ratio at the expense of converting the water-

TABLE 1. RELATIONSHIP OF P_2O_5 WATER SOLUBILITY TO SULFUR REQUIREMENTS AND PRODUCT GRADE IN TVA MIXED-ACID NITROPHOSPHATE PROCESS

Water Solubility of P_2O_5 in Product, % of Total P_2O_5	Ton S Required/ Ton Product P_2O_5	Proportion of Product P_2O_5 from H_3PO_4, %	Highest Possible 1:1:0 Product Grade
94[a]	0.94	100	25-25-0
50	0.55	69	21-21-0
40	0.58	62	20-20-0
30	0.53	56	20-20-0
25	0.51	54	20-20-0
20	0.35	38	19-19-0

a. All ammonium phosphate.

insoluble P_2O_5 to apatite which, even though citrate soluble, is probably less reactive in the soil than dicalcium phosphate.

In one modification of the PEC mixed-acid process, dicalcium phosphate is precipitated as the dihydrate, $CaHPO_4 \cdot 2H_2O$, by cooling during ammoniation. The dihydrate is claimed to be agronomically more effective than anhydrous dicalcium phosphate. However, the dihydrate is unstable at temperatures prevailing in warm climates and reverts to the anhydrous form, releasing the water of crystallization and, thereby, causing deterioration of the physical properties of the product.

Technology of Nitrophosphate Processes

Selection of Phosphate Rock

In general, reactivity of the phosphate rock is no problem; even igneous apatites dissolve readily in nitric acid. The rock need not be finely ground; rock finer than 1 mm is satisfactory. In general, the rock need only be fine enough to prevent rapid settling in stirred reaction vessels. High-silica rock can be used if the equipment is designed for that purpose. Depending on the amount of silica, a "sand trap," a filter, or other means for separating acid-insoluble materials may be used. Coarse silica particles can be very abrasive to pumps and piping, and this fact should be considered in plant design.

It is desirable that the $CaO:P_2O_5$ ratio in the rock should be as low as economically feasible since an increase in that ratio increases the amount of calcium that must be removed or offset (in mixed-acid processes). While additional calcium requires additional nitric acid, it does not necessarily involve a direct economic penalty since the nitrate is subsequently converted to ammonium nitrate either in the nitrophosphate product or in a coproduct.

Carbonates in phosphate rock cause foaming which is usually dealt with by using mechanical foam breakers. However, foaming can be a difficult problem with some rocks.

Organic matter is undesirable in nitric phosphate processes; it reacts with nitric acid with loss of nitrogen as NO_2 or other nitrogen oxides and causes a difficult problem in pollution control.

Iron and aluminum oxides present no special problem within the range of occurrence in commercial phosphate rocks; these oxides usually are dissolved in nitric acid and reprecipitated during ammoniation as citrate-soluble phosphates. TVA has used "leached-zone" Florida phosphate containing a high percentage of aluminum phosphate minerals in a special nitrophosphate process (12). The process was operated on a demonstration scale for several years with technically satisfactory results.

Extraction

Figure 4 shows a flow diagram of the TVA demonstration-scale plant (10). The extraction step was carried out in two stirred reaction vessels in series with a total retention time of about 1 hour. The rock, Florida flotation concentrates, was used as received without crushing, grinding, or screening. The nitric acid concentration was 60%-65% HNO_3, usually about 65%. The extraction tanks were made of type-316 stainless steel, but tests indicated that type 304 (a less-expensive alloy) was equally suitable. The temperature in the extraction step was about 85°C when producing 20-20-0. Foaming was controlled by mechanical foam breakers and thorough agitation. Gases released from the extraction vessels were vented through a scrubber. Nitrogen oxide losses were small but probably too high to comply with present atmospheric pollution control standards.

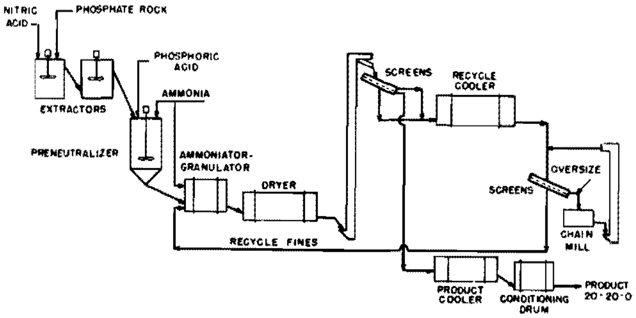


Figure 4. Flow Diagram of TVA Mixed-Acid Nitrophosphate Process.

Calcium Nitrate Removal

In processes using calcium nitrate removal, the usual procedure is to cool the solution stepwise and slowly enough to form large calcium nitrate crystals that can be separated readily by centrifuging or filtration. The cooling may be batchwise or continuous. The first stage normally utilizes water from available sources, such as streams, lakes, or sea. If the water supply is limited, it may be necessary to reuse it through the use of cooling towers; in warm climates, the cooling water may be chilled; vaporization of the ammonia used in other steps of the process can supply the refrigeration requirement. Cooling to 15°C usually will remove enough calcium nitrate so that the water solubility of P_2O_5 in the final product is about 40%, depending on the $CaO:P_2O_5$ ratio in the rock, the concentration of the nitric acid, and other factors. If more complete calcium nitrate removal is desired, cooling by refrigerated brine may be used.

Heat-exchange surfaces, if used in the cooling step, are likely to become coated with calcium nitrate crystal, thereby slowing the heat transfer rate. One way to cope with this problem is to use a temperature cycle so that the coating is redissolved in each cycle.

In a process developed in Czechoslovakia, cooling is accomplished by direct contact of the refrigerant with the process solution (13). The refrigerant is a volatile liquid which is injected into the solution and cools by absorbing heat for evaporation. The refrigerant in vapor form disengages from the liquid and is collected, cooled, and compressed to liquefy it again for reuse. Suitable refrigerants mentioned are butane, propane, and carbon dioxide. Alternatively, a nonvolatile supercooled refrigerant, such as a light hydrocarbon, can be used as the coolant and separated from the solution by decantation.

The process as developed in Czechoslovakia uses an immiscible, light hydrocarbon liquid, "white spirit," which is supercooled by refrigeration, injected into the nitrophosphate liquor and then withdrawn from the upper level of the vessel for recirculation through the cooler. The process was developed for the use of Kola apatite; when phosphate rock containing organic matter is used, it must be calcined before it becomes a suitable feedstock.

The calcium nitrate crystals are separated from the solution by centrifuging or by filtration using a special filter with a stainless-steel filter medium. The crystals are washed on the filter or centrifuge with nitric acid, and the wash solution is returned to the extraction step.

Ammoniation

When the $CaO:P_2O_5$ ratio is adjusted to the desired level by calcium nitrate removal, sulfate precipitation, or phosphoric acid addition, the next step is ammoniation. Two general methods are in use. The method developed by TVA involves ammoniation in two steps, first in a preneutralizer and then in an ammoniator-granulator. The other method consists of ammoniation in a series of stirred reaction vessels.

When the ammoniation is all carried out in the liquid phase, it must be carried out very carefully to prevent formation of apatite in a citrate-insoluble form. Four or more stages are required for best results. In TVA pilot-plant studies, four-stage ammoniation to a final pH of 4.5 resulted in products with a citrate solubility of 98% or more (14). The percentage distribution of ammonia to the first, second, third, and fourth stages was 57%, 26%, 13%, and 4%, respectively. In the PEC multistage ammoniation process, a small amount of magnesium sulfate is added which acts as a stabilizer to prevent formation of citrate-insoluble compounds.

In the TVA process, about 85% of the ammonia was added in the preneutralizer (pH 1.8) (10). The temperature reached the boiling point (about 150°C), and about half of the water was evaporated. A large volume of freeboard space above the liquid level was required to control foaming.

In most other nitrophosphate processes, the heat of ammoniation is utilized to evaporate water as in the TVA process. However, in one version of the PEC process, the slurry is cooled during ammoniation, and this prevents evaporation.

Finishing Processes

The final slurry after ammoniation is granulated, with or without addition of potash salts, by a variety of methods including granulation in a pugmill or blunger and granulation and drying in a Spherodizer; ammoniation and granulation in a rotary drum; and evaporation to a melt followed by prilling. These granulation methods will be described in more detail under granulation of compound fertilizers in chapter XIX. In nitrophosphate processes involving calcium removal, the slurry often has a high water content due to introduction of wash water. In this case some (or all) of the water may be evaporated in steam-heated evaporators before granulation.

Some Other Nitrophosphate Processes

A process known as the "carbonitric process" has been used on a commercial scale but is not known to be in use now. It consists of four steps:

1. Dissolving phosphate rock in nitric acid.
2. Ammoniating the solution from the first step to precipitate essentially all of the P_2O_5 as dicalcium phosphate, leaving the remainder of the calcium in solution as calcium nitrate.
3. Adding ammonia and carbon dioxide to convert the calcium nitrate to ammonium nitrate and calcium carbonate.
4. Granulating and drying.

The final product consists of a mixture of dicalcium phosphate, ammonium nitrate, and calcium carbonate. The grade is about 16-14-0. None of the P_2O_5 is water soluble, but nearly all of it is citrate soluble. The product is not popular because of its relatively low analysis and generally poor agronomic results.

A proposed variation of the carbonitric process was studied by TVA experimentally. In this study the slurry from the second step was filtered to produce dicalcium phosphate as a separate product, and the remaining solution was treated as in the third step to separate ammonium nitrate solution from calcium carbonate.

In a proposed variation of the Odda process, the calcium nitrate crystals were decomposed by heat to form calcium oxide and nitric acid which was recycled. One of the difficulties was that nitric acid recovery was incomplete because nitrogen oxides formed.

As indicated in equation 2, dissolution of phosphate rock in nitric acid yields a solution containing mainly phosphoric acid and calcium nitrate. Various studies have been made on the possibility of separating phosphoric acid by solvent extraction. At least two processes were developed experimentally that were apparently technically feasible. In a process developed in Finland, the solvent was tertiary amyl alcohol (15). Addition of ammonia produced an aqueous slurry containing ammonium phosphate and ammonium nitrate crystals in their saturated solution which was separated from the solvent. The product grade was 26-26-0. The solution remaining after solvent extraction contained essentially all of the calcium nitrate; it was converted to ammonium nitrate according to equation 4. Although plans for a full-scale plant to use the process were announced, the plans apparently were cancelled.

Some other processes have been developed that provide virtually complete separation of phosphoric acid from both calcium and nitrate, but none are known to have been used commercially.

Nitrophosphate slurry fertilizers have been produced commercially and sold in the United States and perhaps in other countries. In this process, phosphate rock is dissolved in nitric acid, and the solution is ammoniated to a pH of about 4. The resulting slurry containing dicalcium phosphate, calcium nitrate, and ammonium nitrate is sold without further processing.

Economic Evaluation of Nitrophosphate Processes

Economic evaluation of nitrophosphate processes is difficult and complex since it is necessary to select for comparison some alternative method for making equivalent amounts of nitrogen and phosphate fertilizers. Sometimes nitrophosphate processes can be ruled out because they do not meet the needs of the market area. Therefore, any economic evaluation must assume that certain preconditions exist in the market area that will validate an economic comparison. These preconditions are:

1. The overall weight ratio of N:P_2O_5 in nitrophosphates and coproducts is about 2:1 (in calcium nitrate removal processes). Since the general trend in the world as a whole and in many individual countries is toward this range, this precondition may often (but not always) be acceptable.
2. The nitrogen content of both product and coproduct will be mainly in the form of ammonium nitrate (or optionally calcium nitrate). Therefore, a precondition is that this form of nitrogen must be acceptable. Ammonium nitrate is generally regarded to be fully as effective as other nitrogen fertilizers and sometimes preferable to urea, with the important exception of use on flooded rice.
3. The range of N:P_2O_5 ratio in the compound fertilizer is limited to approximately 0.75:1.0 up to about 3:1. This range must be suitable for the market area.
4. Some of the P_2O_5 will be in a water-insoluble form (dicalcium phosphate). However, nitrophosphate processes are available that attain up to 75% or 80% P_2O_5 water solubility, and most agronomists agree that such products are suitable for all soils and crops. Lower water solubility may be acceptable for acid soils.

Ewell has compared the calcium nitrate crystallization nitrophosphate process and the sulfate recycle process for making 28-14-0 fertilizer with production of the same grade by the sulfur-sulfuric acid-phosphoric acid-ammonium phosphate-ammonium nitrate route (16). His conclusions were that capital investment costs were about equal, and production costs would be lower for the nitrophosphate route when sulfur costs were about $10/ton or more.

Slack, et al., compared the cost of producing 20-20-0 nitrophosphate with other NP products in 1967; in the Odda process, byproduct ammonium nitrate in solution form was credited at the estimated cost of production directly from nitric acid and ammonia (17). The cost of sulfur was assumed to be $26/short ton ($28.67/mt) delivered. The results of the comparison are tabulated below.

Process	Nitrophosphate (Odda)	Nitrophosphate (Mixed Acid)	Ammonium Phosphate-Nitrate	Ammonium Phosphate-Urea
Grade	20-20-0	20-20-0	26-26-0	29-29-0
Capital investment, $ U.S. million	12.53	10.08	9.09	13.82
Bulk price,[a]				
$/20 lb of N + P_2O_5	1.325	1.409	1.400	1.407
$/kg of N + P_2O_5	0.149	0.155	0.154	0.155

a. Price includes 20% return on investment.

The authors noted that the Odda process showed a clear advantage in price per unit of plant nutrient at the factory, but the urea-ammonium phosphate might have the lowest delivered cost, depending on cost of transportation and price of sulfur.

Hignett compared production of nitrophosphate having a high P_2O_5 water solubility by the Odda process with production of an equivalent amount of N and P_2O_5 as DAP and urea under the following conditions (18):

	Nitrophosphate	TSP + Urea
Product grade	23-23-0	18-46-0
Product capacity, tpd	1,000	500
Coproduct grade	26-0-0 (CAN)	46-0-0 (Urea)
Coproduct capacity, tpd	950	841
Total N production, tpd	477	477
Total P_2O_5 production, tpd	230	230
Cost of ammonia, $/ton	200	200
Cost of sulfur, $/ton	-	60

The estimated plant costs based on early 1975 data for a U.S. location follow:

Battery-Limits Cost, $ US Million

Nitrophosphate		Urea + DAP	
Nitric acid	10.0	Sulfuric acid	8.0
Nitrophosphate unit	13.9	Phosphoric acid	9.3
CAN unit	2.7	DAP	3.9
Storage	5.8	Urea	14.5
		Storage	3.8
Total	32.4		39.5

It should be noted that in each case it was assumed that the production units were part of a complex containing an ammonia plant and various auxiliary and offsite facilities; therefore, the total cost of the complex would be much higher than the totals shown above. Also, present (1978) costs would be higher because of inflation. Therefore, the difference in capital cost might be a relatively small percentage of the total.

By using the estimates and estimating procedures given in other chapters of this manual and by adding 21% to the estimated cost of the nitrophosphate units to update them from 1975 to 1978, the following estimated investment costs for a developed country location are obtained:

Sulfuric Acid Route

Item	Cost, $ Million
Sulfuric acid, 656 tpd (H_2SO_4)	6.7
Phosphoric acid, 230 tpd (P_2O_5)	9.2
DAP, 500 tpd (18-46-0)	5.1
Urea, 841 tpd (46-0-0)	17.0
Total, battery limits	38.0
Total plant (battery limits x 1.5)	57.0
Storage facilities	3.8
Total	60.8

Nitrophosphate Route (80% P_2O_5 Water Solubility)

Item	Cost, $ Million
Nitric acid, 1,000 tpd (HNO_3)	14.5
Nitrophosphate, 1,000 tpd (23-23-0)) CAN, 950 tpd (26-0-0))	20.1
Total, battery limits	34.6
Total plant (battery limits x 1.5)	51.9
Storage facilities	5.8
Total	57.7

Nitrophosphate Route (30%-40% P_2O_5 Water Solubility)

Item	Cost, $ Million
Nitric acid, 1,000 tpd (HNO_3)	14.5
Nitrophosphate, 1,150 tpd (20-20-0) CAN, 715 tpd (26-0-0)	16.0
Total, battery limits	30.5
Total plant (battery limits x 1.5)	45.8
Storage facilities	5.6
Total	51.4

Thus, the nitrophosphate route requires slightly less investment than the sulfuric acid route in the case of 80% P_2O_5 water solubility; for nitrophosphate of 30%-40% water solubility, the required investment is considerably lower. However, when nitrophosphate of the lower water solubility is made, less CAN coproduct is produced. Thus, the total production of plant nutrients is less. For this reason, the estimate for facilities to produce the 30%-40% water-soluble product is not precisely comparable with the other two estimates.

Under the conditions assumed in the 1975 estimates, the production cost and the gate sale price (bagged), with 20% return on investment, were:

	$/ton of N + P_2O_5	
	Nitrophosphate + CAN	Urea + DAP
Production cost	325	337
Gate sale price	365	393

The results of this estimate, like the two previous ones, show a small cost advantage for the nitrophosphate process as compared with the sulfuric acid route, which may be offset by higher transportation costs due to lower concentration of products. Hence, factors other than cost are likely to be decisive. For instance, for countries that do not have sulfur or sulfuric acid, the saving in foreign exchange may be an important factor. Also, the sulfur supply has been subject to recurrent shortages which have limited fertilizer production; this is another factor that might favor nitrophosphate processes in countries dependent on sulfur imports.

The mixed-acid (phosphonitric) process is particularly well suited for relatively small satellite plants, where either ammonia or phosphoric acid or both are imported. Davis, et al., have discussed the economics of the mixed-acid process in comparison with an ammonium phosphate-nitrate process (10). A 20-20-0 nitrophosphate product (50% water solubility) would have a cost advantage over a 25-25-0 ammonium phosphate nitrate, per unit of plant nutrient, when sulfur cost is more than about $35/ton, under conditions assumed in the estimate. The advantage is increased by using less phosphoric acid (lowering the P_2O_5 water solubility) or by increased price of sulfur.

Detailed estimates for specific conditions are necessary to guide a choice between alternative processes. It may be pointed out that nitrophosphate processes are especially popular in several European countries where the following conditions exist:

1. A large tonnage of fertilizer can be marketed in a small market area; therefore, high nutrient concentration is not a vital factor.
2. Ammonium nitrate is generally preferred as a source of nitrogen.
3. A high percentage of P_2O_5 water solubility is not considered necessary.
4. There are few or no indigenous raw materials for the production of sulfuric acid.
5. Compound fertilizers are preferred to straight materials.

To assist those who may wish to make a rough feasibility study, the following process requirements for the Odda-type nitrophosphate process are suggested as typical for a scale of 230 tons of P_2O_5 per day. Two options are shown--the production of a nitrophosphate product of high P_2O_5 water solubility (80% or more) or a product of lower water solubility (30%-40%). The latter option is more economical (lower steam and electricity requirements) and would be preferable where high P_2O_5 water solubility is not essential. The coproduct is shown as CAN (26-0-0), but straight ammonium nitrate could be produced without extra cost.

Requirements per ton of Nitrophosphate and Accompanying Coproduct

	1 ton of 23-23-0[a] and 0.95 ton of CAN (26% N)	1 ton of 20-20-0[b] and 0.715 ton of CAN (26% N)
Phosphate rock (33% P_2O_5), tons	0.719	0.624
Nitric acid (100% basis), tons	1.069	0.838
Ammonia, tons	0.333	0.235
Carbon dioxide[c], tons	0.280	0.143
Calcium carbonate[d], tons	0.276	0.160
Labor, man-hours[e]	0.407	0.35
Electricity, kWh	210	80
Steam, tons	1.66	1.22
Cooling water[f], tons	79	68
Fuel oil, kg	7.3	7.3

a. 80% P_2O_5 water solubility (actual grade may be between 23-23-0 and 22-22-0, depending on phosphate rock impurities).
b. 30% P_2O_5 water solubility.
c. Usually available from an ammonia plant.
d. Byproduct of process.
e. Operating labor and supervision.
f. Once-through basis.

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XVI Other Phosphate Fertilizers

Single Superphosphate

Single superphosphate (SSP), also called normal or ordinary superphosphate or acid phosphate, has been the principal phosphate fertilizer for more than a century and supplied over 60% of the world's phosphate as late as 1955. Since then its relative importance has declined steadily; in 1975 it supplied only 20% of the fertilizer phosphate in the noncommunist world (data for some communist countries are incomplete). The decline in actual tonnage has been small, but most of the new facilities have been built to produce other, higher analysis products. For the world as a whole, including communist countries, TVA estimated 1972 SSP production at 7.87 million tons of P_2O_5, about 35% of total P_2O_5 fertilizer production, and projected production of 7.4 million tons in 1978 which would be about 25% of the total phosphate fertilizer production (1). Thus, SSP is still an important phosphate fertilizer and is likely to remain so even though its relative importance will decrease.

The advantages of SSP are:

1. The process is simple, requiring little technological skill and small capital investment.
2. The economies of scale are minor, thus small plants can be economical.
3. Since the process is not capital intensive, there is little advantage in a high percentage utilization of capacity; in fact, many SSP plants operate on a planned seasonal schedule.
4. The fertilizer effectiveness of SSP is unquestioned; in fact, it is a standard of comparison for other phosphate fertilizers.
5. SSP supplies two secondary elements, sulfur and calcium, which are sometimes deficient in the soil.

Despite these impressive advantages, the disadvantage of low analysis, 16%-22% P_2O_5, and consequent high distribution costs have caused declining interest in its production because the delivered cost at the farm level is usually higher per unit of P_2O_5 than that of TSP or ammonium phosphates.

SSP will still be a logical choice in several situations such as:

1. Where both P_2O_5 and sulfur are deficient, SSP may be the most economical way to meet these needs. This is the case in much of Australia and New Zealand, some parts of the United States, and Brazil. It is likely that more locations where sulfur is deficient will be identified.
2. In small countries or remote regions where the demand is insufficient to justify an economical scale of production of concentrated phosphate fertilizers and where importation is expensive, SSP can be the most economical means for supplying local needs.
3. In many cases, SSP can be an attractive way to utilize byproduct sulfuric acid which cannot be used to produce more concentrated products because the quality or quantity of the acid is unsuitable. Likewise, SSP can utilize deposits of phosphate rock that are too small to justify a more expensive plant.

Suitability of Phosphate Rocks

Since the grade of the rock determines the grade of the product SSP, a high-grade rock is desirable. Reactivity is also important; unreactive rocks must be ground more finely. It is extremely difficult to produce SSP from some igneous apatites. Iron and aluminum compounds can be tolerated up to a point, although they decrease the P_2O_5 water solubility. Silica has no adverse effect other than decrease in grade. An increase in $CaO:P_2O_5$ ratio increases the sulfuric acid consumption per unit of P_2O_5 and decreases the grade. High-chloride rocks (up to 0.5% Cl and perhaps higher) can be used without serious disadvantage since corrosion is not a serious problem in SSP production.

Chemistry of SSP

The main overall chemical reaction that occurs when finely ground phosphate rock is mixed with sulfuric acid in the manufacture of SSP may be represented by the following equation.

$$\underset{\text{(fluorapatite)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(sulfuric acid)}}{7H_2SO_4} + 3H_2O \rightarrow$$

$$\underset{\text{(monocalcium phosphate)}}{3Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{(calcium sulfate)}}{7CaSO_4} + \underset{\text{(hydrofluoric acid)}}{2HF}$$

It is generally agreed that the reaction proceeds in two stages: (1) the sulfuric acid reacts with part of the rock, forming phosphoric acid and calcium sulfate and (2) the phosphoric acid formed in the first step reacts with more phosphate rock, forming monocalcium phosphate. The two reactions take place concurrently, but the first stage is completed rapidly while the second stage continues for several days or weeks.

The calcium sulfate is mainly in the anhydrous form. The hydrogen fluoride reacts with silica in most rocks, and part of it is volatilized, usually as SiF_4. The remainder may form fluosilicates or other compounds in the SSP. Usually 25% or more of the fluorine is volatilized and must be recovered to prevent atmospheric pollution. In some cases recovery as salable fluorine compounds is feasible, but more often the scrubber liquor is disposed of in a pond by neutralizing it with lime or limestone.

"Kotka superphosphate" is a mixture of superphosphate and phosphate rock. It is named for the city of Kotka, Finland, where it was originally made. It has the advantages that little curing is needed, and the free acid content is low. Its effectiveness generally is equal to that of equivalent amounts of fully acidulated superphosphate plus raw phosphate rock applied separately.

Table 1 shows the chemical composition of one sample of Kotka superphosphate and five typical samples of SSP. SSP usually contains 6%-10% moisture; therefore, its grade can be increased by drying.

TABLE 1. COMPOSITION OF SINGLE SUPERPHOSPHATES

	Composition, % by Weight								
	P_2O_5								
Source of Rock	Total	Available	Water Soluble	Free Acid	H_2O	CaO	SO_3	R_2O_3	F
Florida	19.9	19.6	17.5	2.4	5.9	27.1	28.4	1.3	-
Florida (granular)	21.5	20.7	17.4	0.6	1.1	30.5	30.7	2.3	1.6
Morocco	19.8	-	18.8	2.0	8.4	-	-	-	-
Morocco	21.4	20.2	-	1.7	9.8	-	-	-	-
Ocean Island	22.8	-	20.8	4.6	10.6	-	-	-	-
Morocco and Kola (Kotka)[a]	22.8	14.6[b]	14.5	1.3	8.9	-	-	-	-

a. Superphosphate plus additional phosphate rock.
b. Alkaline citrate soluble.

"Serpentine superphosphate" has been produced in New Zealand by mixing serpentine (a mineral consisting of hydrous magnesium silicate) with SSP. The usual proportion is one part of serpentine to four parts of SSP. The serpentine improves the physical properties of SSP by reacting with the free acid, and it supplies magnesium to crops. Various other minerals or chemical compounds sometimes are added to supply magnesium or micronutrients that may be needed locally.

Production Methods

The manufacture of superphosphate involves the following three (or four) operations.

1. Finely ground phosphate rock (90% <100-mesh) is mixed with sulfuric acid. With rock of 34% P_2O_5 content, about 0.58 kg of sulfuric acid (100% basis) is required per kilogram of rock. Sulfuric acid is available commercially in concentrations ranging from 77% to 98% H_2SO_4. The acid usually is diluted to 68%-75% H_2SO_4 before it is mixed with the rock, or in the case of the cone mixer, the water may be added separately to the mixer. When concentrated sulfuric acid is diluted, much heat is generated; many plants cool the acid in heat exchangers to about 70°C before use.
2. The fluid material from the mixer goes to a den where it solidifies. Solidification results from continued reaction and crystallization of monocalcium phosphate. The superphosphate is excavated from the den after 0.5-4.0 hours. At this time it is still somewhat plastic, and its temperature is about 100°C.
3. The product is removed from the den and conveyed to storage piles for final curing, which requires 2-6 weeks, depending on the nature and proportions of the raw materials and the conditions of manufacture. During curing, the reaction approaches completion. The free acid, moisture, and unreacted rock contents decrease, and the available and water-soluble P_2O_5 contents increase. The material hardens and cools. The product from storage is fed to a disintegrator, usually of the hammer-mill or cage-mill type. The product from the mill is discharged onto an inclined screen of about 6-mesh size. The material that fails to pass the screen is returned to the mill for further grinding.
4. If granular superphosphate is desired, the product is granulated either before or after it is cured. Granulation before curing has the advantage that less water or steam is required. After granulation, the product is dried in a fuel-fired dryer and screened; the fines are returned to the granulation unit.

For many years SSP was produced only by batch-mixing methods; however, most modern plants use continuous mixing and denning processes. There is a wide variety of both batch and continuous mixers and dens; no attempt will be made to describe them all. More detail may be found in the book, *Superphosphate: Its History, Chemistry and Manufacture* (2).

One popular batch system is shown in figure 1. The rock and acid are weighed and discharged into a pan mixer which may have a capacity of 1-2 tons per batch. After mixing about 2 minutes, the fluid mix is discharged into a box den, which may hold 10-40 tons. When the den is filled, one side is removed and the den is advanced slowly on a track to a mechanical cutter which shaves thin slices of superphosphate from the block and discharges them to a conveyor or elevator.

With automated weighing and pan discharge, a 3-minute mixing cycle is feasible; with a 2-ton mixer, a 40-ton den can be filled in 1 hour. Some plants have two dens so that one is being filled while the other is being emptied; this gives a production rate of 40 tph.

Figure 2 shows a flow diagram of a popular type of continuous den; the Broadfield den is a well-known example. The mixer may be a cone mixer, as shown, a paddle mixer (pugmill), or sometimes a cone mixer discharging into a paddle mixer. Retention time in such dens usually ranges from 30 minutes to 1 hour and can be varied by varying the speed of the slat conveyor. This type of den is also suitable for making triple or enriched superphosphate.

The production of a ton of SSP of 20% available P_2O_5 content would require 626 kg of ground phosphate rock (34% P_2O_5), 390 kg of sulfuric acid (93% H_2SO_4), and 90 kg of water. The reaction generates considerable heat. Approximately 8%-10% of the weight of the ingredients (water vapor and volatiles) is lost in the manufacturing and curing steps.

A typical continuous mixer plant to produce 20 tons of nongranular superphosphate per hour would have a 60-kW electrical load. One operator, two

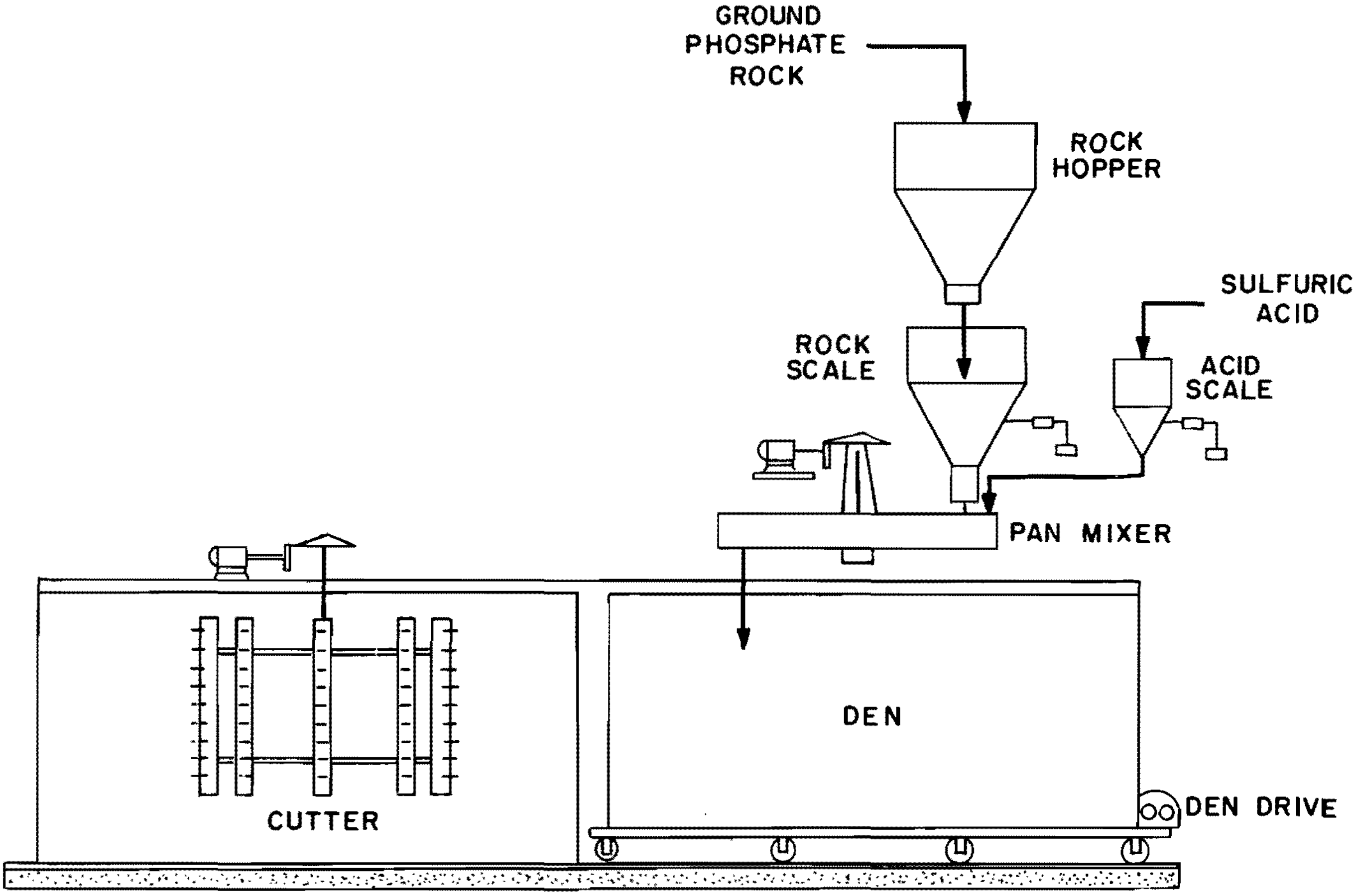

Figure 1. Batch Manufacture of Single Superphosphate.

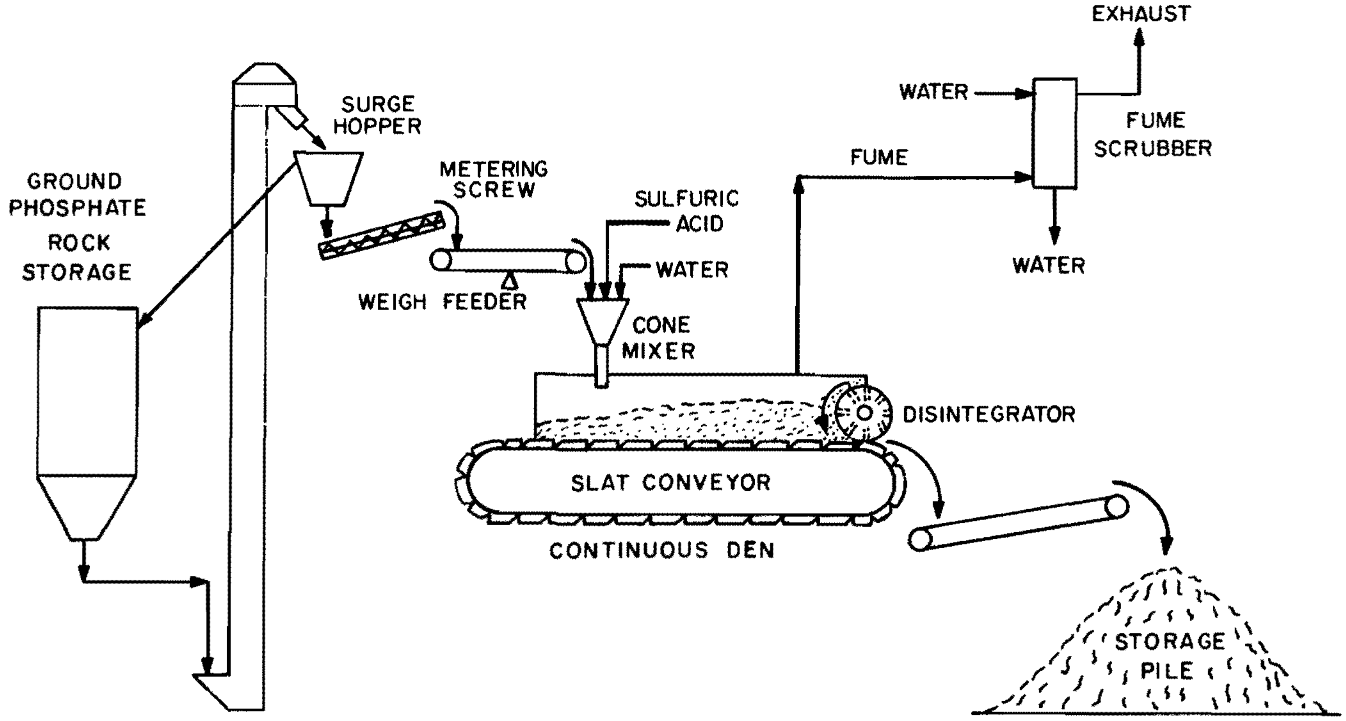

Figure 2. Continuous Manufacture of Single Superphosphate.

laborers, and a part-time supervisor per 8-hour shift would be required to operate the plant.

By applying prevailing unit costs, a rough approximation of the direct cost of producing superphosphate in a specific location can be obtained. The operating requirements per ton of superphosphate are:

Phosphate rock, ton	0.626
Sulfuric acid, (93% H_2SO_4), ton	0.390
Water, ton	0.1
Electricity, kWh	3[a]
Operating labor, man-hour	0.15
Supervision, man-hour	0.017

a. Does not include rock grinding, which requires 7-25 kWh/ton of rock depending on rock hardness and desired fineness.

The capital cost for SSP production will vary widely. While the process equipment itself is relatively inexpensive, a self-sufficient plant including sulfuric acid production, phosphate rock grinding, storage curing, and granulation could be as expensive as a plant for making concentrated fertilizers (TSP or DAP) for an equal P_2O_5 output. However, SSP plants often use byproduct sulfuric acid derived from a plant that is not a part of the SSP plant. Also, small SSP plants may purchase sulfuric acid from a larger plant that supplies several customers.

When several SSP plants are planned or in use, the phosphate rock may be ground at the mine or at a port and shipped to individual plants to take advantage of economies of scale in grinding. When in-plant rock grinding facilities are necessary, the cost depends on the initial size and hardness of the rock.

Storage curing costs will depend in part on the extent of fluorine emission control that is required.

Whether the SSP should be granulated depends on local preference. In some countries nongranular SSP is acceptable. Also, in many cases the SSP will be used as an ingredient for producing granular compound fertilizer.

When granular SSP is desired, the ex-den granulation system described in chapter XIV is suitable. According to Sinte Maartinsdijk, the recycle ratio in this plant was 0.63:1.0 (3). Referring to figure 14, chapter XIV, the battery-limits cost of a plant for granulating 800 tpd would be about $3.2 million. In accordance with table 2, chapter XIV, the battery-limits cost of the plant, not including sulfuric acid production facilities or final product storage, would be:

Item	Cost, U.S. $ Million
Phosphate rock grinding	1.0
Acidulation	0.8
Granulation	3.2
Storage curing	1.2
Total	6.2

Typical process requirements for granular SSP (800 tpd) and illustrative costs are:

	Requirement per ton of SSP	Example of Cost	
		Unit Cost, $	$/ton of SSP
Phosphate rock (33% P_2O_5)	0.626 tons	25	15.65
Sulfuric acid (93% H_2SO_4)	0.390 tons	27.90	10.88
Electricity[a]	33.5 kWh	0.015	0.50
Labor[a]	0.208 man-hour	15.40[b]	3.20
Fuel	62 kcal	0.008	0.50
Steam[a]	55 kg	0.02	1.10
Water[a]	85 kg	neg.	neg.
Capital-related costs[c]			6.21
			38.04

a. Requirements from reference 3.
b. Labor-related costs including overhead and chemical control.
c. Battery-limits cost x 1.5 x 17.67% ÷ 264,000 tpy.

The production cost, $38.04/ton of SSP (20% P_2O_5), is equivalent to about $190/ton of P_2O_5 which may be compared with $200-$213 for TSP, estimated in chapter XIV by similar methods and unit costs. This small advantage would be more than offset by the cost of bagging, transportation, and storage. If these costs amounted to only $20/ton, they would add $100/ton of P_2O_5 to SSP as compared with $43.50 for TSP.

Thus, it may be concluded that large-scale production and distribution of SSP is seldom economical in comparison with TSP or DAP, unless there are special circumstances such as an agronomic requirement for sulfur which would render the SSP more valuable.

On the other hand, small SSP plants to serve small local markets can be economical where suitable raw materials are available, and the alternative of importing more concentrated materials is very expensive.

Enriched Superphosphate

"Enriched" superphosphate is essentially a mixture of SSP and TSP, usually made by acidulation of phosphate rock with a mixture of sulfuric and phosphoric acids. Theoretically, any grade between SSP and TSP can be produced, but the usual range is 25%-35% P_2O_5. Processes and equipment are about the same as for SSP (4).

Enriched superphosphate may be a useful product for application in sulfur-deficient areas where SSP would supply more sulfur than necessary. One advantage is that mixed acid of the proper concentration can be obtained by mixing concentrated sulfuric acid (93% or 98% H_2SO_4) with dilute phosphoric acid (30% P_2O_5), thereby avoiding the need for concentrating the latter.

Basic Slag

Basic slag, also called Thomas slag, is a byproduct of the steel industry. Iron made from high-phosphorus ore is converted to steel in a Thomas converter by oxidation in contact with a basic (high CaO) slag. The usual range of P_2O_5 content in slag that is used for phosphate fertilization is 10%-20%. Sometimes phosphate rock is deliberately added to the blast furnace charge to increase the phosphorus content of the iron and thereby increase the P_2O_5 content of the slag.

Basic open-hearth slag also may contain P_2O_5 up to 10%-12%, and it is used in agriculture in some countries, both for liming and phosphorus supply.

Since most of the high-phosphorus iron ores occur in western Europe, most of the basic slag is produced and used there. A typical range of composition for high-grade basic slag is:

Composition, % by Weight						
P_2O_5	SiO_2	CaO	MnO	Al_2O_3	MgO	Fe
15-20	4-6	42-50	3-6	0.5-2.5	2-4	9-13

The P_2O_5 in basic slag is mainly present as calcium silicophosphates--silicocarnotite ($5CaO \cdot P_2O_5 \cdot SiO_2$) and nagelschmitite ($7CaO \cdot P_2O_5 \cdot 2SiO_2$). Small amounts of fluorspar (CaF_2) may be added to slags to decrease their viscosity during the steel-refining process. Such slags contain fluorapatite and are likely to be less suitable for fertilizer use.

The Wagner test, which measures the solubility of P_2O_5 in 2% citric acid, is widely accepted for evaluating the suitability of basic slag for fertilizer use. P_2O_5 solubility in this reagent ranges from 85% to 98% for English basic slags (5).

The consumption of agricultural-grade basic slag was equivalent to 1.2 million tons of P_2O_5 in 1973 and varied only slightly from this level for many years. However, the available supply recently has decreased because of changes in steel-making processes and importation of low-phosphorus iron ore. In 1977 world production was about 572,000 tons of P_2O_5, less than half of the 1960-65 average (6). Further decreases were forecast in the 1978-81 period.

The slag is regarded as a good phosphate fertilizer on acid soils and is also valued for its liming effect and for micronutrient content. It is usually applied in a finely ground state although granulation with potash has been practiced to some extent.

Potassium Phosphates

Potassium phosphates are excellent fertilizers, and their very high analysis is an advantage that has stimulated much research in an effort to find an economical production process. However, no process has been developed that is economical enough to result in widespread production; therefore, present use is limited to special purposes for which the high cost can be justified.

At present, most of the potassium phosphates used in fertilizers are produced from potassium hydroxide or carbonate and phosphoric acid and are used in liquids for foliar application or other specialty uses.

Some of the potassium phosphates are:

		Approx. Grade
Monopotassium phosphate	KH_2PO_4	0-52-35
Dipotassium phosphate	K_2HPO_4	0-40-54
Tetrapotassium pyrophosphate	$K_4P_2O_7$	0-43-57
Potassium metaphosphate	KPO_3	0-60-40

In addition, a potassium polyphosphate solution of 0-26-27 grade has been produced from superphosphoric acid and potassium hydroxide; it contains a mixture of ortho, pyro, and higher polyphosphates.

TVA, SAI, and others have produced potassium metaphosphate in pilot plants by high-temperature reaction of KCl and phosphoric acid. The pure material, KPO_3, has a grade of about 0-60-40 and, thus, a 100% nutrient content (on an oxide basis).

In a recently developed process originated jointly by Goulding (Ireland) and Pennzoil (United States), potassium chloride is treated with concentrated sulfuric acid to produce potassium bisulfate (7, 8):

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$

The hydrogen chloride is recovered as a dry gas and can be used for certain oxychlorination reactions or other industrial purposes for which elemental chlorine is now used. The potassium bisulfate is used, with more sulfuric acid, to make monopotassium phosphate and phosphoric acid. A simplified equation, representing phosphate rock as tricalcium phosphate, is:

$$KHSO_4 + 2H_2SO_4 + Ca_3(PO_4)_2 + 6H_2O \rightarrow 3CaSO_4 \cdot 2H_2O + KH_2PO_4 + H_3PO_4$$

After removal of the gypsum by filtration, the mixture of phosphoric acid and monopotassium phosphate can be ammoniated to produce a chloride-free NPK fertilizer such as 8-48-16, or monopotassium phosphate can be separated from the phosphoric acid by precipitation in methanol solution and marketed separately. If desired, the monopotassium phosphate can be converted to a pyro- or polyphosphate by pyrolysis.

The process is being carried out by Pennzoil on a small commercial scale in a plant in California. The obvious advantage of the process is the recovery of HCl in a useful form. Another advantage is that a standard wet-process phosphoric acid plant can be adapted with a minor change. Numerous other processes for making potassium phosphate from KCl have been proposed, patented, or developed on a commercial scale, but none are known to be in commercial use for fertilizer purposes.

Bone Meal

A relatively small amount of bone meal is used as fertilizer mainly by home gardeners. It is much too expensive for farm use. Most of the bone meal is marketed for use in animal feeds.

Fused Calcium Magnesium Phosphate

In a process developed by TVA, a mixture of phosphate rock and olivine or serpentine (magnesium silicate) is fused in an electric furnace (9). The molten product is quenched with water and used in a finely divided state as a fertilizer. The product, a calcium magnesium phosphate (CMP) glass, contains about 20% P_2O_5 and 15% MgO. Over 90% of the product is soluble in citric acid.

CMP is produced in several plants in Japan where the annual production is about 500,000 tons. It is also produced in Korea, Taiwan, China, Brazil, and South Africa. Either electric or fuel-fired furnaces are used.

The theoretical compositions of some magnesium-containing minerals that can be used to produce CMP are:

Olivine	$(Mg,Fe)_2SiO_4$
Serpentine	$Mg_3H_4Si_2O_9$
Garnierite	$(Mg,Ni)H_2SiO_4$
Magnesite	$MgCO_3$

The minerals are variable in composition; iron, nickel, and sometimes manganese may substitute for magnesium. A sample of Japanese serpentine contained 38% MgO, 38% SiO_2, 8% Fe_2O_3, and 14% ignition loss (10). Magnesium oxide, obtained by calcining magnesite or extracting it from sea water, can be used in the process; in this case, silica must be added in sufficient quantity to give about 20%-30% SiO_2 in the product. Huang reported that ratios of serpentine to phosphate rock in the range of 6:10 to 8:10 gave the highest P_2O_5 solubility in citric acid, using phosphate rock from Christmas Island (39% P_2O_5) or Lao Kay (33% P_2O_5) (10). Moulton reported using ratios of olivine to phosphate rock of 1:2 with Montana phosphate rock (30%-32% P_2O_5) (11). Walthall and Bridger recommended a ratio of olivine to phosphate rock of 0.46:1.00 using Tennessee phosphate rock (33% P_2O_5) and North Carolina olivine (45% MgO and 44% SiO_2) (9). About 30% of the fluorine was volatilized, but the product P_2O_5 solubility was not related to its fluorine content. In tests in which magnesia and silica were supplied separately, it was found that 0.24 kg of MgO and 0.25 kg of SiO_2/kg of phosphate rock gave product P_2O_5 solubility of 96% (in citrated ammonium nitrate solution). Also, 0.28 kg of MgO and 0.21 kg of SiO_2 gave essentially complete solubility.

In Japan, CMP is produced in electric-arc furnaces of the type used for the manufacture of calcium carbide. The furnace charge is prepared by crushing and mixing phosphate rock and serpentine or olivine. About 850 kWh/ton of product is required for the fusion process. It is essential to quench the molten material rapidly, and this is usually accomplished in a trough provided with high-velocity jets of water. Approximately 10 tons of quench water, which may be recycled, is required per ton of product. The quenched material is allowed to drain and is then dried and ground. The specified fineness is at least 70% through a 100-mesh screen.

Ando reported tests in which charges of garnierite, phosphate rock, gypsum, and coke were fused in a blast furnace or electric furnace to produce CMP and nickel matte, a mixture of sulfides of nickel and iron containing 20%-25% Ni, 60%-66% Fe, and 14%-17% S (12). The nickel matte was processed further to recover the nickel. The coke reduced the gypsum and the iron and nickel oxides to form the sulfides. When the process was carried out in the blast furnace, combustion of additional coke supplied the necessary heat for the fusion process.

A blast-furnace process is used in China also to produce CMP with separate recovery of iron and nickel.

Greenhouse tests made by the U.S. Department of Agriculture showed that the product is, on the average, more effective than superphosphate when used on acid soils. Field tests in Japan have given favorable results on many different crops and soils. The product has a liming value equivalent to 0.5-0.7 ton of calcium carbonate per ton of material. The magnesium oxide content is available to growing plants. In some situations, the soil-soluble silica may be an advantage.

Defluorinated Phosphate Rock

There is a substantial production of defluorinated phosphate rock for fertilizer usage in Japan (about 100,000 tpy). Ground, high-grade rock is mixed with small proportions of sodium carbonate or sulfate and wet-process acid. The mixture is calcined at a temperature of 1350°C in an oil-fired rotary kiln 45.0 m in length and 2.7 m in diameter. The product contains 38%-42% P_2O_5 of which over 90% is soluble in 2% citric acid by the method used in Japan to evaluate this product. About 85%-90% is soluble in neutral ammonium citrate solution. Substantially all of the fluorine is driven off. Sodium bifluoride ($NaHF_2$) is recovered as a byproduct. A similar product is made in the United States, but it is mainly used for animal-feed supplement. The principal phosphate compound in the product is tricalcium phosphate.

Requirements per ton of product containing 41%-42% total P_2O_5 are:

Phosphate rock (37% P_2O_5), kg	900
Wet-process acid, kg (as P_2O_5)	95
Sodium carbonate, kg	120
Heavy fuel oil, liters	200

The product is said to be an effective fertilizer when applied in finely ground form on acid soils.

TVA has studied defluorination of lower grade phosphate rock through fusion processes. Ten pilot plants and two demonstration-scale plants were built and operated. The more successful plant operated for 10 years (1945-55) and produced about 170,000 tons of product containing 28% P_2O_5 from low-grade Tennessee rock. The results of the studies have been published (13).

Rhenania Phosphate

Rhenania phosphate is another thermally produced phosphate fertilizer. It is made by calcining a mixture of phosphate rock, sodium carbonate, and silica in a rotary kiln at 1250°C (14). Enough sodium carbonate is used to form the compound $CaNaPO_4$ and enough silica to form Ca_2SiO_4 with the excess calcium. Typical charge proportions are one part of sodium carbonate to three parts of phosphate rock, plus enough silica to raise the SiO_2 content of the product to about 10%. The product contains 28%-30% P_2O_5 which is nearly all soluble in neutral or alkaline ammonium citrate solution even though much of the fluorine remains in the product. It is applied to the soil in pulverized form or granulated in small granules with potash salts. Some grades are produced containing magnesium or boron which are added during granulation as kieserite or borax, respectively. A substantial quantity is produced in European countries, particularly West Germany.

A somewhat similar product, Roechling phosphate, uses a soda slag that is a byproduct from the steel industry as the source of sodium. Also, the naturally occurring minerals, trona (sodium sesquicarbonate) or natron (sodium carbonate), may be used.

Experiments have shown that a similar product can be made by sintering potassium carbonate with phosphate rock and silica to give a product grade of 0-25-25. The phosphate compound in this product is presumed to be $CaKPO_4$.

The overall reaction in producing Rhenania phosphate is assumed to be:

$$Ca_{10}F_2(PO_4)_6 + 4Na_2CO_3 + 2SiO_2 \rightarrow 6CaNaPO_4 + 2Ca_2SiO_4 + 2NaF + 4CO_2$$

Any grade of phosphate rock can be used, but since the grade of the product is determined by the grade of the rock, a high grade is preferred.

Estimated requirements, using an igneous apatite, are:

	Requirement per ton of 0-29-0 Product
Phosphate rock, 38.7% P_2O_5	0.749 tons
Soda ash, 100% Na_2CO_3	0.289 tons
Sand, 97% SiO_2	0.077 tons
Electricity	36 kWh
Steam	10 kg
Fuel oil	66 kg

The product has been reported to be substantially more effective than superphosphate on several acid tropical soils in Costa Rica, Liberia, Congo, Zaire, Ghana, and Malawi perhaps because of its alkalinity and resistance to fixation by the soil (15). In some crops or soils the sodium or soil-soluble silica may be beneficial.

Calcium Metaphosphate

For several years TVA produced calcium metaphosphate, $Ca(PO_3)_2$, in a demonstration-scale plant. The process consisted of burning elemental phosphorus and reacting the resulting P_2O_5 vapor with phosphate rock. The molten product was tapped out of the furnace and solidified on a water-cooled steel drum (16). The resulting vitreous flakes were cooled further and crushed to pass a 10-mesh screen (about 1.6 mm).

Development of a process for production of calcium metaphosphate involved three pilot plants and three demonstration-scale plants, as well as a considerable amount of laboratory- and bench-scale work (17). The third demonstration-scale plant was technically successful and operated about 16 years, starting in 1949. A total of nearly 1 million tons was produced, including relatively small amounts from the first and second demonstration-scale plants. The process was economically competitive with TSP when both products were based on elemental phosphorus made by electric-furnace process.

Pure calcium metaphosphate contains 71.7% P_2O_5; the TVA product contained about 65% P_2O_5 because of impurities in the rock. The material was not water soluble but hydrolyzed slowly in water or moist soil, forming water-soluble compounds (18). About 98% or more of the P_2O_5 was soluble in neutral ammonium citrate.

The main disadvantage of the process was its dependence on elemental phosphorus which has become too expensive for fertilizer use in most situations. Also its agronomic effect depends on the rate of hydrolysis in the soil which may be too slow for short-season crops.

Calcium metaphosphate glass may also be produced by heating TSP to fusion; crystalline structures, which are not citrate soluble, are formed at lower temperatures.

Dicalcium Phosphate

Dicalcium phosphate is a common constituent of nitrophosphate fertilizers and of compound fertilizers formed by ammoniation of superphosphates. There is a relatively small but substantial production of straight dicalcium phosphate in Europe which is based on utilization of byproduct hydrochloric acid. The process consists of dissolving phosphate rock in hydrochloric acid and then precipitating dicalcium phosphate by stepwise addition of limestone and slaked lime. The product is recovered by filtration and washing, and the remaining solution of calcium chloride may be utilized or discarded.

Various other methods for producing dicalcium phosphate are known, but none are known to be used commercially for fertilizer production. Direct neutralization of pure or defluorinated phosphoric acid with lime or limestone is used to produce feed- or food-grade dicalcium phosphate.

Magnesium Phosphates

Monomagnesium, dimagnesium, and trimagnesium phosphates are known to be effective fertilizers, but there is no known commercial production of these materials for fertilizer use. No doubt small percentages of these compounds are formed in processing phosphate rock containing magnesium.

A process has been developed by Israel Mining Industries (IMI) on a pilot-plant scale in which impure carnallite is heated to 400°C with phosphate rock (19). The presumed reaction is:

$$\underset{\text{(phosphate rock)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(carnallite)}}{10KCl \cdot MgCl_2 \cdot 6H_2O} + \rightarrow$$

$$3Mg_3(PO_4)_2 + MgF_2 + 10CaCl_2 + 10KCl + 60H_2O$$

The reaction product is leached with water to wash out the calcium and potassium chlorides, and the remaining solid consisting mainly of trimagnesium phosphate is dried for fertilizer use. Potassium chloride can be recovered from the leach liquor.

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XVII Some Factors Influencing Choice of Phosphate Fertilizers

Phosphate fertilizers described in previous chapters cover a wide range of solubilities in water and soil. In contrast, all popular nitrogen and potassium fertilizers are water soluble. Also, the most popular phosphate fertilizers contain other primary or secondary nutrients--nitrogen (ammonium phosphates and nitrophosphates), calcium, magnesium, and/or sulfur. Selection of a phosphate fertilizer is therefore relatively complex.

The first step in the selection process should be an accurate estimate of present and future requirements of the country, province, or region involved. For the reasons mentioned above, the estimate should include nitrogen and secondary nutrient requirements as well as phosphorus.

The next step should be an assessment of the types of soils, crops, and climate to determine what kind of phosphate fertilizer is acceptable. Water-soluble phosphate fertilizers are usually satisfactory, but insoluble or partially soluble products are often equally effective and cheaper. In general, phosphate that has a high percentage of its phosphorus in a water-soluble form is needed on high-pH soils. As an exception calcined aluminum phosphate ore is satisfactory on some high-pH soils. On acid soils, on the other hand, water solubility is much less important, and even completely water-insoluble products may be suitable.

The acceptability and advantages of compound fertilizers, including the most useful $N:P_2O_5$ ratios, need to be evaluated. Where compound fertilizers are acceptable, fertilizers based on ammonium phosphate or nitrophosphate may be the most economical source.

The need for secondary elements should enter into consideration; where sulfur is needed, single or enriched superphosphate or ammonium phosphate-sulfate may be preferred. A need for calcium suggests that ground rock, basic slag, or Rhenania phosphate could be considered. Of course, the best way to supply secondary elements may not be in combination with phosphate fertilizer, but the possibility should be considered.

Concurrently with an assessment of fertilizer needs, there should be an assessment of the country's resources to produce phosphate fertilizers. Phosphate rock is a key resource, but the mere presence of a known phosphate deposit does not automatically ensure that it can be profitably converted to fertilizer. Phosphate rock deposits vary widely in their amenability to profitable mining and beneficiation and in their adaptability to various fertilizer processes. Other resources that may be considered are materials for producing sulfuric acid, possible byproduct sulfuric or hydrochloric acid, and energy sources and raw materials for thermal processes including sodium minerals for Rhenania phosphate and magnesium silicate minerals for fused calcium magnesium phosphate.

If a country has neither phosphate rock nor the materials needed to treat it, the question becomes what should be imported--basic raw materials, intermediates, or finished products. The answer will depend on several factors which are discussed in other chapters. Importation of phosphate rock for grinding and direct application will likely be the lowest cost solution in both capital and operating costs. However, ground rock is not a satisfactory source of phosphorus for some soils and crops, thus agronomic tests are needed to determine its usefulness. Importation of intermediates (phosphoric acid or nongranular MAP) for further processing may be attractive when the demand is sufficient to support an economical scale of operation. Nitrophosphates may be considered when the products are suitable for agricultural needs.

When there are indigenous sources of phosphate rock, its use for direct application or for conversion to phosphate fertilizer may be considered. The choice is likely to depend on the character of the rock, the estimated market demand, distribution costs, and agricultural needs.

When indigenous resources include either phosphate rock of satisfactory quality and cost, byproduct sulfuric acid, or low-cost sulfur, production of phosphate fertilizer for export as well as domestic use can be considered.

It is evident that the problem of how to supply the phosphate fertilizer needs of any country or region at least cost is a complex one that requires much study. It is hoped that the information supplied in the preceding chapters, XII through XVI, will be helpful in solving this problem.

In the previous chapters, the productions of sulfuric acid, phosphoric acid, and final product (TSP, DAP, or MAP) have been considered separately. In many cases, the three operations will be carried out concurrently at the same plant location. The operation of such a plant may involve some problems and opportunities that are not evident when the plant processes are considered separately.

Example of Economic Study

As an example of the economic and technical factors involved in planning a phosphate plant complex, a hypothetical case will be assumed in which a developing country has a relatively small phosphate deposit such as 5-10 million tons which it wishes to use to produce phosphate fertilizer for domestic consumption. The rock can be beneficiated by simple size-separation methods to 30% P_2O_5, and tests have shown that it is suitable for producing phosphoric acid of satisfactory quality without unusual technical difficulty. Further beneficiation of the rock to a grade of 34% by flotation to remove silica has been considered. However, this option has been discarded because this step would be costly on a relatively small scale, and losses during further beneficiation would seriously decrease the useful life of the deposit.

The prospective demand for phosphate fertilizers is 120,000 tons of P_2O_5 per year. The country also has a substantial demand for nitrogen fertilizer which is supplied from another source, mainly as urea with smaller amounts of ammonium sulfate. Use of potash is small but growing. Little information is available about the need for supplying sulfur in fertilizers. It has been decided that supplying phosphate fertilizer in the form of an NP compound would be acceptable, provided the minimum $N:P_2O_5$ ratio does not exceed 0.5:1.0 since all crops require at least this proportion of nitrogen as a basal application. For crops requiring a higher ratio, urea can be added by blending.

A study of agronomic and economic factors has indicated that high-analysis, soluble fertilizers would be preferable, and the choice has been narrowed to TSP, DAP, and MAP. The problem, therefore, is to obtain a preliminary indication of whether production of phosphate fertilizer would be economically attractive and, if so, which would be preferable.

It is estimated that the phosphate rock containing 30% P_2O_5 can be delivered to a plant site for $20/ton and that the delivered cost of sulfur is $65/ton. Ammonia is available at $120/ton and bulk urea at $145.

It is assumed that the proposed phosphate plant will operate at 90% of capacity, equivalent to 297 days/year at full capacity. Calculations of daily capacity requirements and capital cost are shown in table 1 and production cost estimates in table 2.

TABLE 1. CALCULATION OF CAPITAL COST AND DAILY MATERIAL REQUIREMENTS

	Production of 120,000 tons of P_2O_5 per year, 297 Operating days per year		
	TSP	DAP	MAP
Grade	0-44-0[a]	18-46-0	11-55-0
Tons of product/year	272,727	260,870	218,182
Tons of product/day	918	878	735
P_2O_5 recovery, %[b]	96	97	97
P_2O_5 required, tpd	420.9	416.5	416.5
P_2O_5 as acid[c]	307.2	416.5	416.5
P_2O_5 as rock[c]	113.6	-	-
H_2SO_4 required, tpd[d]	854	1,158	1,158
Capital cost, U.S. $ million			
Sulfuric acid plant[e]	14.4	17.8	17.8
Phosphoric acid plant[f]	20.8	25.6	25.6
Granulation[g]	18.9	13.3	11.8
NH_3 storage	-	2.5	2.5
Product storage[h]	2.3	2.2	1.9
Total	56.4	61.4	59.6

a. Using 30% P_2O_5 rock with a $CaO:P_2O_5$ ratio of 1.50, TSP contains 44% available P_2O_5.
b. Assume 2% product loss and overage in analysis, plus 2% unavailable P_2O_5 in TSP, 1% in DAP and MAP.
c. Assume 73% P_2O_5 from acid, 27% from rock for TSP (chapter XIV).
d. Based on a $CaO:P_2O_5$ ratio in rock of 1.5 (chapter XIII).
e. See chapter XII.
f. See chapter XIII.
g. See chapter XIV.
h. Based on 45 days' bulk storage at $40/ton, plus 10-day bagged storage at $75/ton.

As shown in table 2, the cost per ton of product is lowest for TSP, but the net cost per ton of P_2O_5, after allowing for the value of the nitrogen content, is lowest for DAP by a substantial margin. Allowance for distribution costs would increase this margin.

Calculations should be made to determine whether the project would be profitable in comparison with importing phosphoric acid or importing bulk TSP, DAP, or MAP. This would require a forecast of world market prices plus transportation costs. Present (mid-1978) prices are somewhat depressed. Prices (f.o.b.) are about $135/ton for bulk DAP, $95/ton for bulk TSP, and $205/ton of P_2O_5 for phosphoric acid.[1] The prospective costs in table 2 are somewhat higher, but depending on location, the delivered costs of imported materials may still be higher. Thus, the project might be considered potentially profitable, particularly in view of probable future increases in cost of imported materials.

Flexibility for possible production of compound fertilizers would be a point in favor of either DAP or MAP. For instance, by adding sulfuric acid and more ammonia in the DAP process, a grade such as 18-36-0 could be made containing sulfur for sulfur-deficient areas. Potash could be added to produce NPK grades such as 14-35-14. Relatively little additional equipment would be required.

The example calculation provides an illustration in which three plant units (sulfuric acid plant, phosphoric acid plant, and granulation plant) are interdependent. Taking TSP as an example, the plant capital cost is $470/annual ton of product P_2O_5 for operation at 90% of capacity. Capital-related costs included in production costs amount to 17.67% of $470 or $83.05/ton of P_2O_5 or $36.54/ton of TSP, about 36% of total production cost of the bulk product. If a return on investment of 10% were required, $47/ton of P_2O_5 (about $20.68/ton of TSP) would have to be added. Increasing the operating rate from 90% to 100% would decrease production cost of TSP by 3.6% while decreasing the rate to 60% would increase costs by about 18%. Thus, the complex as a whole is moderately capital intensive. Raw materials (sulfur and phosphate rock) account for about 49% of the production cost of bulk TSP. In the case of DAP, the cost of the raw materials, sulfur, phosphate rock, and ammonia accounts for about 59% of the production cost of the bulk product.

In practice, the situation is seldom as simple and well defined as in the above hypothetical example. However, a calculation of this sort can be a helpful first step in assessing the feasibility of a phosphate project and selection of a product. A much more detailed feasibility study should, of course, be made before approving a project.

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[1] "International Price Trends," Fertilizer International, No. 111, September 1978, page 4.

TABLE 2. ESTIMATED PRODUCTION COSTS

	TSP	DAP	MAP
Sulfuric acid, \$/ton of H_2SO_4[a]	31.70	30.60	30.60
Phosphoric acid, \$/ton of P_2O_5[b]	217.83	210.17	210.17
		\$/ton of product	
Phosphoric acid	72.89	99.66	119.17
Phosphate rock (.4123 tons at \$20)	8.25	-	-
Ammonia (.224 and .137 tons at \$120)	-	26.88	16.44
	81.14	126.54	135.61
Utilities	2.00	1.45	1.45
Labor-related costs	3.36	3.50	4.19
Capital-related costs[c]	13.73	12.19	13.12
Total bulk cost	100.23	143.68	154.37
Bags and bagging	12.00	12.00	12.00
Cost of bagged materials	112.23	155.68	166.37
Credit for N at \$341.30[d]		61.43	37.54
Net cost of P_2O_5, \$/ton of product		94.25	128.83
Net cost, \$/ton of P_2O_5	255.07	212.50	234.24

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a. Estimated from data in chapter XII, assuming sulfur at \$65/ton.

b. Operating cost estimated from figure 8, chapter XII, plus 2.78 tons of H_2SO_4 at cost shown on line 1 and 3.55 tons of rock at \$20.

c. Based on granulation plant, ammonia storage, and product storage capital costs.

d. Equivalent to bagged urea at \$157/ton.

PART FOUR

POTASH AND OTHER FERTILIZERS

XVIII Potash Fertilizers

Introduction

Potash was first mined commercially as carnallite ore in the Stassfurt region of Germany in 1861 soon after the investigations of Liebig indicated that potassium salts might be used advantageously as a chemical fertilizer. Within 2 years, 14 plants had come into operation. In 1864 the total production was 110,000 tons of salts, and this value gradually increased to about 3 million tons in 1900 and to about 44 million tons in 1978-79 (calculated as 60% K_2O product).

Potassium is the seventh most abundant element in the earth's crust. In addition to being an essential constituent of plant and animal life, it occurs in very low concentrations in rocks and soils; in the oceans, lakes, and rivers; and in the saline residues of salt lakes. The most widespread economic source of potash is the evaporite deposits--sedimentary deposits formed by the evaporation of seawater under very arid conditions (1). Commercial deposits, such as those in the Elk Point Basin in western Canada, required the flow of large amounts of seawater into a lagoon where the dissolved salts precipitated in the inverse order of their solubilities, first calcium carbonate, calcium sulfate, anhydrite, and sodium chloride, followed by the highly soluble potassium and magnesium salts when the seawater reached about 100 times its original concentration.

The principal potash evaporite minerals of commercial importance are sylvite, langbeinite, kainite, and carnallite. Sylvinite, a mixture of potassium chloride and sodium chloride crystals, is the easiest to process and is mined in the largest quantities. It normally occurs in layers, underlain and overlain with sodium chloride. The sylvinite occurs in more than one stratum.

All North American potash mines recover sylvinite. Two mines in the United States also produce langbeinite, which is sold as a source of water-soluble magnesium as well as potassium and sulfur. One producer also reacts langbeinite with potassium chloride to produce potassium sulfate and the waste product magnesium chloride. Potassium chloride or sulfate is also recovered from brine deposits.

Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) is more difficult to process, but it is refined in Europe, Israel, and the U.S.S.R. to recover its potassium chloride.

Kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) occurs in several European mines, usually in combination with other potash ores.

The purpose of this chapter is to state the importance of potash, to review its mineralogy and principal deposits, to give an overview of the processes for refining it, to indicate trends in its products, to report price levels and typical production costs, and finally to summarize world potash commerce and consumption.

Agronomic and Industrial Significance of Potash

Although some 17 elements are normally required to support healthy plant growth, nitrogen, potassium, and phosphorus (the three primary nutrients) are required in much larger quantities than are the other elements. In order to attain the maximum effectiveness, these primary nutrients have to be supplied to crops in essentially the same proportions as they exist in most plant life, where the ratio of nitrogen to potassium is about 2:1. Thus, among the commercial fertilizers, about half as much potash is used as nitrogen, except when the soil is capable of supplying potash. Thus, the ever-increasing use of nitrogen fertilizers necessitates the application of potash in similarly increasing quantities.

The physiological functions of potassium in plants include at least the following:

1. Promotion of carbohydrate metabolism or formation, breakdown, and translocation of starch.
2. Promotion of nitrogen metabolism and the synthesis of protein in green plants.
3. Control and regulation of activities of various essential mineral nutrients.
4. Neutralization of the physiologically important organic acids.
5. Activation of various enzymes.
6. Promotion of the growth of young meristems.
7. Control of stomatal movement and internal water relationships.

About 95% of all potash mined is used as fertilizers (2). The other 5% is used in various industrial applications. A higher purity (99.92% KCl) chemical grade of potash is used by the chlor-alkali industry in the electrolysis of KCl-water solutions to form chlorine and potassium hydroxide (KOH), commonly called caustic potash. Caustic potash is used in liquid soaps, textiles, greases, catalysts, engraving, alkaline batteries, and rubber fabrication. A substantial amount of caustic potash is further processed to form potassium carbonate and other potassium compounds. More than half of the potassium carbonate produced annually is used in glass manufacture. Caustic potash is also used in relatively small amounts to make potassium phosphates for special fertilizers such as liquid fertilizers for foliar application. Small quantities of agricultural grades of muriate of potash are used with sodium chloride and other chemicals as fluxes in the secondary smelting of aluminum and magnesium. Muriate of potash is included in drill muds used in oil well drilling.

Mineralogy of Potash Ores

Potassium accounts for 2.35% of the earth's crust, where it is mixed mainly with deposits of sodium compounds. But it is also found in feldspars, muscovite (white mica), granite, and gneiss. Sedimentary rocks comprise about 5% of the earth's crust. The sandstones contain about 1.1% potassium, shales about 2.7%, and limestones about 0.27%. Potassium, a monovalent alkali metal, does not occur in nature because it is highly reactive and has a strong affinity for other elements. It has a melting point of 63.5°C, a specific heat of 0.177 cal/mole/°C, and a specific gravity of 0.86.

Potassium mineral deposits are usually the result of evaporation of water from landlocked seas that have become separated from the main oceanic body and from which the contained salts have gradually precipitated. In some cases inland seas have evaporated to form such deposits. Potassium and other alkali metals were brought into the oceans and inland lakes by river water that leached these materials from rocks and soils. Sodium is leached more easily from soils because potassium becomes fixed to clay particles in soil.

Salts crystallize in an inverse ratio of their solubilities; the order of deposition usually is calcium carbonate, magnesium carbonate, calcium sulfate, sodium chloride, magnesium sulfate, magnesium chloride, and finally potassium chloride. Other conditions alter the deposition, and they may account for the various strata encountered.

The mother liquor or bittern of seawater after the moderately soluble salts have precipitated is rich in magnesium chlorides and sulfates and smaller amounts of potassium and bromine.

Bittern salts of marine origin include:

Sylvite	KCl
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Polyhalite	$2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$
Boracite	$5MgO \cdot MgCl_2 \cdot 7B_2O_3$

The minerals associated with brines of lake beds include other minerals such as those found in Searles Lake in California.

Halite	$NaCl$
Hanksite	$9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Borax	$Na_2B_4O_7 \cdot 10H_2O$
Glaserite	$3K_2SO_4 \cdot Na_2SO_4$

The following potash minerals are found in nature. The most important is sylvite which is usually found mixed with sodium chloride; the mixture is called sylvinite. Other ores being used in fertilizer potash production are carnallite, langbeinite, niter and kainite.

Mineral	Composition	% K_2O
Chlorides		
Sylvite	KCl	63.1
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	17.0
Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$	18.9
Hanksite	$KCl \cdot 9Na_2SO_4 \cdot 2Na_2CO_3$	3.0
Sulfates		
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$	15.5
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$	22.6
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	25.5
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	23.3
Krugite	$K_2SO_4 \cdot MgSO_4 \cdot 4CaSO_4 \cdot 2H_2O$	10.7
Glaserite	$3K_2SO_4 \cdot Na_2SO_4$	42.6
Syngenite	$K_2SO_4 \cdot CaSO_4 \cdot H_2O$	28.8
Aphthitalite	$(K, Na)_2SO_4$	29.8[a]
Kalinite	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	9.9
Alunite	$K_2 \cdot Al_6(OH)_{12} \cdot (SO_4)_4$	11.4
Nitrates		
Niter	KNO_3	46.5

a. Assuming equimolecular proportions of K and Na.

Silicates and other nonsoluble minerals (except alunite) are not included in the tabulation above. Potash deposits can be classified into three basic types according to the mineralization of the principal horizons, namely:

1. Carnallitic mineralization including a carnallite-kieserite-halite zone, a carnallite-anhydrite-halite zone, and a carnallite-halite zone.
2. Sylvinitic mineralization, including a sylvite-kieserite-halite zone, a sylvite-anhydrite-halite zone, and a sylvite-halite zone.
3. Kainitic mineralization, containing sulfates, chlorides, and a kainite-langbeinite-picromerite-glaserite-polyhalite zone.

World Potash Reserves

World potash reserves are enormous and sufficient to meet requirements for many centuries to come. The U.S. Bureau of Mines in 1978 estimated the reserves of potash at about 12 billion[1] tons of K_2O at 1976 domestic mine prices, with total resources at 132 billion tons (3). The fact that potash can be recovered from seawater means an additional, almost unlimited, but more costly, resource of this material.

Enormous quantities of potash are present in Canada and the U.S.S.R. These two countries together probably represent more than half the world's reserves and about 80% of the world's resources. The remaining known reserves are distributed among the United States, Europe, the Middle East, Thailand, the Congo, and South America. An estimate of world potash reserves and resources is given in table 1 which was taken from a recent U.S. Bureau of Mines report (3). A similar estimate has been published by The World Bank (4). A brief description of each deposit follows (5, 6).

In the U.S. Bureau of Mines classification, "reserves" are described as ores that can be recovered at or near the current market prices; whereas, "resources" are potentially minable ores which, because of cost or other constraints, could not necessarily be recovered at current prices but might be at a later date (3). The World Bank estimates use a similar classification. The necessary data for making such estimates are not always available or may be subject to different interpretations. Locations of the major potash deposits are indicated in figure 1.

Canada

Saskatchewan--The development of the vast potash deposits in the Devonian Prairie Evaporite formation in Saskatchewan and adjacent Alberta and Manitoba has been the most important event in the potash industry in the last three decades. Three main potash zones in this evaporite have been defined. Zone 1 (Esterhazy), the lowest, attains a maximum thickness of about 21 m and consists of a central sylvinite region surrounded by carnallite-rich mineralization. Zone 2, the Belle Plaine member, reaches a maximum thickness of 23 m with a central sylvinite region, but the center carnallite zone is narrower than in Zone 1. Zone 3, the Patience Lake member, is over 24 m thick, and the carnallite mineralization surrounding the sylvinite is narrower still. In general, the grade in all three zones increases toward the south from 20% to 30% K_2O and is comparable in all three. The depth of the Prairie Evaporite ranges from 660 m along its northern edge to 3,050 m at the international boundary.

Seven organizations operate 10 mines in Saskatchewan with an aggregate annual capacity of 8.0 mil-

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[1] In this manual the term "billion" is equivalent to 1,000 million.

TABLE 1. ASSESSMENT OF WORLD POTASH RESOURCES (MILLION TONS OF K_2O)[a]

Location	Reserves[b]	Other Resources	Total Resources
North America			
Canada	9,000	58,000	67,000
U.S.A.	180	5,260	5,440
Total	9,180	63,260	72,440
South America			
Chile	9	9	18
Peru	0	9	9
Brazil	45	225	270
Total	54	243	297
Europe			
France	35	145	180
Germany, Democratic Republic	270	4,260	4,530
Germany, Federal Republic	180	3,080	3,260
Italy	9	27	36
Spain	27	154	181
U.S.S.R.	1,800	43,500	45,300
United Kingdom	45	225	270
Total	2,366	51,391	53,757
Asia			
Israel and Jordan	218	870	1,088
China, Peoples Republic of	9	9	18
Laos	18	27	45
Thailand	55	9,015	9,070
Total	300	9,921	10,221
Africa			
Congo	0	180	180
Total	0	180	180
Oceania			
Australia	0	18	18
TOTAL	11,900	125,013	136,913

a. U.S. Bureau of Mines. 1978. "Potash," Mineral Commodity Profiles MCP-11, (Converted from short to metric tons).

b. At average 1976 domestic mine price.

lion tons. One of the mines is a solution mine; the others are shaft mines. Total resources may be 74 billion tons of K_2O, of which 18 billion tons may be economically recoverable--5 billion by conventional mining and 13 billion by solution mining (3, 6).

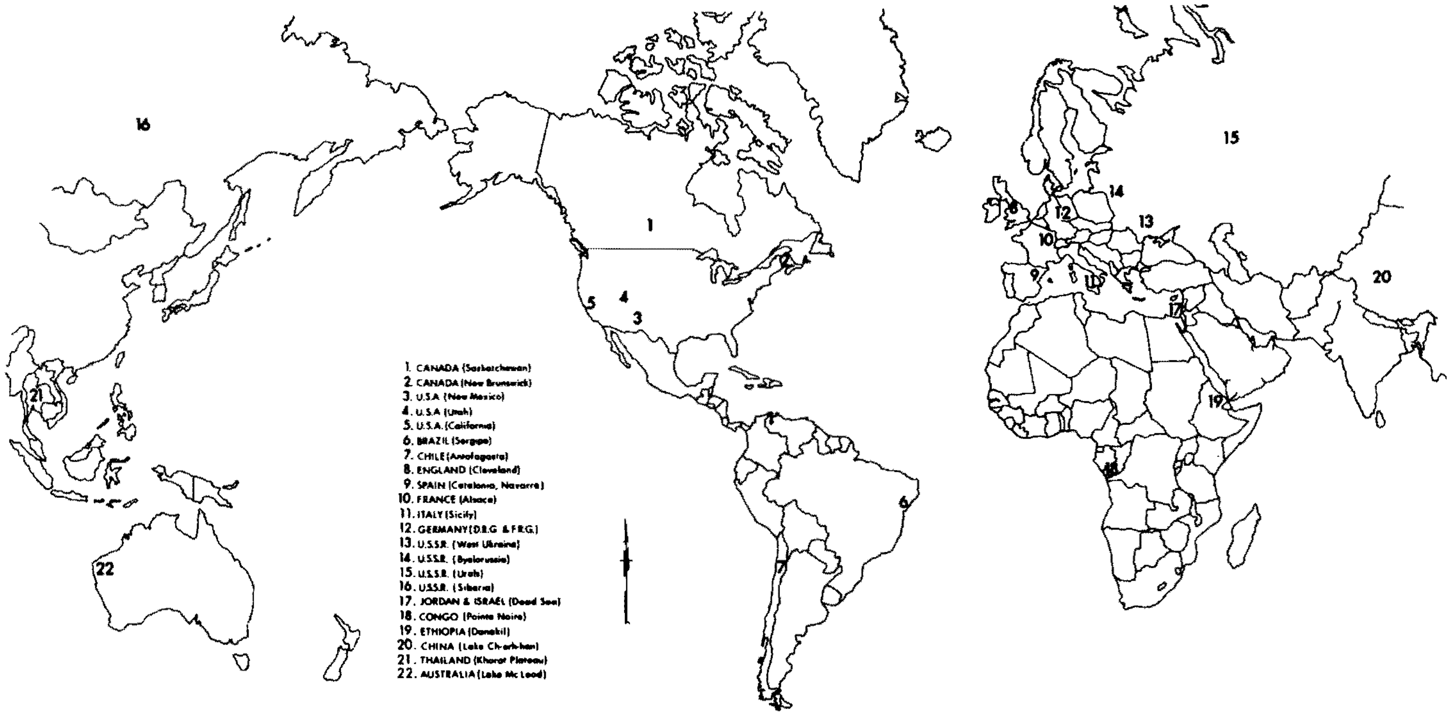
Maritime Provinces--The evaporite deposits of adjacent parts of Nova Scotia and New Brunswick have been known since the beginning of the 20th century; gypsum and rock salt have been mined for many years. Potash was discovered in the Nova Scotia salt deposits in 1919 and again in 1939, but the low grade and unfavorable mining conditions discouraged further interest. More intensive exploration started in 1965. Economic reserves have been found in an adjacent area of New Brunswick in the Moncton Basin at a depth of about 600 m. The potash zones range from 3 to 15 m in thickness, and the average grade is 21%-30% K_2O. One mine is currently (1979) under construction, and plans for a second mine and refinery have been announced. The combined capacity of these two projects is expected to be 2 million tpy or more of muriate of potash. A favorable factor is the location within 50 km of the deepwater seaport of St. John.

Potash deposits have also been found in Newfoundland, and exploration is expected to continue there and in Nova Scotia.

United States

North Dakota--The Prairie Evaporite formation underlies 20,700 km^2 of the North Dakota-Montana section of the Williston Basin at depths of 2,000-4,000 m. This is an extension of the Canadian deposits. The ore beds are thick and high grade, but the depth would require expensive solution mining. PPG Industries reported in 1976 that tests of the effectiveness of solution mining would be made at depths of 3,000-3,600 m which is about twice the depth of the Kalium solution mine in Canada. (Kalium is a subsidiary of PPG Industries.)

New Mexico--A sedimentary basin of Permian age covering some 104,000 km^2 in western Texas and southeastern New Mexico has been outlined by exploratory drilling. The most abundant mineral is polyhalite, but minable sylvinite occurs in the area around Carlsbad. At least 60 potash layers have been encountered, of which 11 ore zones are significant. The productive zones are located 250-610 m below the surface, dipping gently southeast, and are between 1.5 and 3 m thick in the mining area. The ores are sylvinite with more than 3% water-insoluble material and two mixed ore beds containing sylvite and langbeinite. Reserves are estimated to be about 85 million tons of K_2O.



Source: The World Bank.

Figure 1. World Major Potash Deposits.

Seven mines are in operation in New Mexico. Five recover only sylvite, one recovers only langbeinite, and one recovers both. The average grade of the ore is about 16% K_2O.

Utah--The Cane Creek potash deposits near Moab in southeast Utah lie at depths of around 1,200 m. The sylvinite horizon which is exploited is 3-4 m thick, and it contains 25%-30% K_2O. The formation is highly faulted and folded. It is estimated that reserves of 200 million tons of potash-bearing salts are present in a 31 km^2 area.

One mine is in operation in the area. It was originally a shaft mine, but because of difficulties caused by faulting, it was converted to a solution mine in 1972. Water pumped into the mine becomes saturated in 300-350 days and attains a temperature of 32°-33°C after which it is pumped into a series of evaporation ponds. A sodium and potassium chloride mixture is slurried from the ponds to the original refinery for recovery of potassium chloride.

The Great Salt Lake in Utah covers a variable area between 2,600 and 5,200 km^2. It is a remnant of ancient Lake Bonneville. The Bonneville Salt Flats in western Utah are another remnant of Lake Bonneville. They are a desert deposit of salt or mud flats impregnated with a saturated or nearly saturated brine. A 1-m top layer of hard-packed salt is underlain by a layer of fissured clay beneath which lies the brine. The brines which contain about 2.4% K_2O are pumped to evaporation ponds.

Two plants are in operation in this area. In one plant brine from the northern part of the Great Salt Lake is carried by canal to 7,000 ha of evaporation ponds. Sodium chloride, sodium sulfate, and a mixture of kainite, carnallite, and schoenite are successively crystallized. Schoenite is crystallized in settling tanks and converted to potassium sulfate.

In another operation brines in the Bonneville Salt Flats are recovered from a 35,000-ha area in about 145 km of ditches from which they are pumped into 3,000 ha of evaporation ponds. Following a short (about 3 months) evaporation season, sylvinite is trucked to a flotation plant. Standard potash and compacted granular muriate of potash are produced.

California--Searles Lake covers an area of about 104 km^2 and is a remnant of a much larger fresh water lake. Today, it is a mud and sand flat within which are two superimposed crystal bodies of mixed salts permeated with concentrated brines. The upper layer from which the potash is obtained averages 20 m thick and has a total area of 31 km^2. The upper brine contains about 8% K_2O. Muriate and sulfate of potash are produced together with nonfertilizer products.

Central America

Mexico--Potassium minerals have been reported in the Isthmus of Tehuantepec and the Yucatan Peninsula. Carnallite is the most prevalent, but sylvinite is also present. These deposits are not yet being mined, but exploration indicates that they may be economically promising.

South America

Brazil--The potash deposits of northeast Brazil are estimated to contain 500 million tons of sylvinite and 6 billion tons of carnallite at depths in excess of 550 m. Although plans have been announced for recovery of these deposits, near-term commercialization is hampered because of difficult access and its location.

Peru--Brine deposits have been located in the western half of the Sechura Desert Region of northern Peru. It is estimated that 30 billion tons of brines circulate in the desert sediments and that they contain 17 million tons of KCl and 146 million tons of $MgCl_2$. No plans for exploitation are currently under consideration.

Chile--The nitrate deposits of Chile are located on the plateau lying between the coastal range and the Andes, principally in the Atacama Desert in northern Chile. The deposits which vary in thickness from a few centimeters to several meters are patchy, poorly stratified layers of red-brown gravel cemented together with sodium nitrate and other soluble salts. Potassium salts, mainly nitrate, are recovered as a byproduct from sodium nitrate production. The composition and processing of the Chilean ore are described in more detail under the heading "Sodium Nitrate" in chapter VIII.

Africa

Congo--During the course of exploratory work in the Congo Basin between Pointe Noire and Brazzaville, an area of approximately 4.1 km^2 of salt and potash deposits was outlined in 10 evaporite cycles. Carnallite beds are regular and extensive with a cumulative thickness of up to 90 m. The zones are located around Holle-St. Paul where sylvinite occurs in three beds at relatively shallow depths (90-120 m) with K_2O contents at a range of 20%-35%. There are two beds containing sylvinite averaging about 20%-21% K_2O. Large-scale mining operations were started in 1969, but flooding of the mine has terminated production. There are no known plans to resume it.

Ethiopia--The evaporite deposits of the Danakil Depression contain substantial reserves of potash as sylvinite, carnallite, and kainite. In the area south of Dallol, the potash horizon has been found at 730 m. The prospected potash bed is 3-15 m thick and consists of sylvinite grading downward into carnallite, kieserite, polyhalite, and kainite. The deposit has not yet been exploited although several feasibility studies have been carried out in the last few years.

Morocco--The potash reserves in the Khemisset Basin extend over an area of more than 31 km^2. The principal ore is carnallite which occurs in two beds 1-10 m thick. There are also low-grade sylvinite deposits. No exploitation has yet taken place.

Middle East

Israel and Jordan--The Dead Sea lies between Israel and Jordan and now covers an area of about 700 km^2 to a maximum depth of 400 m. It is fed by the Jordan River and natural springs, but it has no outlet. The potassium resources of the Dead Sea are being exploited by Israel, and plans call for exploitation by Jordan also.

Solar evaporation is utilized to crystallize halite, followed by carnallite. The latter salt is harvested and converted to muriate of potash. Bromine is also recovered as a byproduct. The Dead Sea is estimated to contain over 1 billion tons of K_2O of which about 20% may be economically recoverable (3).

Pakistan--Pakistan possesses potential for potassium reserves, both in bedded salts and brine. The salt bed occurrences thus far reported are sporadic zones of sylvite and langbeinite in salt mines. The area of potash-rich beds is believed to include the greater part of the Salt Range and the Potwar and Indus Plains. The brine occurrences were discovered in the Punjab province during oil-drilling operations. The brine is hot and under great pressure and is saturated with carnallite. It contains about 7% KCl, 17% $MgCl_2$, 3% $CaCl_2$, 2% NaCl, and fractional percentages of boron and bromine compounds. Utilization of the brine to recover KCl and other soluble products has been proposed, but no definite plans have been made.

Europe

France--The Alsace potash occurrences lie in a faulted depression of about 210 km^2 between the Rhine River and the Vosges mountains. Two sylvinite beds are found in three separate basins. The Mulhouse Basin is a source of the present production where the beds are 400-1,100 m below the surface. The upper zone contains 20%-25% K_2O as sylvite 1-3 m thick, and the lower bed is 2-5 m thick with 15%-20% K_2O as sylvite. Total resources for the French deposits are estimated at about 300 million tons. The potash deposits also extend across the French border into the Buggingen district of Germany, but mining has now ceased in this area.

Federal Republic of Germany--In West Germany, the Kali und Salz mines the Zechstein deposits in the southern Werra district and the north German plain near Hannover. Kali-Chemie has a mine nearby at Friedrichshall where it mines hartsalz (a rock composed of sylvite, halite, anhydrite, and/or kieserite) at about 900 m depth. Muriate of potash and a 12% K_2O product, magnesia-kainite, are produced at Friedrichshall. All the mines of the Hannover region exploit the highly concentrated potash beds of salt domes in the Permian Zechstein evaporites.

No further changes are anticipated in the potash production capacity of this country in the next few years.

Democratic Republic of Germany--VEB Kombinatkali operates mines in four groups:

Kalibetrieb Werra
Kalibetrieb Zielitz
Kalibetrieb Sud-Harz
Kali und Steinsalzbetrieb Saale

Various ores are mined to produce muriate and sulfate of potash as well as kieserite and minor amounts of miscellaneous products. The total annual production is now slightly over 3 million tons of K_2O. In the early 1980s with the Zielitz mine operating at full capacity plus other minor expansions, the East German potash industry should have a capacity of nearly 4 million tons of K_2O (7).

England--All four Zechstein evaporite cycles have been found in the coastal areas between Durham and Scarborough and have been correlated with the German deposits. The evaporite beds thicken from the northwest and south to a central area around Whitby and Scarborough where the lower, middle, and upper evaporites occur. In the Whitby area sylvinite deposits occur at depths of 1,000-1,200 m and at 1,500 m. One mine is in operation at a depth of 1,160 m where the ore grade is 27% K_2O. The operation has been hampered by a badly faulted seam, but production is gradually increasing.

Denmark--Potash-bearing evaporite beds have been found to be up to 0.46 m thick in North Jutland at depths of 800-1,300 m.

Poland--The eastern extension of the Zechstein formation from Germany contains bedded potassium deposits in the vicinity of Klodawa. The known deposits contain low-grade (8% K_2O) carnallite ores that are 500-1,600 m in depth.

Spain--In Spain there are up to four potash beds which contain carnallite and sylvinite ore within the range of 15%-29% K_2O in the area between Barcelona and Pamplona. These mines are operated at depths of 300-500 m. Further west, the deposits are mined in an area south of Pamplona. These beds also consist of carnallite and sylvinite, but they are less faulted than those in the Catalonian field. Two potash beds occur in the Navarre district at depths of 130-650 m. The upper seam contains principally carnallite with an average grade of 14% K_2O. The grade of the sylvinite bed is 18%-20% K_2O. Four mines are in operation in Spain.

Italy--Potash deposits in Italy are found only in Sicily. It is one of the few areas of the world where kainite is the principal ore mineral although some sylvite and carnallite occur in the ore mined. The four mines in operation produce potassium sulfate and potassium-magnesium sulfate.

U.S.S.R.

In the U.S.S.R. potash is produced in three main regions: the north Urals, southern Byelorussia, and the western Ukraine. Sylvinite occurs in the first two of these regions, while both sylvinite and kainite are mined in the Ukraine. Muriate of potash is the principal product. Actual production in the U.S.S.R. in 1975 was 8.7 million tons of K_2O from the following sources:

Byelorussia	3.8
Urals	4.3
Ukraine	0.6

These three major projects will probably increase the Russian potash production significantly during the next 10-15 years.

The deposits near Stebnik and Kalush in the west Ukraine contain hartsalz, sylvinite, kainite, and langbeinite. These deposits are inclined, and mining in steeply dipping beds is common.

Additional potash deposits are present in east and south Russia. In Siberia, comparatively deep-bedded deposits are known at Irkutsk, Krasnoyarsk, and Yakutsk. Widespread mineralization exists north and east of the Caspian Sea, and several beds of potassium minerals have been found in salt deposits in Turkmenistan. Total resources are estimated at 45 billion tons of K_2O, of which about 1.8 billion tons is currently classified as reserves (3).

Asia

China--Potash has been recovered from salt lakes in China for several years, and production from underground mines began in the early 1960s. Potash is also recovered from underground brine seams and from sea salt operations. Over 3,000 salt lakes are found in northwest China in Tsinghai Province. Lake Cha-erh-han is one of the lakes from which potash is recovered. The brines which occur in Szechuan Province have been processed for many years to recover potash.

There are deposits of potash in west central China containing 10%-20% K_2O. These are currently being exploited.

Thailand--A potash deposit has been discovered in northwest Thailand extending into Laos. This deposit is essentially carnallite which lies at depths between 80 and 400 m. Sylvite is also present in some areas. Only a small area of the potential deposits has yet been explored, but it is believed that the deposits may be extensive. The deposit has been estimated to contain 10 billion tons of K_2O, of which 60 million has been classified as reserves (3).

Australia--Several extensive evaporite basins have been found in Australia. Lake McLeod in western Australia contains about 6.5 billion tons of rock salt below the dry surface of the lake. Underground water dissolves the salt and produces a saturated brine which contains 3% K_2O. Langbeinite was recovered from the brines in a plant that was recently destroyed by a typhoon. There are no known plans to rebuild it.

Mining

Potash is very largely extracted from underground deposits of sylvinite, primarily mixed crystals of potassium chloride and sodium chloride. The shaft-room-and-pillar method of mining is generally practiced. Long-wall mining is used in limited instances. Solution mining technology is well developed and is practical on a limited scale; the cost of energy required is the main deterrent. Shaft mining is generally practiced when the ore body is less than 1,300 m from the surface. At greater depths solution mining is necessary. Potash is also recovered in much lesser quantities from brines, such as those in the Great Salt Lake and the Dead Sea.

Shaft Mining

Shaft excavation and construction are generally conventional and costly. In Canada the Blairmore zone of high water pressure and unstable formations necessitated freezing the material to be removed before the shaft could be excavated and tubbed. Similar difficulties were experienced in Yorkshire.

The success of underground room-and-pillar mining is dependent on the character of the ore body; thick, flat beds are preferred. A thin sylvinite or other potash-bearing ore zone necessitates mining sodium chloride above and/or below the sylvinite, and this dilutes the ore grade. Equally difficult and expensive is a badly faulted mine, which also results in the excavation of an undue amount of debris in order to operate mobile equipment or to install conveyor belts.

The proportion of ore removed (rooms) during the initial mining depends upon mine depth, roof condition, and other factors. Primary mining often removes in the range of 40%-50% of the ore. Secondary mining can increase the removal to the 80%-90% range.

Ammonium nitrate and oil mixtures have virtually displaced dynamite as the blasting agent because they result in a substantial cost saving. Improved drill patterns increase the yield per charge and thereby further reduce cost. More recent installations use continuous mining machines having the capability of up to 5 tons of ore per minute.

Mechanical loaders gather the fragmented ore, whether dislodged by blasting or by continuous miners. Conveying from the mine face to the hoist shaft has traditionally been by railcars. Belt haulage is rapidly replacing rails, thus reducing labor and other costs, especially as the distances increase from mine face to hoist shaft. Mine maintenance and other underground services are usually rendered from facilities located underground. Working conditions, including temperature, freedom from harmful dust, utility services, and mechanization, are nearly ideal in most potash mines.

Ore storage and facilities for primary crushing to a maximum of about 15 cm are located at the hoist shaft. The crushed ore is automatically loaded into skips for hoisting to the surface.

Solution Mining

This method of mining involves the application of phase chemistry as well as large amounts of increasingly expensive energy. Techniques include investigations of the salt solution, brine flow, selective extraction of KCl from sylvinite, and control of cavity geometry. Advantages are reportedly that the method (1) avoids the construction of shafts which are also costly and (2) permits the mining of land or marine deposits without regard to overburden and at depths not feasible by shaft mining. With solution mining the preferred approach is to employ multiwells circulating the solvent between the wells. Most of the solution can take place from the cavern roof. Achieving a high level of dissolved potassium chloride per unit of solvent is the key to efficiency. One technique to assist in controlling contact of the brine with the potash ore is to inject diesel fuel to blanket the brine. Drilling costs for identifying the ore zone as well as for production holes are high; yet, solution mining is an established technology.

A hole is drilled to a level near the upper level of the potash strata and is then cased down to this level. A pipe is placed in the casing to a level below the lower level of the potash strata. An aqueous medium is pumped between casing and pipe to the potash bed where a cavity is established. When the cavities of two adjoining cased holes meet, water unsaturated with regard to potassium chloride and sodium chloride is added through one cased hole, and the saturated solution is withdrawn through the other. The concentration of the solution can be partially controlled by the rate of pumping which determines the retention time in the cavity, which can be very lengthy.

Brine Recovery

The recovery of potash from natural brines is practiced in a few locations, most notably the Dead Sea where the net evaporation rate is exceptionally high. At both the Dead Sea and the Great Salt Lake, brine is taken from that part of the lake where retention has been longest and, thus, the brine concentration is the highest. Brines can be accumulated from certain "dry" lakes by ditching and accumulating brines that move laterally through the soil to the ditches from which the brine can be pumped to solar evaporation ponds.

Beneficiating - Refining

Beneficiation of Sylvinite Ores

There are three principal methods of beneficiating sylvinite ores: flotation, heavy-media separation, and solution-crystallization (8).

Froth Flotation--This method of refining is the most widely practiced and the most economical method of recovering sylvite (KCl) from sylvinite, a mixture of potassium chloride and sodium chloride crystals with some attendant clay and clay slimes. Flotation, as the name suggests, is a method of floating off either the potassium chloride or the sodium chloride on a froth. Flotation of the potassium chloride is the preferred commercial method.

The steps in flotation of sylvite from sylvinite after the ore is hoisted include the following:

1. Crushing and classifying.
2. Adding a saturated brine of NaCl and KCl to produce a pulp containing 50%-75% solids.
3. Wet grinding the ore to a size that liberates the sylvite from the sodium chloride crystals. This size varies according to the size of the crystals.
4. Adding the chosen sylvite conditioning agents usually including an amine to make the potassium chloride more hydrophobic. A blinder is also added to depress slime flotation and an alcohol to act as a frothing agent.
5. Diluting with brine to 20%-25% solids.
6. Introducing the sylvite-containing brine into a series of rougher flotation cells, providing agitation and introducing air which adheres in the form of bubbles to the sylvite particles and causes them to float to the surface. The sylvite float is raked off mechanically from the top of the flotation cells. This flotation process in the rougher cells is repeated usually through five cells.
7. Harvesting the flotation concentrate from the top of the rougher cells. The concentrate contains some sodium chloride as well as a high percentage of the sylvite in the raw ore. For that reason it is introduced into a "cleaner" flotation circuit which further refines the sylvite. The unfloated particles from the cleaner circuit can be and usually are recycled to the rougher cells.
8. Drying the sylvite either in a rotary dryer or in a fluid bed dryer.
9. Screening the dried sylvite according to the sizes chosen to be marketed.
10. Compacting the offsize material from the screening operation. Screened-out fines are processed through a compactor which produces "flakes" of potash. These flakes are crushed to the desired size, and the fines and oversize are recycled to the process.

Both flotation and compaction involve the application of considerable chemistry and mechanics. There is, however, substantial art to achieving high recoveries, good production rates, and stable particles in each chosen size range of products.

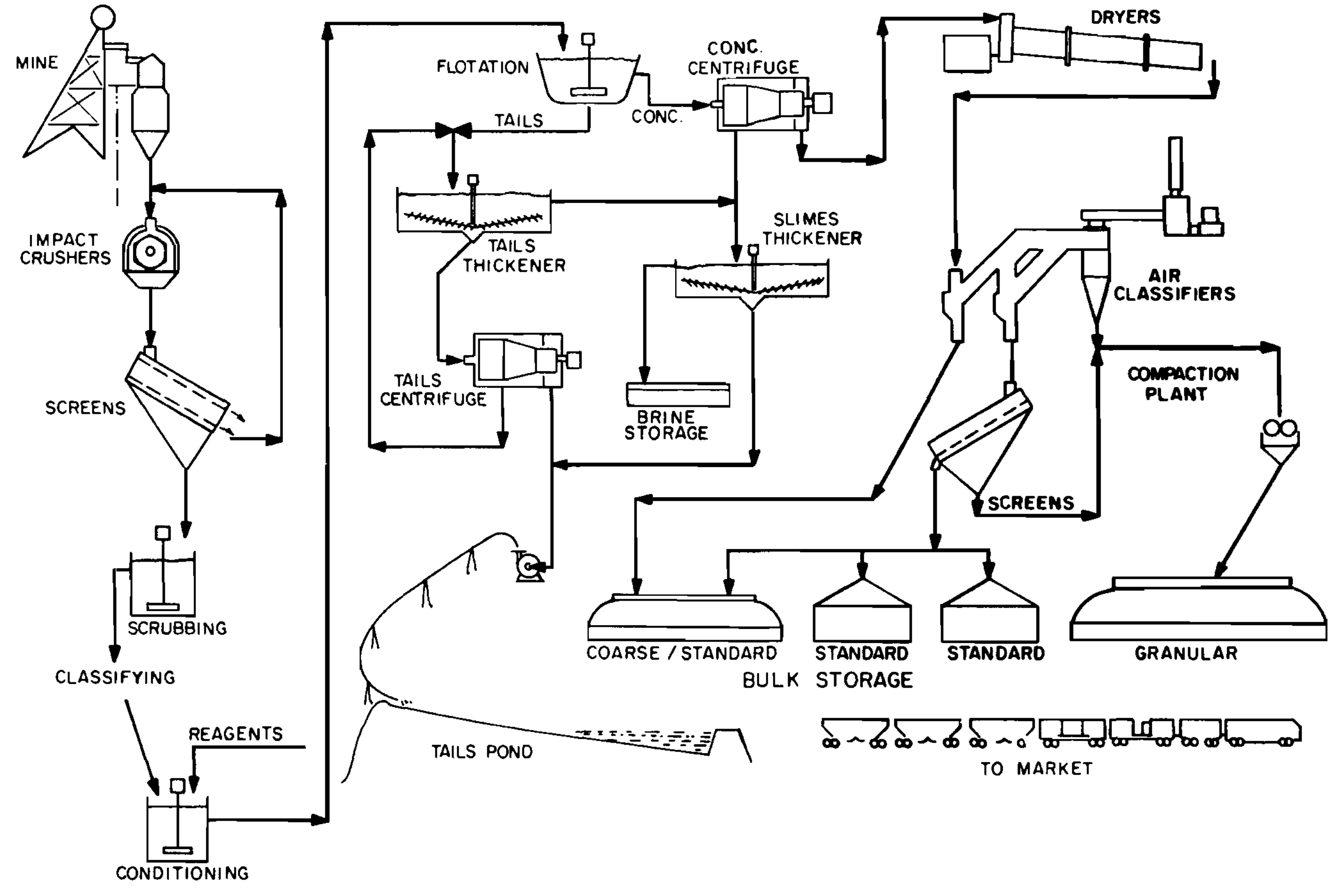
Beneficiation of sylvinite ores by flotation (figures 2 and 3) necessitates conditioning the ores with selective collectors and depressing agents before they enter the flotation cells. Amines are used to make potassium chloride more hydrophobic; a blinder is used to depress slime flotation; and an alcohol serves as a frothing agent.

A clay and slimes impurities range of 3.5%-4.0% requires more extensive mechanical desliming. Above this recoveries decrease, and this necessitates more equipment to recover slime-entrained sylvite.

Flotation techniques for removing insoluble slimes from potash ore can become complex. One arrangement is four flotation stages for insoluble flotation and one cell for potash rougher and cleaner flotation. Reagents for insoluble slime flotation can include Superfloe 127-Aero 870 at a rate of about 68 g of each reagent per ton of ore. Armeen TD at about 100 g and Barrett's oil 634 at about 45 g/ton can be used in potash rougher flotation while about 20 g each of Armeen TD and Barrett's oil 634 can be used in potash cleaner flotation. High insolubles removal is encouraged by recycling potash cleaner tails back to insoluble flotation.

Slimes have been removed from low-grade ores containing 5% water insolubles using nonionic or cationic polyacrylamide flocculants and cationic, anionic, and/or nonionic collectors. Subsequent potash flotation recovers a high percentage of the potash.

Heavy Media Beneficiation--This modification of the beneficiation technique is especially useful in preserving large potassium chloride crystals which may be classified without further processing to products for use in blended mixed fertilizers or for direct application (8). The process utilizes the difference in specific gravity of sylvite (KCl) and halite (NaCl). Halite is the more dense (specific gravity 2.13 versus 1.98 for sylvite); therefore, in a liquid of intermediate specific gravity, halite will sink and sylvite will float. U.S. patent No. 3,638,791 to International Minerals and Chemical Corp. describes this technique as "Ore beneficiation by treatment with a heavy media, e.g., an aqueous liquor and a very finely divided weighting agent, typically magnetite or ferrosilicon of minus 200-mesh. The efficiency of the magnetite separation operation is restored by treating the rinse liquor in a second hydrocyclone. The density of the rinse liquors is much less than the density of the ore constituents, and the ore constituents in the wash liquor report to the hydrocyclone underflow while the overflow comprises a suspension of the finely divided weighting



Source: Amax Chemical Corporation.

Figure 2. Simplified Flowsheet of Potash Refining System Using Flotation.

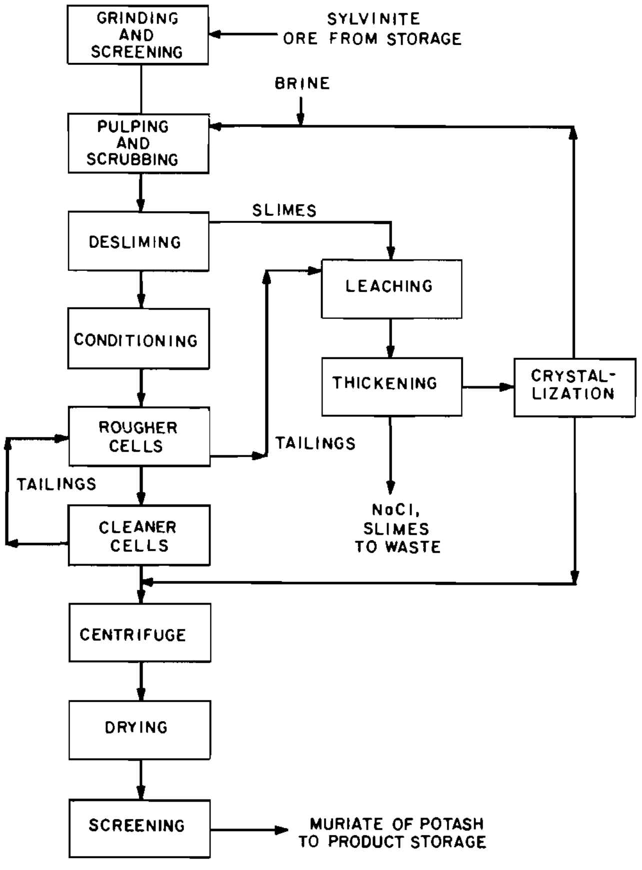


Figure 3. Diagram of Flotation Process for Recovery of Muriate of Potash.

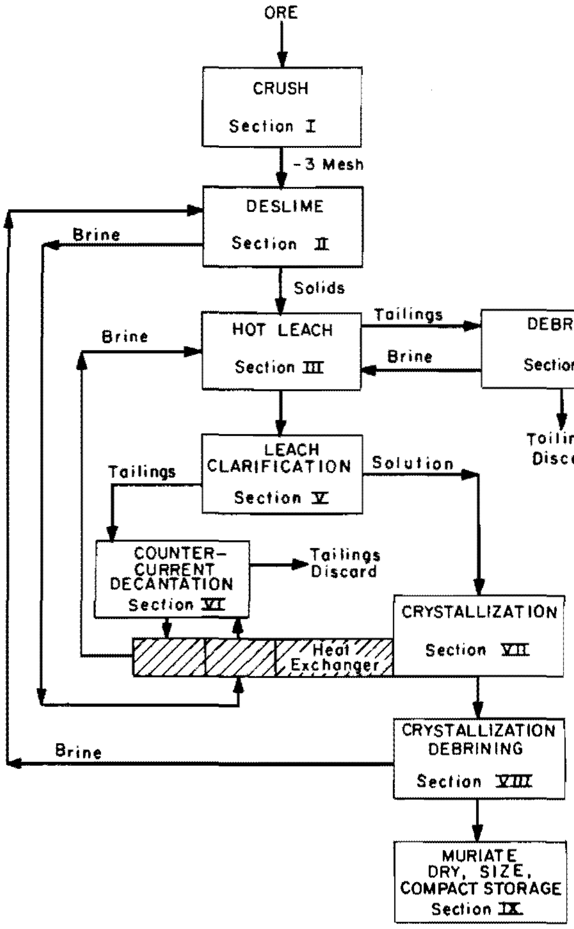
agent in the liquor. This liquor is suitable for separation in the magnetic separator at high efficiency. The underflow is treated to separate ore impurities from the weighting suspension. This may be accomplished by means of a fine screen."

Solution-Crystallization--Dissolution of the ore with recovery of KCl by crystallization is necessarily used in solution mining. It is also used to some extent for beneficiating shaft-mined ore. Its advantages are that it can utilize ores with a high percentage of insoluble materials such as clay, and it produces a high-grade (62%-63% K_2O) product that is fully soluble and hence suitable for use in liquid fertilizers. The beneficiation process is based on the solubilities of NaCl and KCl in hot and cold water which are:

	Solubility, g/100 ml of Water at 20°C	Solubility, g/100 ml of Water at 100°C
KCl	34.7	56.7
NaCl	35.4	39.1

The data shown above are the separate solubilities of KCl and NaCl. For solutions containing both salts, the solubility of NaCl decreases slightly as the temperature increases. Thus, when a brine that is saturated with both NaCl and KCl at 20°C is heated to 100°C, it is capable of dissolving substantial amounts of KCl but no NaCl.

Figure 4 shows a typical flow diagram of a solution-crystallization process. Sylvinite ore is crushed to minus 3-mesh and washed with a cool, saturated



Source: U.S. Bureau of Mines.

Figure 4. Diagram of Solution-Crystallization Process for Recovery of Muriate of Potash.

NaCl-KCl solution. Most of the clay is carried off in the solution to a desliming step where the clay is discarded as tailing. The clarified solution is then heated and used to dissolve the KCl from the washed ore. As mentioned earlier, NaCl is not soluble in the hot brine, and the undissolved NaCl is discarded as tailing. The brine is then cooled, crystallizing KCl which is separated from the brine, washed, and dried. The remaining brine is recycled. When a high-purity product for chemical use is desired, the crystalline KCl is redissolved and recrystallized to provide a double-refined product containing more than 99.9% KCl.

Electrostatic Beneficiation--This method of beneficiating potash utilizes mutual triboelectric charging of the salt components. This can be done by heating the material to 300°-700°C, followed by cooling to 100°-200°C, or by treatment with specific conditioning agents. These agents selectively alter the electrical properties of the individual minerals to separate one or more components from a salt mixture. Preferred agents are aliphatic and aromatic monocarboxylic acids, ammonium salts, or aliphatic monocarboxylic acids. The raw material is ground, conditioned, and treated in a heating apparatus with air of a specific moisture content and simultaneously triboelectrically charged by friction. A charged residue and a preconcentrate are obtained in the preseparator.

Beneficiation of Carnallite Ores and Brines

Carnallite ore is the source of a small percentage of the world's potash supply even though there are large deposits of such ores in many regions. One disadvantage of carnallite ores is their low grade; even pure carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) contains only 17% K_2O. A second disadvantage is that dissolution and recrystallization methods must be used which are energy intensive. A third disadvantage is the large volume of byproduct magnesium chloride solution which is likely to pose a difficult disposal problem. The magnesium chloride can be hydrolyzed to magnesium oxide at elevated temperatures.

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

Magnesium oxide is useful as a material for manufacture of refractories and other purposes, but disposal of HCl is another problem.

In spite of its disadvantages, ores or brines containing carnallite are processed to recover KCl in several countries including Spain, Israel, and East and West Germany and may be utilized in the future in developing countries such as Brazil, Thailand, Congo, Jordan, and Pakistan.

Processing methods vary widely and depend on what accessory minerals are associated with the carnallite. Halite (NaCl) is a common accessory mineral, and there are various other combinations as mentioned in the preceding description of world potash deposits. Because of the wide variety of carnallite-containing ores, no attempt will be made to describe any specific beneficiation process in detail. A recent article summarizes methods for treating carnallite ores (9).

There are two general types of processes: cold leach and hot leach. Cold leach processes are carried out at 20°-25°C. Carnallite ore, which usually contains some NaCl, is leached with water or dilute brine which dissolves $MgCl_2$ preferentially. Actually, KCl dissolves and reprecipitates as the $MgCl_2$ content of the solution increases. The rates of dissolution and recrystallization affect the size of the crystals; relatively coarse crystals which may be separated from the $MgCl_2$ solution by centrifuging are preferred. If the ore contains insoluble material such as clay, it remains in suspension in the solution. The mixture of NaCl and KCl crystals may be separated by either of two previously described methods that are used for refining sylvinite--by flotation or by a hot leach which dissolves the KCl preferentially. The $MgCl_2$ solution is clarified and then evaporated to a high concentration to recover potash by crystallizing carnallite which is recycled. The $MgCl_2$ solution can then be discarded or utilized.

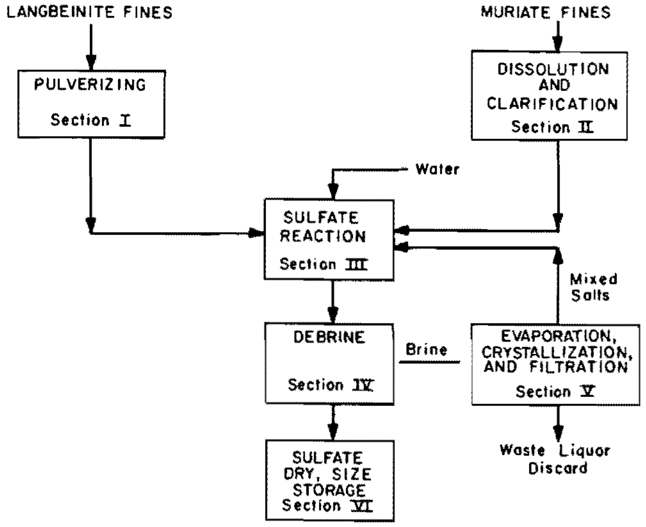
Alternatively, carnallite ores may be treated by a hot leach at about 100°C which dissolves both $MgCl_2$ and KCl and also any NaCl that may be present. The hot solution is clarified to remove solid impurities and then cooled and evaporated; after the KCl and NaCl crystals are recovered, one of the above-described separation techniques is employed. Part of the mother liquor, which has a high $MgCl_2$ content, is diluted, heated, and returned to the hot leach step. The remaining mother liquor is evaporated further to recover the remaining KCl as carnallite and then discarded.

The Dead Sea brine typically contains 11.5 g/liter of KCl. The concentration of the other salts in grams/liter is $MgCl_2$, 130; NaCl, 87; $CaCl_2$, 37; and $MgBr_2$, 5. At the Dead Sea Works in Israel, brine from the sea is first fed into large shallow ponds covering about 155 km^2 where the brine is concentrated by solar evaporation until about 90% of the NaCl crystallizes. The brine is then transferred to a second series of evaporation ponds where the carnallite crystallizes and is recovered by dredging. The brine is then pumped as a slurry to the refinery. The carnallite slurry is treated by a cold leach process similar to that described above to separate KCl and NaCl from the brine. Both flotation and hot leach processes are used to separate NaCl from KCl. The KCl is dried and marketed in several grades differing mainly in particle size; all grades contain 60%-61% KCl. The grades are granular (compacted), coarse (crystalline), "standard," "fine," and "highly soluble."

The firm also markets table salt, industrial salt (NaCl), and bromine compounds. Part of the brine remaining which contains $MgCl_2$ and $CaCl_2$ is used to produce HCl for phosphoric acid production and refractory grade MgO, and part of it is returned to the Dead Sea.

Beneficiation and Utilization of Sulfate Ores

Langbeinite--Langbeinite ($K_2SO_4 \cdot 2MgSO_4$) is separated from sylvite and halite by selective washing, froth flotation, or heavy media. The langbeinite may be marketed as such as a source of K, Mg, and S, or it may be converted to other products. Potassium sulfate is produced by reacting one molecule of langbeinite with four molecules of muriate of potash (figure 5).



Note: Langbeinite and muriate fines are concentrate products from the langbeinite leach and sylvite flotation circuits.

Source: U.S. Bureau of Mines.

Figure 5. Diagram of Process for Production of Potassium Sulfate from Langbeinite and Muriate of Potash.

Potassium magnesium sulfate is produced by refining langbeinite. The reaction to produce potassium sulfate from langbeinite is:

$$(1)\quad \underset{\text{langbeinite}}{K_2SO_4 \cdot 2MgSO_4} + \underset{\text{mur. of potash}}{4\ KCl} \rightarrow \underset{\text{potassium sulfate}}{3K_2SO_4} + \underset{\text{magnesium chloride}}{2MgCl_2^{*}}$$

$$(2)\quad \underset{\text{langbeinite}}{2(K_2SO_4 \cdot 2MgSO_4)} + \underset{\text{mur. of potash}}{2KCl} \rightarrow \underset{\text{potas. magnesium sulfate}}{3(K_2SO_4 \cdot MgSO_4)} + \underset{\text{mag. chloride}}{MgCl_2}$$

---

*Discarded.

For each 100 tons of potassium sulfate

56.7 tons of muriate of potash is required for 100% conversion

70.9 tons of muriate of potash is required for 80% conversion

79.3 tons of potassium-magnesium sulfate is required for 100% conversion

99.1 tons of potassium-magnesium sulfate is required for 80% conversion

Alunite--Alunite [$K_2 \cdot Al_6(OH)_{12} \cdot (SO_4)_4$] is a potential source of potassium sulfate, alumina, and sulfur dioxide byproduct. The economics of its production hinges on the value of the alumina. Technology has been developed in the U.S.S.R. (10, 11). A major operation utilizing a large alunite deposit in southwestern Utah has been intensively investigated technically and economically without reaching any satisfactory solution to date, mainly because of the lower cost of alumina from Australia.

It was proposed that the alunite ore would be mined in an open pit operation. The ore, after it has been stockpiled, would be crushed to minus 2-mm size before drying and further grinding of the ore that is coarser than 14-mesh. This would be roasted to convert the potassium to a salt soluble in water or dilute alkali. Leaching would follow to recover potassium sulfate solution. Washed, filtered solids would be transferred to a Bayer-type plant for alumina recovery.

In a Bayer alumina plant, the filtered solids are digested with caustic soda to dissolve alumina. Alumina is precipitated as aluminum hydrate followed by calcining. To recover sulfuric acid from the sulfur dioxide stream, a double absorption acid plant is installed. The sulfuric acid can be used in the manufacture of the concentrated phosphates or other products using massive quantities of sulfuric acid.

Production of 1 million tpy of alumina (Al_2O_3) would require about 10 million tons of alunite ore and would yield about 500,000 tons of potassium sulfate and nearly 800,000 tpy of sulfuric acid. The magnitude of the coproducts tends to limit the potential for the production of alumina from alunite.

Complex Sulfate Ores--Complex mixtures of potash ores have been successfully beneficiated in Russia (10, 11). These ores may contain any or all of the following minerals: anhydrite, epsomite, halite, kainite, kieserite, langbeinite, polyhalite, and sylvite, along with clay. Extraction of potassium salts from such ores becomes quite complicated because the mineralogical forms of the various components are unstable, and the chemical composition of the group as a whole varies considerably. The process used to extract the ore depends upon the various proportions of the different minerals present. For example, whenever potassium sulfate is the desired product, free sylvite and kainite must be present in the same molecular proportions or the potassium chloride must be added if there is an excess of kainite. Ideally, the reaction is:

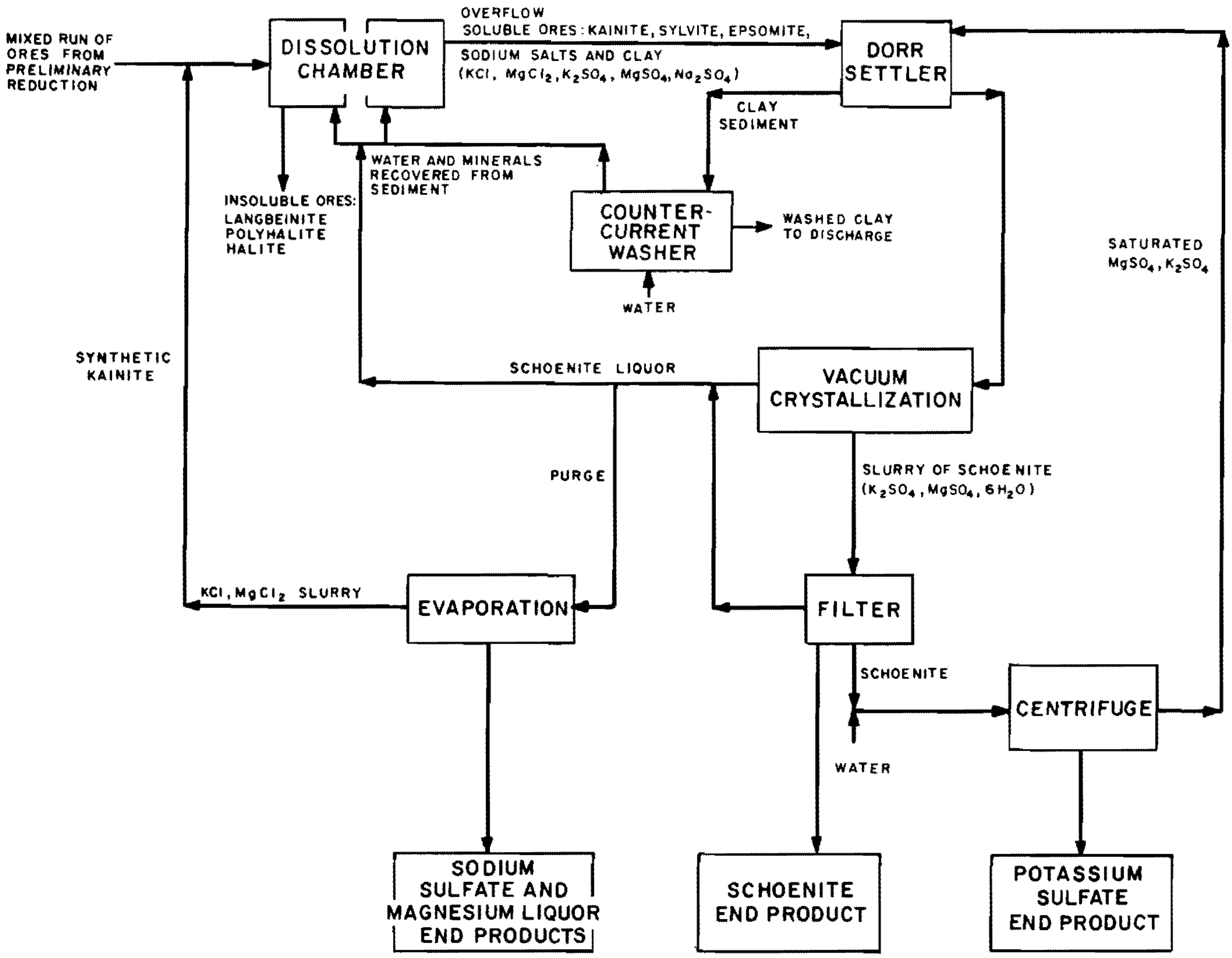
$$KCl + KCl \cdot MgSO_4 \cdot 3H_2O \rightarrow K_2SO_4 + MgCl_2 + 3H_2O$$

When the ore is deficient in sylvite, schoenite is produced.

$$\underset{\text{(kainite)}}{2KCl \cdot MgSO_4 \cdot 3H_2O} \rightarrow \underset{\text{(schoenite)}}{K_2SO_4 \cdot MgSO_4 \cdot 6H_2O} + MgCl_2$$

(In both equations above the interaction of the solvent has been omitted.) Thus, the product varies between potassium sulfate and schoenite according to the composition of the ore.

A new method for extracting potassium compounds from Carpathian ores that contain several minerals is being extensively tested on an industrial scale at Kalush. A flowsheet of the process is shown in figure 6. In this process natural ore containing about 9% potassium is ground and leached in two steps, with a hot "synthetic kainite" solution (described later) in dissolving tanks. The leach dissolves epsomite, kai-



Source: Phosphorus and Potassium, 59, 1972.

Figure 6. Flowsheet for the Processing of Carpathian Polymineral Ores.

nite, and sylvite as well as any other readily soluble mineral, but langbeinite, halite, and polyhalite are practically insoluble in this liquor. If the ore contains significant quantities of langbeinite and polyhalite, then the residue from the leaching process should be treated to recover them. The ore as mined normally contains about 15% clay which remains suspended in the hot leach liquor until it is clarified in Dorr settling tanks. As the liquor begins to cool, potassium salts begin to crystallize out. Normally, potassium chloride and sodium chloride would precipitate first, but since the desired product is schoenite, the precipitation of these chlorides is inhibited by the addition of a solution that is saturated with magnesium and potassium sulfate. (This solution is obtained from the later decomposition of part of the schoenite to form relatively pure potassium sulfate.) This, in effect, leaves a solution that is saturated with respect to schoenite but unsaturated with respect to the chlorides. Under these circumstances, only schoenite will precipitate.

$$2KCl + 2MgSO_4 + 6H_2O \rightarrow K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O + MgCl_2$$

The clarified liquor, plus the added sulfate solution, is cooled in a vacuum crystallizer to 20°C. The schoenite so formed is thickened and filtered. Part of the filtered schoenite is mixed with water to produce potassium sulfate according to the reaction:

$$K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O \rightarrow K_2SO_4 + MgSO_4 + 6H_2O$$

The potassium sulfate is removed as an end product by centrifugation, and the hot liquor is recycled to the settling tanks.

The thickened slime from the settling tanks contains salty clay which is washed with a countercurrent flow of water in a washer to minimize losses of potassium. This washing liquor along with the filtrate from the schoenite filtration is sent to the dissolving tanks to act as a solvent for the original ore.

During the conversion of kainite to schoenite (second equation above), magnesium chloride is also formed. If the concentration of this magnesium chloride were allowed to increase indefinitely, the process would not function properly. To circumvent this problem, a part of the schoenite filtrate is withdrawn and sent to an evaporator where enough of both sodium and potassium are removed to maintain a constant concentration of these materials in the system. The remaining slurry is recycled to the dissolving tanks as "synthetic kainite." The concentrated magnesium chloride liquor is used to make products that require magnesium.

This process permits the use of Carpathian ores to produce several commercially valuable products, such as potassium sulfate, potassium-magnesium sulfate, potassium chloride, sodium sulfate, and magnesium chloride liquors.

Production of Potassium Sulfate by Thermal Processes

Mannheim Process

This process for the manufacture of potassium sulfate from potassium chloride and sulfuric acid involves a two-stage reaction. The following first reaction is exothermic:

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl$$

However, the second reaction is endothermic:

$$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl$$

The first reaction proceeds at a relatively low temperature to produce potassium bisulfate ($KHSO_4$) which is heated in a Mannheim furnace to complete the second reaction. The process is used in Belgium and the United States.

Hargreaves Process

In this process, the finely ground potassium chloride is briquetted, dried, screened, and then charged into a conversion chamber. Hot sulfur dioxide from a sulfur burner flows into the chamber together with enough excess air and water vapor to complete the reaction which is:

$$4KCl + 2SO_2 + O_2 + 2H_2O \rightarrow 2K_2SO_4 + 4HCl$$

In practice, the gas flows through a series of conversion chambers which are charged and discharged batchwise. The flow of the SO_2-containing gas is such that it first contacts a converter in which the potash has most nearly been converted to K_2SO_4, and the gas lastly flows through a converter containing a fresh charge of KCl briquettes.

HCl Utilization

Both the Mannheim and Hargreaves processes produce byproduct hydrochloric acid which must be utilized or disposed of. In Belgium the HCl is used to make dicalcium phosphate by reaction with phosphate rock followed by neutralization with limestone or lime (see chapter XVI). A $CaCl_2$ solution is a byproduct of this reaction and may pose a disposal problem. In the United States the principal use for the byproduct HCl is for acidulating oil wells to increase oil recovery. The K_2SO_4 plant may be built in an oil field to minimize transportation of HCl. Other possible fertilizer-related uses for HCl are to produce ammonium chloride (see chapter VIII) or to produce phosphoric acid by a solvent extraction process (see chapter XIII).

Uses of Potassium Sulfate

The sulfate or other nonchloride forms of potash are preferred for fertilizing certain crops for which the quality may be adversely affected by chloride. Examples are tobacco, potatoes (in some cases), and grapes. Also nonchloride potash sources are needed in areas where chloride accumulation in the soil is a problem as in the Netherlands or in many arid regions where chloride salts in irrigation water accumulate in the soil. Potassium sulfate may be preferred because of its sulfur content where soils are deficient in both potassium and sulfur.

Production of Potassium Nitrate[2]

Southwest Potash Process

Potassium chloride is slurried with 65% nitric acid which has been previously chilled to prevent a reaction occurring before the slurry is fed into the reactor (figure 7) (12). In the reactor, which operates at about 25 psig (1.76 kg/cm²), the slurry is heated with nitric acid vapor to about 75°C, whereupon reaction takes place, according to the following equation:

$$3KCl + 4HNO_3 \rightarrow 3KNO_3 + Cl_2 + NOCl + 2H_2O$$

Some 90% of the chlorine is removed in gaseous form. Because of the extreme corrosiveness prevailing

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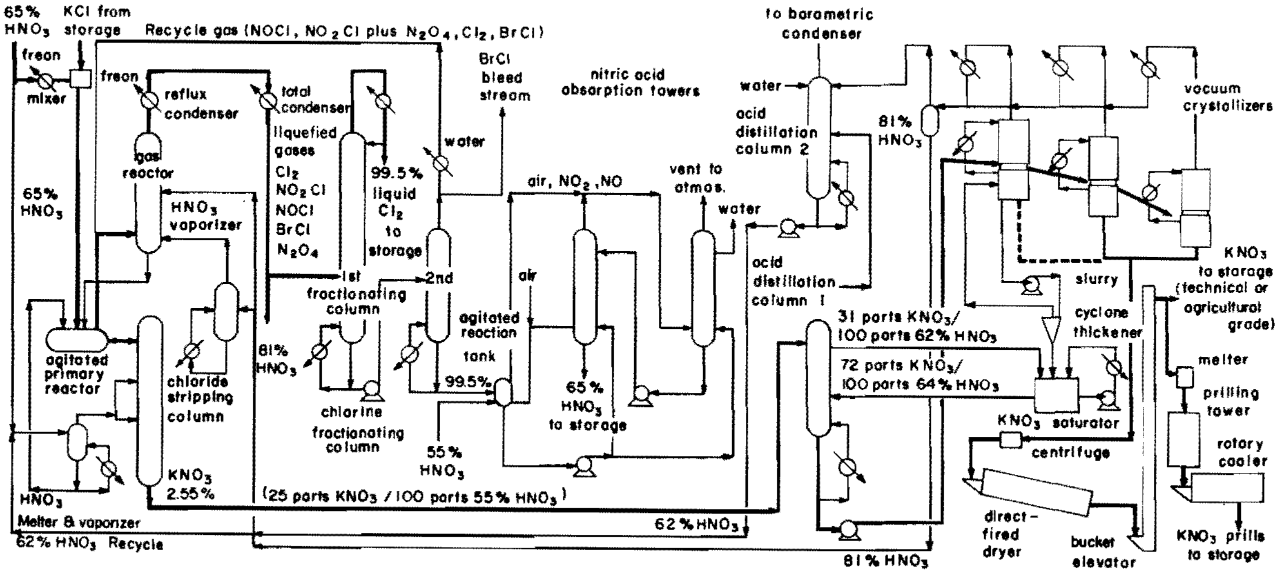
[2] This section has been abstracted from Phosphorus and Potassium, volume 52, with the permission of the British Sulphur Corporation (12).



Source: Phosphorus and Potassium, 52, March/April, 1971.

Figure 7. Flow Diagram of Southwest Potash Process for Production of Potassium Nitrate.

in the reactor, this vessel, which is in fact an agitated autoclave, has to be fabricated from titanium and lined with acid-resistant brick.

The solution from the reactor flows to the chloride-stripping column where it is heated with more nitric acid vapor to its boiling point of around 150°C. This treatment takes the reaction to completion and gives rise to a stripped solution containing less than 10 ppm of chlorine. For this degree of completion to be obtained, it is necessary to maintain an excess of nitric acid corresponding to a concentration of 55% in the solution.

The gaseous mixture, containing nitrosyl chloride and chlorine, coming from the agitated reactor, is oxidized in the gas reactor by means of hot nitric acid at a concentration of at least 80% at 150°C. The reaction which takes place yields nitrogen dioxide and more chlorine as follows:

$$NOCl + 2HNO_3 \rightarrow \tfrac{1}{2}Cl_2 + 3NO_2 + H_2O$$

Water formed in the oxidation is condensed and fed to the primary reactor. The chlorine and nitrogen dioxide are separated into liquid products; the chlorine is fed to storage, while the nitrogen dioxide is oxidized with air and absorbed in water to produce 65% nitric acid. This oxidation step is characterized by the following chemical equation:

$$2NO_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2HNO_3$$

The overall reaction through the process is given by:

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \rightarrow 2KNO_3 + Cl_2 + H_2O$$

In the gas section of the process, two distillation columns are used to separate the pure chlorine from pure nitrogen dioxide. Chlorine is removed from the top of the first column and nitrogen dioxide from the bottom of the second column while in the wet section the potassium nitrate-nitric acid solution is concentrated in the acid distillation column. It has been practical to concentrate the solution up to 81% nitric acid; the weak acid vapors in the overhead fraction are subsequently concentrated to around 62% HNO_3 in a second distillation column. Bottoms from the first acid distillation column are fed to a battery of vacuum crystallizers where potassium nitrate is precipitated and separated by a centrifuge. The product is dried and may be stored direct or melted and prilled at 340°-350°C in a 35-ft (10.7-m) tower. Both technical grade (99.3%) and an agricultural grade (99%) potassium nitrate are produced for the process.

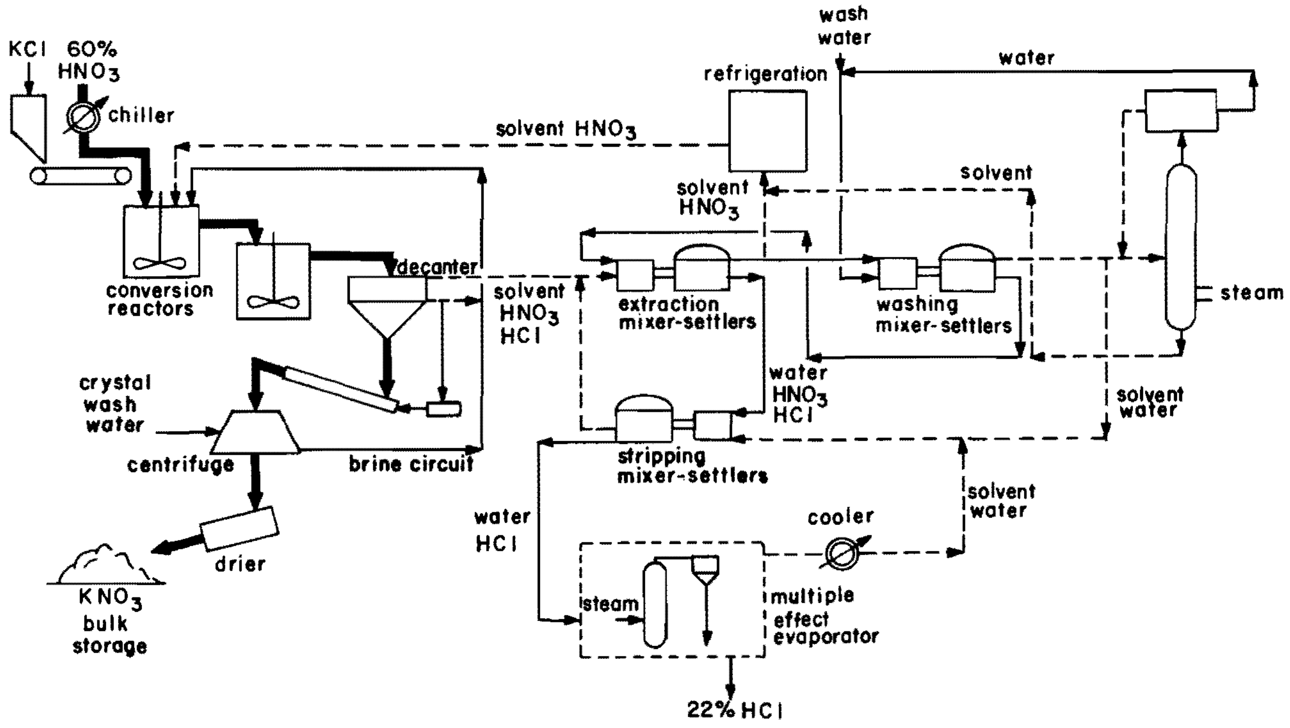
IMI Process

The alternative to a high-temperature, distillation-based process for manufacturing potassium nitrate by direct acid attack is solvent extraction at relatively low temperature. At low temperatures, the potassium nitrate formation reaction proceeds, with the aid of solvent extraction and with no side reactions occurring, according to the equation:

$$KCl + HNO_3 \rightarrow KNO_3 + HCl$$

In this way the solvent extraction route obviates some of the intense corrosion problems which are an inherent feature of the process previously described. However, solvent extraction installations, with the associated regeneration facilities, are fairly expensive; thus, the economic advantage of reduced corrosion is at least partially offset.

In this process developed by Israel Mining Industries, potassium chloride, together with stoichiometric quantities of chilled 60%-70% nitric acid, is fed into the first of a series of conversion reactors at 5°-10°C (figure 8). Recycled brine and solvent are also added. The reaction between potassium chloride and nitric acid is, under normal circumstances, reversible, but in this case because of the presence of solvent, the reaction goes almost entirely to completion. Potassium nitrate is produced in the solid phase. Both hydrochloric acid and the unreacted nitric acid dissolve into the solvent phase and are removed, while



Source: Phosphorus and Potassium, 52, March/April, 1971.

Figure 8. Flow Diagram of IMI Process for Production of Potassium Nitrate.

the potassium nitrate crystals are separated, by decantation and centrifugation, and dried for storage. Part of the product is melted and prilled.

The remainder of the process is concerned with the treatment of the solvent phase to recover hydrochloric acid of reasonable purity and to recycle the solvent-nitric acid mixture to the reactor system. Both hydrochloric and nitric acids are soluble in the solvent, but fortunately the distribution coefficients differ sufficiently for the hydrochloric acid to be removed separately in a countercurrent liquid-liquid extraction system. The hydrochloric acid is utilized to produce phosphoric acid by the IMI solvent extraction process as described in chapter XIII.

Other Processes

Potassium nitrate may be recovered as a coproduct in certain nitrophosphate processes as described in chapter XV.

Waste Disposal

The beneficiation of sylvinite results in byproduct sodium chloride containing a small amount of potassium chloride. The waste product slurry usually is pumped to a storage area bounded by an earthen retaining wall to solidify gradually as the entrained water evaporates. A few mines are located where the slurry can be pumped to an ocean or river. The latter disposal method is coming under increasing environmental criticism and banning. The refining of other potash ores incurs other byproduct salts that are treated similarly. If sufficient solid, level land is available near the refinery, the cost of containment is not excessive. However, suitable land is not always available, and this presents a serious problem. Also, the net evaporation rate differs with salts, and this affects the time required for solidification.

Carnallite byproduct liquor contains primarily $MgCl_2$. One ton of carnallite ore produces 0.3-0.5 m^3 of brine. Byproduct liquors from potassium sulfate production also contain largely $MgCl_2$. Utilization of $MgCl_2$ by hydrolysis and calcination is practiced in Israel. The reaction is:

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

The MgO is useful for production of refractories, and the HCl is used to produce phosphoric acid by the IMI solvent extraction process.

Chemical Grade Potash

Chemical grade potash, a highly refined potassium chloride, is used almost entirely in the production of chlorine and potassium hydroxide (KOH), commonly called caustic potash.

High purity of chemical grade potash is important for at least three reasons:

1. Certain unacceptable impurities in the chemical grade potassium chloride are carried forward in the process into the caustic potash.
2. Efficiency of caustic potash manufacture in an electrolytic cell is impaired by undue presence of diluents.
3. Presence of heavy metals causes release of hydrogen in the electrolytic cells in the presence of chlorine, giving rise to the formation of explosive mixtures.

Refinement of muriate of potash to produce the chemical grade is achieved by redissolving and recrystallizing an already crystallized potassium chloride.

Most chemical-grade potash is used in the production of potassium hydroxide (KOH). The process entails electrolysis of a KCl brine to yield KOH and chlorine. The main use of caustic potash is in the manufacture of liquid soaps which are becoming increasingly popular. Other uses are in textile operations, greases, catalysts, engraving, alkaline batteries, and rubber fabrication. In addition to direct use of caustic potash in liquid soaps or other products, a substantial tonnage is used in the production of potassium carbonate (K_2CO_3) and other potassium compounds. More than half of the potassium carbonate is used in glass manufacture. Some potassium carbonate is carbonated further to form potassium bicarbonate, $KHCO_3$, used largely in foods and medicine. KOH is also used to make potassium phosphates for use in specialty fertilizers.

About 4% of the world potassium consumption is for industrial applications, as follows:

Detergents and soaps	35%
Glass and ceramics	25%
Textiles and dyes	20%
Chemicals and drugs	13%
Other	7%
	100%

Refined potassium chloride is shipped in bags or in bulk form in modified hopper cars called sparger or solution cars. Anticaking agents are not added to chemical-grade KCl since they may cause explosions in the electrolytic cells. With a sparger car the chemical-grade potassium chloride is slurried out of the car, and with a solution car it is fully dissolved and pumped out of the car. Table 2 gives the product characteristics of a typical chemical-grade potassium chloride. Note that it is guaranteed to contain a minimum of 99.9% KCl.

TABLE 2. POTASSIUM CHLORIDE (CHEMICAL GRADE)

Component	Unit	Guaranteed	Typical
KCl	%	99.9 (min.)	99.92
K_2O	%	63.12 (min.)	63.13
H_2O (@ 105°C)	%	0.07 (max.)	0.02
H_2O (@ 700°C)	%	0.67 (max.)	0.30
Water insoluble	ppm	75 (max.)	12
Acid insoluble	ppm	75 (max.)	8
Sodium, Na	ppm	150 (max.)	100
Bromine, Br	ppm	700 I(max.)	600
Sulfate, SO_4	ppm	10 (max.)	5
Calcium, Ca	ppm	10 (max.)	
Calcium and Magnesium, Mg	ppm	30 (max.)	
Iron, Fe	ppm	5 (max.)	2
Lead, Pb	ppm	3 (max.)	0.5
Copper, Cu	ppm	0.5 (max.)	0.05
Nickel, Ni	ppm	0.5 (max.)	0.05
Chromium, Cr	ppm	0.1 (max.)	0.01
Molybdenum, Mo	ppm	0.1 (max.)	0.01
Vanadium, V	ppm	0.1 (max.)	0.01
Titanium, Ti	ppm	nil (max.)	0.01

Bulk Density, Loose--1,041 kg/m^3

Color - White

Potash Particle Size

During much of the history of potash production in Europe and North America, particle size was of little consequence. Each company shipped for agricultural purposes the size range most easily produced, approximating what is now classified as "standard" grade (13). Agricultural potash was then either applied as a straight material or used in production of "pulverized" or later "ammoniated" nongranular compound fertilizers. In the early 1950s when granulation of compound fertilizers was being developed in the United States and the initial equipment proved to be sized too small, Southwest Potash Corporation introduced "coarse" grade as an aid to granulation. Coarse potash is now offered by most North American producers; its particle size is mainly between 0.8 and 2.0 mm. The use of larger particle size muriate of potash did assist in the agglomeration wanted and thereby reduced the recycle of particles finer than the bottom size screen being used. This practice led to increased production rates in many plants with undersized equipment. Granulation units installed during the latter 1950s or later in Europe, the United States, Japan, and other countries were better engineered with respect to incorporating "standard" grade potash materials into granular compound fertilizers.

The advent of "bulk blending" in about 1960 led to the introduction of "granular" materials. This trend was fostered by the introduction of granular diammonium phosphate, largely in the 6- to 14-Tyler mesh (1.2- to 3.3-mm) range. As the trend to bulk blending in small plants located in immediate consuming areas developed, the demand for large particle size materials increased similarly. Bulk blending is most commonly practiced in the United States and Canada, but its use is growing in Latin America and some other regions. Granular potash is also preferred for direct application.

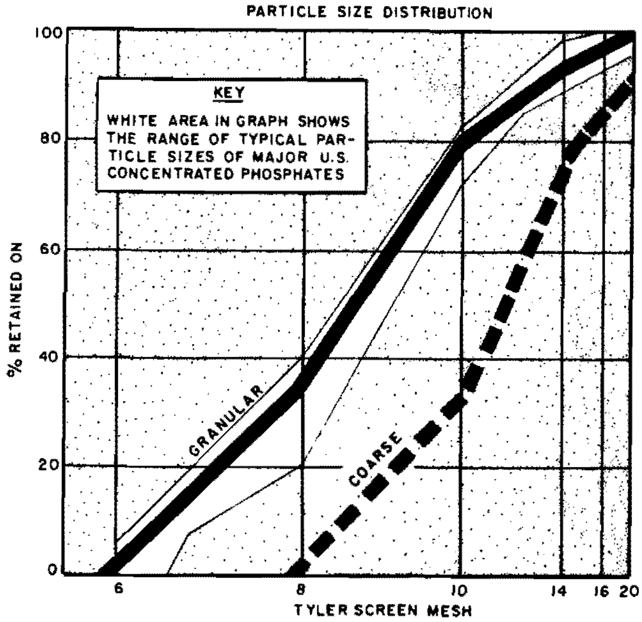
Both "coarse" and "granular" grades of potash are used by bulk blenders. However, the "coarse" grade does not match well the particle size of nitrogen and phosphate materials commonly used in bulk blending, leading to unsatisfactory analysis control of bulk-blend mixtures (see chapter XXII).

Gradually the potash industry, in North America especially, is increasing its granular grade compaction capacity. Likewise, blend plant owners are recognizing the need for using potash of a size that is similar to that of the other materials in the mixture and, therefore, are more generally choosing "granular" potash. Figure 9 illustrates the similarity of "granular" potash to other granular materials and the dissimilarity of "coarse" grade potash. Studies at the National Fertilizer Development Center, Muscle Shoals, Alabama, demonstrate that all materials in a blend mixture should be within ±10% range of particle size on each screen size to avoid undue segregation.

In Germany, where potash was first produced, the kieserite, carnallite, and insoluble anhydrite are finely grained, and the crystals are intergrown, making separation by grinding and flotation almost impossible. Crystallization is the principal method of beneficiation used in Germany. Some flotation units are now in use. More recent crystallization units installed in Europe are capable of producing a rounded grain of about 1-mm diameter. Compaction of fine particles to granular size range has been introduced in Europe. In North America coarse grade and, with certain ores, some granular potash can be produced by flotation.

In North America granular grade ranges in size between 1.2 and 3.3 mm. In France compacted potash ranges between 0.8 and 5.0 mm. A screened fraction sold as "granular" is 1.5-5.0 mm with the major percentage of particles between 1.8 and 4.0 mm.

The West German plants have compaction units for "granular" grade (13). Swenson crystallizers are used to produce a semicoarse particle at most West German plants.



Source: AMAX Chemical Corporation.

Figure 9. Particle Size of Granular and Coarse Potash in Comparison with Granular Phosphates Available in the United States.

In the German Democratic Republic, the Unterbreizbach plant has granulating facilities to produce about 250,000 tons annually on a K_2O basis. This product ranges from 0.5 to 4.0 mm but can be screened at Wismar, a port, to 0.5-1.5 mm and 1.5- to 4.0-mm fractions for export.

The potash industry in the U.S.S.R. intends to increase the proportion of granulated product to 75% of total output. Only about 1.0 million tpy was produced in 1977. Both Uralkali and Byeloruskali mines have compaction units.

Price Differential for Grades

The following prices are illustrative of the various "grades" of muriate of potash offered by North American producers (14):

	Price (Feb.-June 1977)[a]		
Grade	Typical Size Range, mm[b]	\$/Short Ton Unit of K_2O[c]	\$/kg of K_2O
Standard	less than 0.8	0.80	0.088
Coarse	0.8-2.0	0.84	0.093
Granular	1.2-3.3	0.86	0.097
Soluble 62%-63% K_2O	less than 0.8	0.86	0.097

a. List price from Phosphorus and Potassium, 83:14 (1976), f.o.b. mine in Canada.
b. Specifications vary somewhat from one producer to another.
c. Short-ton unit of K_2O = 20 lb (1% of short ton).

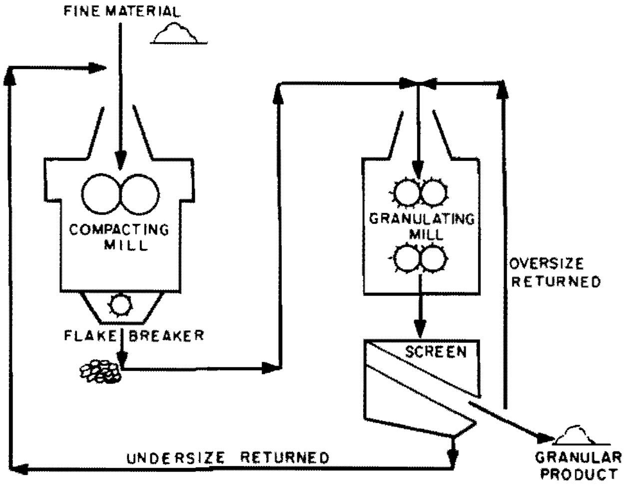
The prices shown above amount to a premium for granular potash over a standard of about \$4 per metric ton of muriate of potash containing 60% K_2O. "Soluble" potash commands a similar premium; it contains no insoluble impurities and is used mainly in fluid fertilizers. A fine particle size is preferred for rapid dissolution or, in the case of suspensions, to prevent rapid settling.

The premium for granular potash has varied considerably since 1976. In mid-1979 the premium for international sales of granular Canadian or European potash was about $10/ton, but for sales within North America the premium varied from $10 to less than $5/ton, presumably in response to supply and demand factors.

Sulfate of potash also is offered in standard and granular sizes; the price of the granular grade in 1976 was about $8.60/ton more than the standard grade. For potassium magnesium sulfate, the premium for granular grade was $6.60/ton. Granular potash products may be obtained by screening flotation product or by roll compaction as described elsewhere in this report. However, granular sulfate of potash is produced only by compaction.

Granulation of Potash Salts

Granulation of fine potash salts is carried out on a commercial scale by compaction. Some other methods have been tried, but there is no known commercial use. A typical flowsheet of a roll compaction unit for producing granular muriate of potash is shown in figure 10. The feed is fine potash plus recycled fines from the process. The feed is preheated in a steam-heated conveyor and fed to a hopper above a pair of smooth rolls. The rolls turn toward each other and compress the material into a continuous sheet. The sheet is broken into flakes by a "flake breaker." The flakes are screened to remove fines and then fed to two "granulating mills" in parallel. The granulating mills are corrugated rolls with sharp-edge corrugations designed to break the flakes in such a way as to form a maximum percentage of the desired particle size. Other types of crushers, such as cage mills, may be used. The product from the primary mills is screened to remove fines (which are recycled to the compactor), product size (1.2-3.3 mm), and oversize (which goes to a third granulating mill). The product from the mill is screened to recover more product size. Oversize is recycled to the mill, and fines are recycled to the compactor. Of the total throughput, 40%-60% is recovered as granular product, and the remainder is recycled as fines to the compactor.



Source: Allis Chalmers.

Figure 10. Simplified Flowsheet for Granulation of Potash by Roll Compaction.

In a similar process, the incoming potash is formed into briquettes by pressing the material between rolls that have matching pockets rather than smooth rolls. The shape of the briquettes may be long and narrow like a cigar. The briquettes are then crushed and screened to recover the desired size.

The roll compaction machines consist essentially of a set of two, powered, inward-turning rolls. One roll has a fixed bearing; the other is floating in a slide arranged so that it can be forced toward the fixed roll by hydraulically actuated pistons acting on the bearing blocks. The material to be compacted is fed continuously into the nip of the rolls from above. Very high pressure can be exerted on the material as it is forced or drawn between the rolls where a momentary phase change to a plastic flow condition takes place. The crystals are fused together into an almost continuous sheet of product which is ejected beneath the rolls. The void content of the sheet may approach zero, and the thickness may vary from 1/8 in to 3/4 in (0.3-1.9 cm), depending on the feed texture and compaction machine in use. Compaction machines vary in size (table 3), but the mechanism of compaction is the same. One of the very few in-depth studies on compaction has been published by B. E. Kurtz and A. J. Bardunhn (15).

Factors affecting compaction of potash are as follows:

Feed Texture--The optimum particle size distribution lies on the slope of approximately 8% plus 14-mesh to 8% minus 200-mesh. This includes minus 12-mesh fines and dust recycle from the compaction circuit, in addition to fresh crystalline feed. Excessively coarse crystalline feed may result in a weaker, grainy-textured sheet. A high minus 200-mesh content increases the void content in the sheet and produces severe mechanical stresses on the drive gears of the compactor due to "chattering" in which the rolls vibrate and slip under load. Segregation can be a serious problem. It is minimized by using a small volume feed bin so that fresh feed is constantly blended with recycled material.

Feed Condition--An oil or amine residual film on the crystal from previous treatment inhibits fusion of the surfaces and results in weak sheet and heavy recycle to the rolls. The film can be removed by high temperature drying. Some producers add a small amount of moisture to the feed; others find that trace additives, such as starch, improve the quality of the product.

Feed Temperature--Optimum feed temperature without water-cooled rolls is 120°-150°F (49°-65°C). Higher temperatures result in additional maintenance problems throughout the plant. Hot feed (300°-500°F) (150°-280°C), however, can be compacted into an extremely dense sheet at somewhat lower pressures when the high temperature conditions can be tolerated.

Methods of Introduction--Feed to compactors can be introduced either by gravity or with assistance by force feeding screws.

High bulk density of the feed is important to successful compaction when rolls are fed by gravity. The density, however, is altered drastically by the presence of air entrapped in the material, and the quantities of this air must be decreased to tolerable levels. The deaeration of feed might be accomplished by vibration of the feed hopper above the rolls, by vacuum, or by mechanical stirring. In varying degrees, all of these methods help by decreasing the void content of the feed. Some operators claim that deaeration and increased bulk density resulting therefrom are quite effectively obtained by using a high, shaft-like hopper directly over the rolls.

Force feeding utilizes one or more vertical screws to introduce feed into the angle of nip under pressure. This serves two purposes, namely, it assists in displacement of the entrapped air and increases the coefficient of friction between the feed

TABLE 3. ROLL COMPACTION MACHINES IN CURRENT USE

	Allis-Chalmers	Komarek-Greaves	Humboldt	Vulcan-Koppers
Roll diameter, cm	61	71	91	102
Roll width, cm	61	69	119	127
RPM	24	42	25	14
Peripheral speed, m/min	46	94	72	47
Roll construction	Cast iron-alloy shell. Solid steel shaft.	Cast iron roll 2" alloy shell. Hollow shaft.	Cast steel. Internal water cooling.	Monobloc body and shaft. Water cooled under roll surface.
Bearings	Sleeve or roller	Roller	Roller	Roller
Motor capacity (kW)	149-224	373	2 x 186	448
Applied pressure, kg/cm	3,575	3,932	4,182	5,362
Feeding method	Either gravity or vertical twin screw force feeder.	Tapered-screw, twin-force feeder (4:1 ratio).	Hydraulic variable-speed, twin-force feeder.	Five 22-kW hydraulic motor-driven force feeders.
Throughput, tph	27	45	77	91
Approximate production rate (6 x 14 mesh), tph	11	20	26	27

material and smooth surfaces of both rolls. The benefits claimed for the force feeding method are:

(1) decreased sensitivity of compaction rolls to fluctuations in texture of the feed; (2) increased angle of nip, which is reflected in increased thickness of the compacted sheet and higher production rate by the compactor resulting therefrom; and (3) greater effectiveness of automation by use of screw feeders, e.g., by controlling force feeder speed to maintain a specific loading on the compactor motor or to produce a constant sheet thickness by transducer signal to a varispeed force feeder drive.

Roll Speed--This variable must be regulated in relation to feed texture, method of its introduction, and roll diameter. High-speed rolls generally produce a thinner sheet with less recycle, but they are sensitive to feed texture changes. Slower turning rolls (10-25 rpm) are more stable, but they produce a narrow sheet.

Roll Pressure--All other variables are controlled to permit the highest possible roll pressure consistent with a sustained operation. This is the most critical factor in the successful agglomeration of free-flowing potash between compaction rolls. Roll pressure on the potash is normally quoted in pounds per linear inch and is commonly in the range of 20,000-30,000 lb/linear in (about 3,500-5,400 kg/linear cm). Pressure is applied to the bearing blocks of the floating roll by a hydraulic system which is either set manually or automatically controlled to maintain optimum pressure.

Roll Surface--Smooth rolls are standard, with a provision for scraping fused material from the surface. The rolls may be solid or ducted for cooling water, but a common practice in the industry is to apply external cooling by water sprays, damp sponges, etc. Application of moisture results in severe corrosion of the roll surfaces.

Roll Diameter--Sensitivity to particle size distribution and residual air content in the feed is decreased as roll diameter is increased, thereby permitting increased circumferential speed. One manufacturer of large diameter rolls utilizes a grating immediately above the angle of nip. The air is drawn down into the rolls instead of escaping above with some turbulent effect. The resulting sheet leaves the rolls as longitudinal strips.

The flowsheet (figure 10) shows a 24 by 24 in (61 by 61 cm) Allis-Chalmers compaction unit running in an independent closed-circuit system. The equipment is common in the industry, and this flowsheet, although not standard, is particularly illustrative because of its simplicity.

Most recent compaction installations are designed to recycle all or part of the near sized granular material back to the mill product screening plant to recover a percentage of the product as coarse or standard-grade products.

One drawback of roll compaction processes is that the granules may have thin edges or corners that break off in handling to form fines. To overcome this problem, some producers put the granular product through a tumbler so that fragile edges are broken off and can be removed by screening. Also, a treatment with steam has been developed that helps to round the edges. Other particle stabilizing treatments may involve addition of moisture or brine followed by drying.

Granulation by roll compaction can also be applied to potassium sulfate, ammonium sulfate, and crystalline diammonium phosphates. The process also can be used to granulate some types of compound fertilizers, as discussed in chapter XIX, and to agglomerate a wide range of nonfertilizer products.

As to the cost of granulation by roll compaction, the price differential of about $4-$8/ton for granular potash salts versus the price of standard grade presumably reflects an order of magnitude of the cost.

World Potash Production Capacities

Since the first potash mine was opened in 1861 near Stassfurt, Germany, world potash production capacity has increased to about 32 million tons of K_2O equivalent in 1979 (4), largely as muriate of potash and much lesser amounts of potassium sulfate and small amounts of potassium nitrate. The following tabulation summarizes the present (1978-79) capacities by country.

World Potash Capacity in 1978-79

		Million
	Tons K_2O	Percent
World total	31.96	100
U.S.S.R.	10.00	31
Canada	7.50	24
German Democratic Republic	3.20	10
German Federal Republic	3.30	10
United States	2.86	9
France	2.39	7
Spain	0.88	3
Israel	0.88	3
Others	0.95	3

A World Bank report estimates that world capacity will increase to 39.05 million tons of K_2O in 1985 (4). Over 60% of this forecasted increase will be in the U.S.S.R. The report estimates that the rate of capacity increase will be sufficient to satisfy the increased demand at least up to 1982, when the capacity is expected to be 36.18 million tons of K_2O.

Prices and Production Costs

Historical information in potash prices is not very useful because of the major dip in prices during 1966-72 which resulted from the overambitious development of new mining capacity in Saskatchewan and the U.S.S.R. following:

1. A worldwide campaign to "feed the world."
2. Discovery of large potash reserves and suitable technology in Saskatchewan and the U.S.S.R.
3. Expansion of nitrogen and phosphate production which lent encouragement to investment in new potash production.

Figure 11 shows price trends to date for three major fertilizer materials (16). The potash price, f.o.b. Vancouver, rose from $33/ton of 60% K_2O muriate in 1970 to a maximum of $80/ton in 1974 and then fell below $50/ton in 1977 and rose to about $78/ton

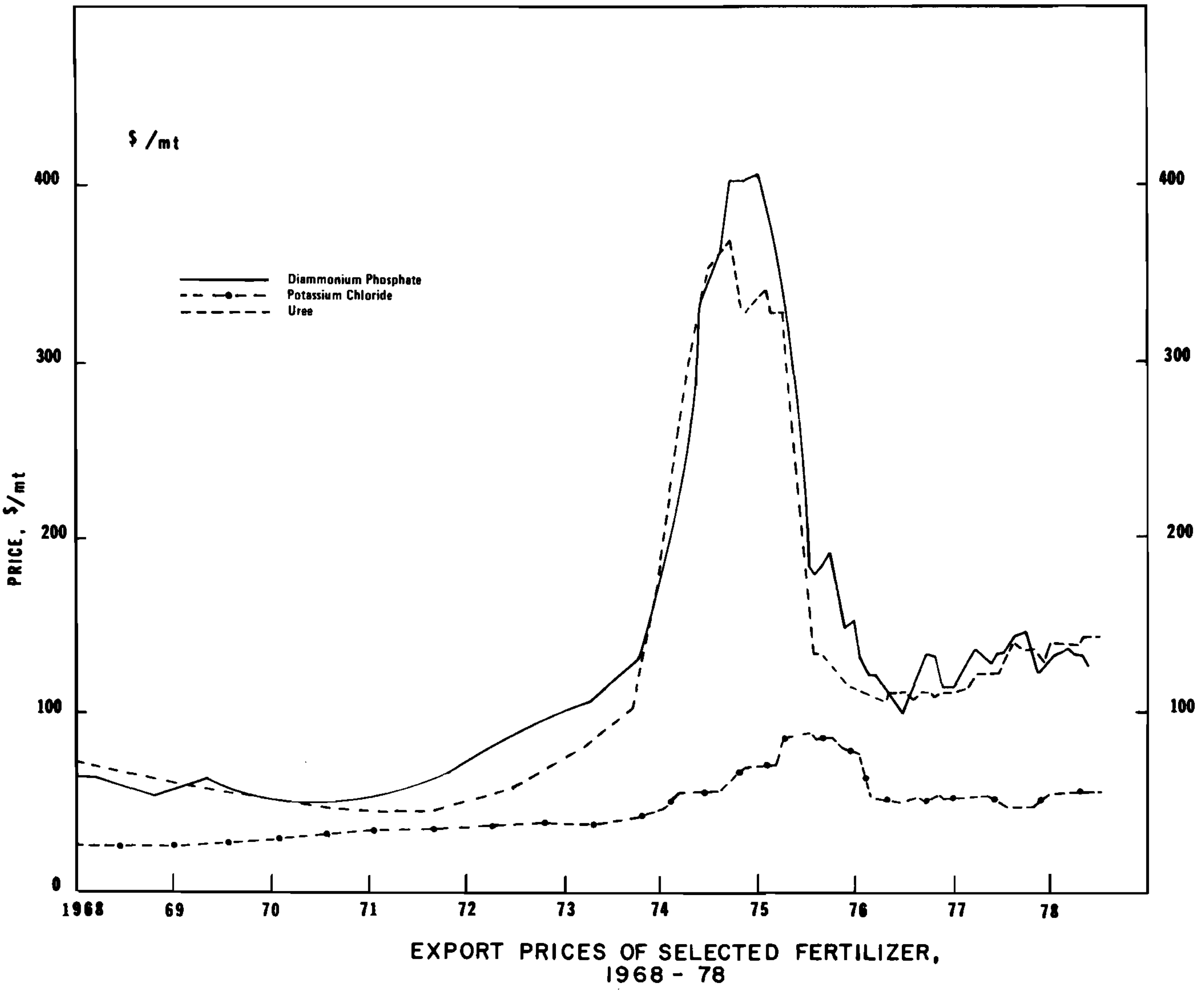


Figure 11. Export Prices of Selected Fertilizers, 1968-78 (Potash Prices, f.o.b. Vancouver, Canada).

in mid-1979. Note that potash prices rose much less during the 1973-75 shortage than did most other fertilizer materials (17). Noting also the modest increase of potash price during the past 14 years, it seems certain that potash prices will have to rise to support the more rapidly increasing construction costs. On a constant-dollar basis, potash price is lower than it was 15 years ago.

Table 4 shows the estimated capital cost of a plant designed to produce 1.13 million tpy of product as muriate of potash at the mine in Saskatchewan. The ore is very high grade and will be used to produce agricultural muriate of potash in all size grades. Some of the product will be used to produce agricultural soluble grade and chemical grade. The estimated cost is $219 million which equates to about $194/annual ton of product expressed in 1977 dollars.

TABLE 4. 1977 CAPITAL COST OF POTASH MINE AND REFINERY IN SASKATCHEWAN 1.13 MILLION TONS OF PRODUCT/YEAR CAPACITY

Facility	Cost, Million U.S. Dollars
Mine	
2 shafts, 16-ft diameter x 3,000 ft, with hoisting equipment	53.0
Mine equipment	30.0
Subtotal	83.0
Surface plant[a]	136.0
TOTAL[b]	219.0

a. Includes eight compactors and a crystallizer circuit.

b. No working capital included.

Table 5 approximates typical operating costs of an operation in Canada as described above. It must be emphasized that ore grade and other conditions are highly favorable in Saskatchewan, and these costs are lower than many other potash operations, substantially lower than some. On the other hand, the capital requirements for opening a mine in Saskatchewan are unusually high because of the depth of the deposits and the difficult geological formation (high pressure aquifer) through which the shafts must be constructed. Also, the severe climatic conditions increase the cost of the ore refining plant.

On the basis of the premises expressed in tables 4 and 5, there are calculated prices necessary to yield 5%, 10%, and 15% after tax return on investment, assuming further the stated 15-year depreciation rate, royalty/taxes, and general and administrative costs. These calculations made with and without the Saskatchewan reserve tax, a business expense peculiar to Saskatchewan, are shown in table 6.

It is difficult to compare the investment and operating costs of solution mining with shaft mining because solution mining is seldom used except where shaft mining is infeasible owing to excessive depths or geological character of the deposit. Also, in solution mining there is no clear-cut separation of mining and beneficiation.

TVA has estimated the energy requirements for three combinations of mining and beneficiation for North American conditions, assuming an ore grade of 26% K_2O (18):

TABLE 5. CANADIAN PLANT, DIRECT OPERATING COSTS

		Annual Cost, $	Cost, $/Ton Product
Mine Personnel			
Office	16		
Maintenance	74		
Production, face	104		
Production, backup and utility	42		
Total	236	4,786,000	3.51
Plant Personnel			
General and administration	48		
Supervisory	19		
Operating	88		
Maintenance	65		
Total	220	4,686,000	3.43
TOTAL PAYROLL (includes 20% fringe benefits)		9,472,000	6.94
General Plant Overhead		643,800	0.48
Mine:			
Operating supplies	876,600		
Maintenance supplies	3,123,600		
Power	957,200		
Expendable and miscellaneous	755,500		
Total		5,712,900	4.19
Plant:			
Operating supplies		2,830,100	
Maintenance supplies		1,146,100	
Power		1,587,000	
Expendable and miscellaneous		377,800	
Total		5,941,000	4.36
Total annual direct operating costs		21,769,700	15.97

TABLE 6. POTASH PRICE CALCULATION

Basis:

1.12 million tons of product per year capacity
Plant includes eight compactors and a crystallizer
Capital cost, \$218.75 million (\$192.50/tpy)
Direct operating cost, \$15.97/ton
Costs expressed in 1977 U.S. dollars/mt of product
Reserve tax, \$15.00/short ton, nondeductible

Costs	Excluding Reserve Tax	Including Reserve Tax
Operating	\$15.95	\$15.95
Depreciation (15-year life)	12.84	12.84
Royalty/taxes	2.20	2.20
Administrative, etc.	2.20	2.20
Reserve tax	0	16.50
Total	\$33.19	\$49.69

Price necessary to yield indicated after tax return on total investment based on current 1977 Canadian taxes:

	Price, \$/mt, f.o.b. Saskatchewan	
% Return on Investment, After Tax	Including Reserve Tax	Excluding Reserve Tax
5	73.59	49.50
10	89.82	65.78
15	106.32	82.12

	Energy Requirement, GJ/Ton of 60%-62% K_2O as Muriate of Potash[a]
Solution mining	6.5
Crystallization recovery	5.4
Total	11.9
Shaft mining	2.2
Beneficiation by flotation	1.0
Total	3.2
Shaft mining	2.2
Beneficiation by crystallization	5.4
Total	7.6

a. 1 GJ = 0.948 million Btu = 0.239 million kcal.

The above energy requirements include both electrical energy and fuel with the equivalent fuel requirement of electrical energy calculated on the basis of a conversion efficiency of 33%. It is evident that solution mining is energy intensive and, if based on world market prices for oil (about \$2/GJ), it would be uneconomical at current potash prices. However, any kind of fuel can be used to generate steam and electricity which are the major forms of energy needed. Thus, where low-cost coal or natural gas is available, solution mining may be economically acceptable. In arid climates solution mining may be modified to take advantage of solar energy; a relatively dilute solution can be produced at moderate temperature, and most of the evaporation and crystallization can be carried out in lagoons by solar energy. This is done at the Texasgulf mine in Utah.

Beneficiation of shaft-mined ore by crystallization methods also requires a substantial amount of energy, but it has the advantage of producing a fully soluble high-grade (62% K_2O or more) product which is preferred for liquid fertilizers and as an intermediate for high purity material for industrial uses. Some plants prepare a portion of their output by crystallization for these markets.

World Potash Commerce

World potash exports in 1976-77 were 13.3 million tons K_2O and 51% of world potash production. Thus, potash is an important item of world commerce. World potash fertilizer exports increased at an average annual growth rate of 7.1% over the 10-year period ending 1975-76. This was 2% faster than the potash production increased on average during this period. Nine countries export over 99% of all potash materials: Canada, the U.S.S.R., East and West Germany, France, the United States, Israel, Spain, and Italy, about as follows:

Exporter	% of Total Exports
Canada	40
United States	7
France	4
West Germany	6
East Germany	19
U.S.S.R.	19
Israel	3

North American exporters account for about half of the exports to lesser developed countries. North American exporters also supply the major portion of the demand in Oceania and Japan. Western European countries are supplied mainly by trade within the region.

International trade patterns for potash are determined largely by:

1. Relative transportation costs.
2. AID and other sales concessions.
3. Political relationships and the European cartel.

This export pattern has been reasonably stable in recent years but may be altered somewhat if the U.S.S.R. materially increases its exports.

Table 7 gives the potash trade in 1976 from nine exporting countries including Spain to developed, developing, and centrally planned economies (19). Imports in 1976 were divided as follows: 60% to developed market economies, 15% to developing market economies, and 25% to centrally planned economies.

TABLE 7. POTASH TRADE IN 1976 ('000 TONS K_2O)

Importers	France	Fed. Rep. Germany	Italy	Spain	Dem. Rep. Germany	U.S.S.R.	Canada	United States	Israel	1976	1975
World Total[a]	476	779	54	239	2,303	2,304	4,923	848	341	12,268	11,721
Developed Market Economies	371	566	16	179	639	597	4,412	323	273	7,377	6,781
North America	-	20	5	15	-	-	4,030	14	48	4,132	3,286
West Europe[b]	283	453	11	150	618	462	25	38	172	2,213	2,237
Oceania	-	2	-	-	-	14	54	175	-	245	210
Others[c]	88	91	-	14	21	121	303	96	53	787	1,048
Developing Market Economies	100	190	38	60	349	104	420	524	68	1,854	1,677
Africa	47	5	1	-	-	-	-	3	8	64	42
Latin America	30	78	4	36	201	101	147	471	19	1,088	821
Near East											
Africa	4	-	25	24	3	-	-	-	-	56	85
Asia	-	-	5	-	10	-	-	-	-	15	8
Far East											
South Asia	-	91	-	-	131	3	110	-	-	335	245
East Asia	19	16	3	-	4	-	163	50	41	296	476
Centrally Planned Economies	5	23	-	-	-	1,315	1,603	91	1	3,038	3,263
Asia	-	-	-	-	-	38	33	91	1	163	292
E. Europe[b]	5	23	-	-	-	1,277	1,570	-	-	2,875	2,971

a. Totals rounded, not always comparable.
b. Yugoslavia included in West Europe.
c. Includes Japan, South Africa, and Israel.

Source: International Phosphate Industry Association (ISMA) (19).

World Potash Consumption

World consumption of potash fertilizers has increased at an average annual growth rate of about 6% during the past 20 years. Table 8 gives the regional and world potash consumption for 1962-77, with projections to 1985. During this 15-year period, the average annual increase of potash consumption for the world was 6.8%.

In 1977 world potash fertilizer consumption was about 23.1 million tons K_2O. North America, primarily the United States, consumed 5.5 million tons and Latin America, 1.1 million tons. In Asia it is estimated that Japan consumed 655,000 tons; China, 400,000 tons; India, 360,000 tons; and South Korea, 200,000 tons while others used 522,000 tons.

During the next 7 years, 1977-85, world potash consumption for fertilizer is projected by TVA to increase about 4.2% annually from 23.1 million tons K_2O in 1977 to 32.1 million tons K_2O in 1985 (16). In terms of muriate of potash, that would be an increase of 15.0 million tons of product in the 7 years (see table 8). To meet this demand, production should be about 10% higher than agricultural consumption in order to allow for industrial consumption and the usual 5% gap between production and consumption (see chapter I). A World Bank report projects a somewhat higher rate of consumption increase, reaching 34.5 million tons of K_2O in 1985 (4).

North American potash exports are expected to continue to increase primarily from Canada but also from Carlsbad, particularly because of its logistic advantage to Central and South America. This adds to the strategic importance of the Carlsbad location.

In a recent AMAX study using three published independent projections of world potash consumption, it was estimated that world consumption will increase to about 64 million tons of K_2O by the year 2007. To supply this demand, production capacity would have to be increased by at least 41 million tons of K_2O during the period 1976-2007. The 41 million tons of K_2O is equivalent to about 68 million tons of muriate of potash. Since new mines will have to supply most of this added potash, there should be strong upward long-term pressure on price, sufficient to justify the investment in ever-increasing potash operations.

Granular grade is best fitted to the largest and still growing share of the U.S. market. The blending of granular materials at small local plants has become standard procedure in much of the major fertilizer use states.

Both granular and coarse grades of potash are used in bulk-blend mixtures, but educational efforts on the benefits of the use of granular grade are increasing as shown in table 9. Granular grade more nearly matches the particle size of other materials used in the blended mixtures of solid materials.

TABLE 8. REGIONAL POTASH FERTILIZER CONSUMPTION

	North America	Latin America	Western Europe	Eastern Europe	U.S.S.R.	Africa	Asia	Oceania	World
					'000 mt K_2O				
1962	2,156.4	193.9	3,474.5	1.244.4	703.0	96.2	683.8	130.3	8,682.6
1963	2,372.7	210.5	3,663.6	1,247.3	826.0	107.1	758.4	91.3	9,277.0
1964	2,585.8	270.3	3,779.0	1,410.4	901.0	124.4	877.6	128.4	10,076.9
1965	2,694.3	268.6	3,895.4	1,522.4	1,421.0	156.5	924.3	152.5	11,035.0
1966	3,064.1	292.7	3,930.0	1,709.5	1,891.0	158.0	1,066.5	171.1	12,282.7
1967	3,465.4	326.7	3,941.2	1,929.6	1,902.0	184.4	1,165.6	174.9	13,089.8
1968	3,606.6	366.1	4,231.3	2,092.4	2,136.0	191.2	1,292.1	157.0	14,072.9
1969	3,698.7	536.4	4,191.8	2,308.7	2,176.0	201.7	1,404.9	175.7	14,693.7
1970	3,835.7	556.5	4,371.1	2,468.0	2,319.0	214.7	1,508.6	194.5	15,468.2
1971	4,022.9	646.5	4,796.4	2,678.4	2,574.0	237.0	1,519.1	196.0	16,670.3
1972	4,120.4	659.3	4,996.2	3,015.9	2,788.0	264.1	1,572.4	193.9	17,610.3
1973	4,398.1	769.6	5,091.2	3,011.3	3,238.0	294.8	1,750.5	240.5	18,794.0
1974	4,803.2	894.7	5,395.7	3,319.4	3,605.0	308.6	2,118.7	287.9	20,733.2
1975	4,246.1	929.6	4,602.3	3,397.4	3,884.0	343.8	2,182.8	237.9	19,824.0
1976	4,968.2	872.0	4,478.1	3,707.6	5,176.0	326.3	1,814.6	195.7	21,538.4
1977	5,545.6	1,097.1	4,741.6	3,499.4	5,577.0	350.1	2,002.0	251.5	23,064.2
					-Forecast-				
1978	5,264.8	1,138.5	4,981.2	3,674.9	5,400.0	376.4	2,364.7	274.0	23,474.5
1979	5,557.4	1,261.5	5,125.2	3,819.0	6,143.0	400.7	2,408.9	283.5	24,999.3
1980	5,743.9	1,362.0	5,269.4	3,949.1	6,650.0	426.0	2,501.2	292.9	26,194.6
1981	5,930.5	1,464.9	5,344.7	4,078.1	7,174.0	453.5	2,594.7	302.4	27,342.8
1982	6,117.1	1,570.2	5,434.2	4,207.3	7,714.0	479.0	2,687.1	311.7	28,520.6
1983	6,302.6	1,676.9	5,515.6	4,336.3	8,270.0	506.5	2,775.8	321.0	29,704.7
1984	6,488.2	1,787.4	5,604.7	4,465.4	8,850.0	534.1	2,868.4	330.3	30,928.6
1985	6,673.8	1,897.3	5,692.9	4,593.4	9,430.0	558.6	2,959.4	339.5	32,145.0

Source: (16)

TABLE 9. AGRICULTURAL SALES OF POTASH BY U.S. AND CANADIAN PRODUCERS IN THE UNITED STATES AND CANADA ('000 TONS K_2O)

	Granular	Coarse	Standard
1973	1,394	2,141	1,394
1974	1,588	2,241	1,476
1975	1,191	2,022	1,046
1976	1,665	2,485	1,174
1977	1,824	2,417	1,119
1973-77 increase--percent	31.1%	12.9%	(19.7%)

AMAX Chemical has successfully promoted the use of granular grade in blend mixtures through the use of the trade name K-Gran and promotional/educational material explaining the merits of its use. Consumption of the granular grade in North America has increased by 31.1% during the 5-year period 1973-77 which indicates that retailers and consumers are becoming aware of the advantages of this grade (table 9). A substantial proportion of the potash used in the United States and some other countries is for direct application. For this purpose, either coarse or granular grades can be used, but the closely sized granular grade is likely to give a more even distribution pattern when broadcast by mechanical application.

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XIX Compound Fertilizers

"Compound fertilizers" is the term used in this manual to denote all fertilizers containing more than one of the three primary nutrients--N, P_2O_5, and K_2O. They may also contain one or more of the secondary elements and micronutrient elements. In the United States, the term "mixed fertilizers" is synonymous with "compound fertilizers" with some exceptions (see "Definitions," Chapter IV). In some European countries compound fertilizers are further subdivided into "mixed fertilizers" and "complex fertilizers," according to whether chemical reactions are involved in the mixing process.

The derivation of the word "compound," as applied to fertilizer use, is related to the dictionary definition "formed by combining parts, ingredients, or elements." "Mixed" in European usage relates to the definition, "formed by mixing"; in U.S. usage it is apparently related to the definition, "consisting of different parts or elements."

In the early stage of development of the industry, "straight" fertilizers predominated in most countries. Phosphate fertilizers were developed first in the 1840s; a potash industry was developed later in the 1870s and a nitrogen industry still later. In the United States compound fertilizers were developed at an earlier stage on the basis of superphosphate mixed with Peruvian guano, Chilean nitrate of soda, potash salts, and byproduct organic materials such as fish scrap, cottonseed meal, and abbatoir waste. In developing countries it is common to start with straight nitrogen and later move on to compounds.

With these diverse beginnings, as the fertilizer industry and agriculture mature, the usual tendency is to supply most of the phosphate and potash and a part of the nitrogen as compound fertilizer. Thus, in many European countries and Japan, over 90% of the P_2O_5 and K_2O and about 50% of the N are supplied as compound fertilizer. This compound fertilizer is commonly applied before or during the planting of farm crops. An additional application of straight nitrogen may be supplied during the growth of the crop as a "topdressing" or "sidedressing." The reason for a "split" application of nitrogen is that nitrogen supplied at the time of planting may be partially lost by leaching or decomposition. In sandy soils, for example, leaching is likely to be serious, and a low-nitrogen compound fertilizer (such as a 1:4:4 $N:P_2O_5:K_2O$ ratio) may be applied at planting time, with additional applications of nitrogen during the growing season.

Choice of Grades

Different grades of compound fertilizers are formulated to supply different proportions of N, P_2O_5, and K_2O in accordance with the needs of various crops, the native fertility of the soil, and the desirability of later supplemental applications of straight nitrogen. Recommendations for $N:P_2O_5:K_2O$ ratios are based on soil analyses, if available, or on general knowledge of the type of soil and its fertility status in a district or region. The estimation of the "best" ratio for any soil-crop combination cannot be made with mathematical precision. Therefore, it is common practice to recommend a few ratios of whole numbers, such as 2:2:1, 4:2:1, 1:1:1, 1:4:4, 1:4:2, and 2:2:3. Very often a few ratios are sufficient for any region.

Low-nitrogen or no-nitrogen grades may be preferred for fertilization of soybeans and other legumes which obtain their nitrogen from the air by symbiotic fixation. Low-nitrogen grades are also preferable when nitrogen can be supplied more economically by separate application of nitrogen as anhydrous ammonia. For this reason, 6-24-24 is the most popular NPK grade in the United States, and various no-nitrogen PK grades (usually blends) are also popular.

Compound fertilizers may also contain one or more of the secondary or micronutrient elements when the need for such elements has been identified. Methods for incorporating these elements in compound fertilizers are discussed in chapter XX.

When suitable ratios have been determined, the grade can be formulated to provide the highest concentration that can be attained with the available or recommended materials. When a variety of materials are on hand, there could be several grades of the same ratio. For instance, a 2:2:3 ratio is popular in Europe. Several grades of this ratio or a close approximation of it have been produced, such as 10-10-15, 12-12-18, 13-13-20, and 15-15-21. In most cases the lower grades have been replaced by successively higher grades as higher analysis materials and improved technology permitted. However, in some cases lower grades are preferred because of some agronomic or economic advantage or better physical properties.

Figure 1 shows how the average analysis of fertilizers has increased during the last 20 years in the United States and the United Kingdom. There was a sharp increase from 1957 to about 1970, after which the concentration tended to level off or even decrease slightly. Similar trends have occurred in many other countries.

Processes for Manufacture of Compound Fertilizers

Compound fertilizers may be classified according to the type of process used in their production as follows:

1. Dry mixing of nongranular or pulverized materials.
2. Granulation of dry-mixed materials by processes in which chemical reactions are not an essential part of the process.
3. Granulation of dry materials with the addition of materials that react chemically, usually ammonia or solutions containing ammonia and often sulfuric or phosphoric acid.

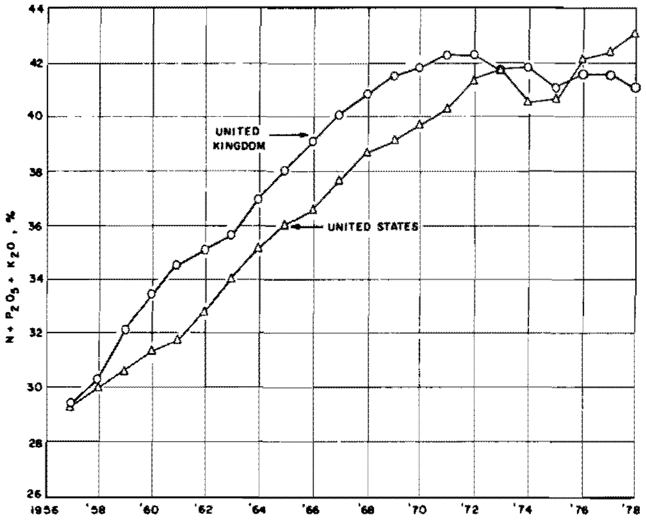

Figure 1. Trends in Concentration of Compound Fertilizers.

4. Slurry granulation in which the materials to be granulated are in the form of a slurry, usually derived from reaction of sulfuric, nitric, or phosphoric acid with ammonia, phosphate rock, or some combination of these materials. In some process modifications, solid materials may be added to the slurry during granulation; in other processes, all incoming materials are incorporated in the slurry.

5. Melt granulation in which all or a major part of the mixture to be granulated is in the form of a hot, fluid melt, usually containing less than about 2% water, which solidifies on cooling.
6. Blending or bulk blending consisting of mechanical dry mixing of granular materials. The materials may be either straight or compound fertilizers. The mixture may be marketed in bulk or bags.
7. Fluid or liquid compound fertilizers of two types:
   a. Liquids in which all or nearly all of the ingredients are in solution, sometimes called "fertilizer solutions" or "clear liquid fertilizers."
   b. Suspensions or slurries which are fluid mixtures containing solids, usually suspended in a saturated solution of fertilizer materials.

Processes 1, 2, and 6 (dry mixing, granulation of dry mixes, and bulk blending) are sometimes referred to as mechanical processes for preparing compound fertilizers, as compared with processes in which chemical reactions are an essential part of the process. Products made by the latter methods may be referred to as "chemically mixed." However, many chemical reactions do occur in mechanically mixed fertilizers. The reactions are sometimes helpful but more often detrimental to the physical properties of the products. The extent and rate of these reactions are greatest in granulation processes in which increased temperature and moisture accelerate the reactions. The extent of reaction is least in bulk blends, but even in blends some reactions may occur which may seriously affect the quality of the products.

Some of the more common chemical reactions that may occur in "dry" mixtures are listed below:

$$Ca(H_2PO_4)_2 \cdot H_2O + (NH_4)_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O + 2NH_4HPO_4 \qquad \text{(Equation 1)}$$

$$(NH_4)_2SO_4 + 2KCl = K_2SO_4 + 2NH_4Cl \qquad \text{(Equation 2)}$$

$$NH_4NO_3 + KCl = KNO_3 + NH_4Cl \qquad \text{(Equation 3)}$$

$$(NH_4)_2SO_4 + CaSO_4 + H_2O = (NH_4)_2\,SO_4 \cdot CaSO_4 \cdot H_2O \qquad \text{(Equation 4)}$$

$$K_2SO_4 + CaSO_4 + H_2O = K_2SO_4 \cdot CaSO_4 \cdot H_2O \qquad \text{(Equation 5)}$$

$$H_3PO_4{}^1 + (NH_4)_2HPO_4 = 2NH_4H_2PO_4 \qquad \text{(Equation 6)}$$

$$Ca(H_2PO_4)_2 \cdot H_2O + 4CO(NH_2)_2 = Ca(H_2PO_4)_2 \cdot 4CO(NH_2)_2 + H_2O \qquad \text{(Equation 7)}$$

The above reactions and many others may occur which result in crystal growth or absorption or release of water, thereby causing caking. Urea forms several adducts; in addition to the adduct with monocalcium phosphate shown in equation 7, adducts with NH_4Cl, $CaSO_4$, and H_3PO_4 have been identified. Also, urea may hydrolyze according to the reaction:

$$CO(NH_2)_2 + H_2O = 2NH_3 + CO_2 \qquad \text{(Equation 8)}$$

The reaction may occur slowly in storage piles depending on temperature, moisture content, and acidity or more rapidly in drying compound fertilizers. The ammonia released in reaction 8 may react with monocalcium phosphate in superphosphate or with monoammonium phosphate:

$$Ca(H_2PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4 \qquad \text{(Equation 9)}$$

$$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4 \qquad \text{(Equation 10)}$$

Many of the reactions are exothermic and cause "self-heating" in storage piles. The increased temperature accelerates the reaction rate and may raise the temperature to the point that rapid decomposition of nitrates occurs, releasing toxic nitrogen oxides. In acidic mixtures containing nitrates and organic matter, rapid oxidation resulting in fires has occurred.

Dry Mixing of Fertilizers

One of the oldest processes for making compound fertilizers is dry mixing. Fertilizer materials such as single or triple superphosphate, ammonium sulfate, sodium nitrate, and potash salts are weighed out in the desired proportions and mixed mechanically, usually in a rotary drum mixer. The materials are usually crushed to pass (for instance) a 6-mesh screen (about 3.3 mm) before or after mixing. In the early history of the industry, the mixing was done manually with rakes, hoes, or shovels; and in some countries manual methods are still used, particularly for small batches.

To alleviate caking which often occurred with such mixtures during storage, bulky conditioners were added, such as ground hulls from cotton, rice, groundnuts, or tobacco stems. Waste organic materials were also used, such as cottonseed meal, fish meal, or "tankage" (ground, dried waste from animal slaughter). These materials also contributed some nutrient value. Ground limestone often was added to neutralize the acidity of superphosphate and thus improve its physical properties.

In an effort to control caking, in many plants the mixtures were stored in bins for several weeks which permitted chemical reactions between ingredients to approach completion. The "cured" material, which was usually severely caked, was crushed to pass a

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[1] Free acid in superphosphate.

6-mesh screen before bagging. This treatment tended to alleviate caking after bagging. In some countries, light ammoniation of the superphosphate was practiced both to improve its physical properties and to supply part of the nitrogen. Either anhydrous ammonia or nitrogen solutions containing ammonia and ammonium nitrate or urea (see chapter X) were used for this purpose. In some cases the superphosphate was ammoniated separately and then used as a base material for preparing other compound fertilizers; in other cases the ammoniation was carried out as a part of the mixing step. Ammoniation decreases the water solubility of the P_2O_5; in countries where water solubility was a criterion of commercial value, ammoniation if practiced at all was limited to that required to neutralize free acid content of the superphosphate.

Granulation of Mixtures of Dry Materials

Two factors influenced the development of granulation of compound fertilizers:

1. The concentration of compound fertilizers was gradually increased in order to minimize costs of transportation, bagging, storage, and handling. In general, the higher the concentration, the worse the caking problems of nongranular compounds.
2. Mechanization of farm fertilizer application equipment developed as farm labor became scarce and more expensive. Mechanical applicators required dependably free-flowing fertilizer and worked best with closely sized material.

The first granulation processes were viewed as an additional step to the previous dry mixing process. The pulverized dry mixture was moistened with water and subjected to mechanical action which caused the mixture to agglomerate in more or less uniformly sized particles. The particles were then dried and screened, the oversize was crushed and recycled either to the screen or to the granulator, and the undersize was recycled to the granulator. In some processes, the product was cooled and coated with a conditioning agent such as clay or kieselguhr to prevent caking. Often a small percentage of oil was sprayed on the granules to ensure adherence of the clay.

In the early development of granulation processes, many diverse types of equipment and processes were tried, and development of new methods and equipment is still continuing. Some of the types of granulators that were more or less successful were: (1) extrusion machines, which produce cylindrical pellets; (2) rotating pans, either horizontal or inclined, some of which were equipped with mixing blades; (3) "pugmills" which are horizontal or inclined U-shaped troughs equipped with rotating blades or pins on one or two shafts to agglomerate the material and move it through the trough; (4) horizontal or slightly inclined rotating drums or tubes, sometimes equipped with internal stirrers; and (5) pear-shaped rotating mixers similar to concrete mixers. In some processes, granulation occurred mainly in the dryer; thus, the function of the mixer was to prepare the material by agitation and moisture addition to a consistency that would promote efficient granulation during drying. Only some of the more common processes and equipment will be described.

The development of processes for granulation by agglomeration of dry materials took place mainly in Great Britain and some European countries. One of the earliest successful processes was the Eirich mixer process, which was widely used in several countries particularly in Europe. The Eirich mixer is a rotating pan, usually horizontal, containing rotating, off-center mixing blades. Granulation is controlled by the addition of water and/or steam. The mixer operates batchwise; successive batches are discharged to a conveyor feeding a continuous dryer. When properly operated, the mixer is capable of doing an excellent job of granulation of compound fertilizers, especially compounds containing superphosphate. It is still used in some plants for making small lots of fertilizer. However, it is not well adapted to large-scale production.

The rotary drum or tube became and still is the most popular method for granulation of compound fertilizers starting with all dry materials. Figure 2 is a flow diagram of a typical granulation plant of this type. The process is often called "steam granulation."

Incoming materials are screened to remove lumps which are crushed. The materials are weighed batchwise to a feed hopper from which the mixture is fed continuously at a controlled rate to the granulator. In some cases, a mixer precedes the granulator. The most common type of granulator is a rotating cylinder with a retaining ring at the feed end but none at the discharge end. It is usually horizontal or very slightly inclined toward the discharge end. Depending on the design capacity, the granulator may be 1.0-2.5 m in diameter by 3-10 m long.

Steam is discharged under the bed of material at the feed end, and water is sprayed on the bed through spray nozzles located at two or more points along the axis. Granulation is controlled by the amounts of steam and water added.

In theory, for each mixture there is a percentage of "liquid phase" at which granulator efficiency is optimum. The liquid phase consists of the moisture content plus the salts that will dissolve in that amount of water. Since the solubility of fertilizer salts increases with temperature, the higher the temperature the less water is required. Thus, for any given mixture there is an optimum moisture content for each temperature which may be described by a curve such as figure 3. The main advantage of steam granulation as opposed to use of water only is that granulation occurs at a lower moisture content. As a result, less drying is required, and the dried granules are more dense and usually stronger.

A. T. Brook has given an excellent account of the development of steam granulation and the important factors in the process (1).

The importance of temperature and moisture content and their interrelation have already been mentioned. Temperatures in the range of 70°-95°C, measured at the granulator exit, are usual. The optimum moisture content depends on the formulation and may be as high as 7% or as low as 2%.

The speed of rotation of the rotary drum granulator is quite important in order to produce a combination rolling and cascading action. Brook determined that the optimum speed is 50% of the "critical speed," which is defined as the speed at which material could just be carried completely around the drum by centrifugal action. Brook's formula for the critical speed in rpm is $76.5/\sqrt{d}$, where d is the drum diameter in feet. If the drum diameter is in meters, the formula becomes $42.3/\sqrt{d}$. Thus, for drum diameters of 1 and 2 m, the critical speeds are 42.3 and 29.9 rpm, and optimum speeds are about 21.1 and 15.0 rpm. There may be some mechanical difficulties in rotating large granulators at relatively high speeds, but satisfactory results can be obtained at somewhat lower speeds.

A common criterion for granulator capacity is its inside cylindrical area; a range of 20-30 ft^2/short ton of product/hour is considered satisfactory (2). The metric equivalent is roughly 3-4 m^2/mt/hour. Thus, a granulator 2.0 m in diameter by 6.0 m long will have an inside surface area of about 37.7 m^2 and a capacity of roughly 9-12 mt of product per hour for best results. Acceptable granulation can be obtained at considerably higher production rates.

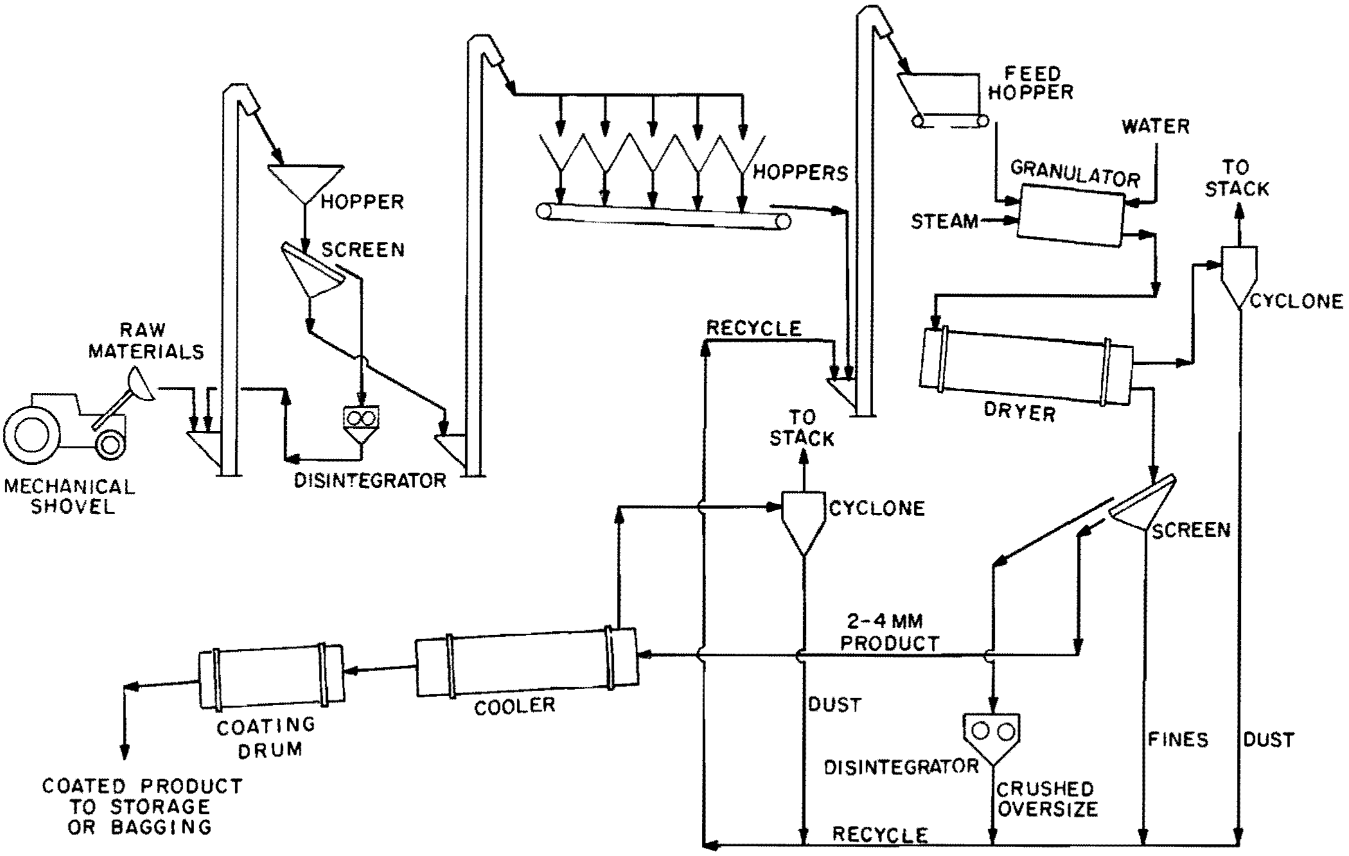

Figure 2. Typical Plant for Granulation of Dry Materials.

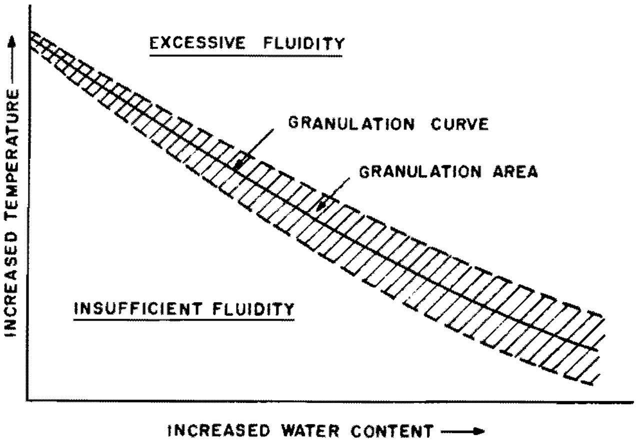

Figure 3. Relationship of Temperature and Water Content to Granulation of Fertilizers.

The bed depth at the feed end should be deep enough to absorb the steam from the steam nozzle. Increasing the bed depth by means of a retaining ring at the discharge end does not appear to be helpful and adds unnecessarily to the power requirement for rotating the granulator.

The plasticity of the mix is important but difficult to define or measure. Pure salts such as potassium chloride or sulfate and ammonium nitrate or sulfate have little plasticity and are very difficult to granulate. Superphosphates (single or triple) have good plasticity, and mixtures containing them are easily granulated. Ammonium phosphates made from wet-process acid have plasticity in proportion to their impurity content. Formulations that are lacking in plasticity can be granulated by addition of binders such as clay.

The particle size of the feed materials has some effect on granulation efficiency (3). It is helpful to have some of the particles in the feed material coarse enough to form nuclei for the granules. Thus, coarse potash salts are preferred for granulation of some grades that are otherwise difficult to granulate.

Brook gives examples in which granulation efficiencies in the order of 80% were obtained consistently (1). Granulation efficiency is defined as the percentage of the product leaving the granulator that falls within the desired size range. In the case of Brook's examples, the desired size range was either 1.8-4.0 mm or 2.0-3.75 mm. The overall granulation efficiency for the entire plant may be greater or less than that measured at the granulator because of disintegration or agglomeration in the dryer, cooler, and accessory equipment. However, recycle:product ratios of 0.3-0.5 can be attained in a well-operated plant.

The steam requirement may vary with the formulation. Brook gives examples of 75-90 kg per ton of product. Low-pressure steam was used.

Methods for obtaining the desired granulation temperature other than steam injection have been used. In some plants, gas flames are directed on the surface of the material in the granulator. The shell of the dryer may be heated. Using hot rather than cold water helps conserve steam. Some plants use hot ammonium nitrate solution as the source of nitrogen. A common practice is to supply heat through chemical reactions. This practice will be described in the next section.

The formulations used in granulation of dry materials during the 1950s contained mainly ammonium sulfate, single and triple superphosphate, and potassium chloride. Gradually analysis has been increased by replacing ammonium sulfate with ammonium nitrate (solid or solution) or urea. Single superphosphate has been gradually replaced by triple superphosphate or by powdered monoammonium phosphate. During this transition, many of the larger European plants shifted to slurry processes based on ammonium phosphate-nitrate (chapter XIV) or nitrophosphates (chapter XV). However, granulation of dry materials is still a useful process for small plants both in Europe and many developing countries.

The remainder of the plant (following the granulator) is generally similar for all granulation processes; it consists of a dryer, a cooler, screening facilities, and facilities for dust collection and for recycling fines and oversize.

In dry-mix granulation plants, the screening unit often follows the dryer, and fines are recycled to the granulator while they are still hot to conserve heat. Oversize is crushed and recycled to the granulator or to the dryer or sometimes to the screening unit. Since oversize may be incompletely dried, it is often preferable to recycle it to the dryer after it is crushed rather than to the screening unit. In most European plants the cooled product is conditioned by coating it with 0.3%-1.0% of oil followed by 1%-2% of clay.

Granulation with steam and water is a useful process for small plants, especially where acids and ammonia are not readily available. Whyte described a modern plant of this type which is located in Scotland (4). Its versatility is illustrated by the four types of products it produces:

1. Single superphosphate-based compounds, such as 9-9-9 and 6-15-6.
2. Compounds based on nongranular monoammonium phosphate, such as 10-20-15, 12-12-18, and 15-10-10.
3. Compounds based on urea and nongranular monoammonium or diammonium phosphate, such as 20-10-10.
4. NPK compounds based on organic materials for horticultural use.

Roll Compaction--A relatively new method for granulating dry-mixed fertilizers is roll compaction. Unlike other granulation processes, compaction works best at low-moisture levels such as 0.5%-1.5%. Therefore, drying and cooling are not necessary.

Compaction is used on a large scale for granulating ammonium sulfate and potassium chloride. The process is described in chapter XVIII (Potash Fertilizers). Relatively little use of the process has been made for granulation of compound fertilizers. However, a recent paper describes a plant used in Germany to produce small lots of granular fertilizers for specialty use at rates of 3-7 tph (5). While some materials are difficult to granulate by compaction, other materials that are difficult to granulate by other methods can be granulated by compaction.

One of the advantages of compaction is that high temperatures are not necessary; heat-sensitive organic materials may be included in the formulation without danger of harm. Although large-scale units are in use, the economies of scale are relatively unimportant; thus, small units can be economical. Small lots of different grades may be made easily since the time required to change from one grade to another is short, and there is little in-process material.

One disadvantage of compaction of compound fertilizers is that the different materials in the formulation may react with each other after granulation, which may cause disintegration of the granules in some cases. Some possible reactions of dry mixed fertilizers are mentioned in an earlier part of this chapter.

Granules made by compaction tend to be blocky and angular rather than round. The shape is not particularly important but may be viewed with disfavor by farmers who are accustomed to well-rounded granules.

Granulation of Dry Materials With the Addition of Materials That React Chemically

Granulation developed later in the United States than in England and other European countries and followed a different course. With the exception of a few early plants, U.S. granulation was based on chemical reactions. Ammoniation of superphosphates was the principal reaction at first; the addition of sulfuric acid or phosphoric acid with more ammonia followed.

Some reasons for the different course of development are:

1. Ammoniation of superphosphates was already a common practice in the United States before granulation. Nitrogen solutions containing ammonia and ammonium nitrate or urea were available and were usually the lowest-cost form of nitrogen available to compound fertilizer manufacturers.
2. Ammoniation of superphosphate decreases its water solubility which is of little concern in the United States where solubility in neutral ammonium citrate is the standard for phosphate fertilizers. In contrast, England and some other countries use water solubility for evaluating P_2O_5 content of fertilizers.

The reactions occurring during ammoniation of superphosphate and their effect on water solubility have been described by Keenan and later by White, Hardesty, and Ross (6, 7). The reactions are listed below in the sequence in which they are believed to occur.

$$H_3PO_4 + NH_3 = NH_4H_2PO_4$$
(Equation 11)

$$Ca(H_2PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4$$
(Equation 12)

$$NH_4H_2PO_4 + NH_3 + (NH_4)_2HPO_4$$
(Equation 13)

$$3CaHPO_4 + 2NH_3 = (NH_4)_2HPO_4 + Ca_3(PO_4)_2$$
(Equation 14)

$$2CaHPO_4 + 2NH_3 + CaSO_4 = Ca_3(PO_4)_2 + (NH_4)_2SO_4$$
(Equation 15)

$$NH_4H_2PO_4 + NH_3 + CaSO_4 = CaHPO_4 + 2(NH_4)_2SO_4$$
(Equation 16)

Equations 11 and 12 apply to both single and triple superphosphate.
Equations 13 and 14 apply to triple superphosphate ($CaSO_4$ absent).
Equations 15 and 16 apply to single superphosphate ($CaSO_4$ present).

In ammoniation of triple superphosphate, in which calcium sulfate is absent or present in minor proportions, reactions 11 and 13 do not affect P_2O_5 water solubility, reaction 12 decreases water solubility to about 50%, and reaction 14 increases water solubility. In pilot-plant experiments, Yates, et al., determined the effect of ammoniation of TSP on P_2O_5 water solubility experimentally (8). The results are shown in figure 4. It is evident that the experimental results agreed roughly with the theory; as the extent of ammoniation increased, water solubility decreased to a minimum of about 50% and then increased slightly.

In ammoniation of single superphosphate, the calcium sulfate participates in the reaction as shown in reactions 15 and 16, with the result that P_2O_5 water solubility continues to decrease with increasing

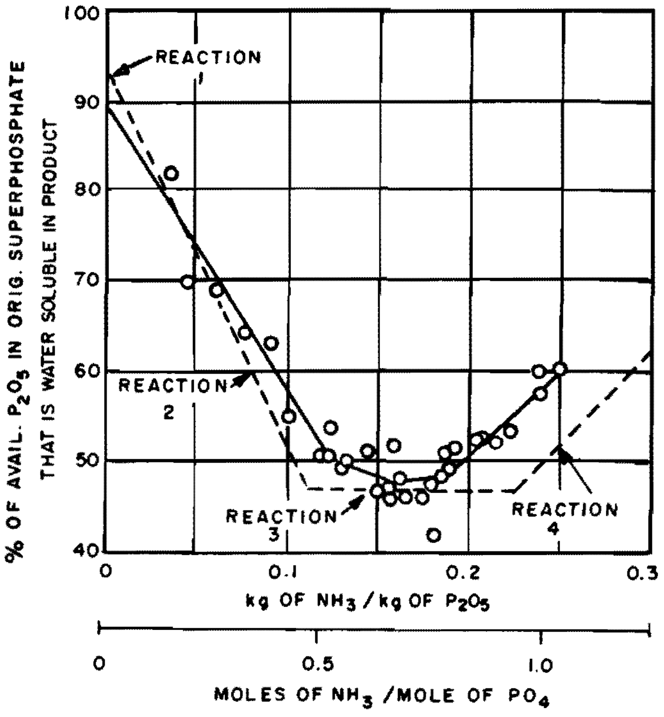

Figure 4. Effect of Ammoniation on Water Solubility of P_2O_5 in Triple Superphosphate.

extent of ammoniation. Experimental data shown in figure 5 confirm this effect; water solubilities as low as 20% were obtained when the extent of ammoniation reached an $NH_3:P_2O_5$ mole ratio of 2.8. The phosphate compound formed in reactions 14 and 15 is shown as tricalcium phosphate, $Ca_3(PO_4)_2$. However, more recent studies have indicated that an apatitic compound is formed which is soluble in neutral ammonium citrate but not in alkaline ammonium citrate. Dicalcium phosphate (formed in reactions 12 and 16) is soluble in either neutral or ammonium citrate.

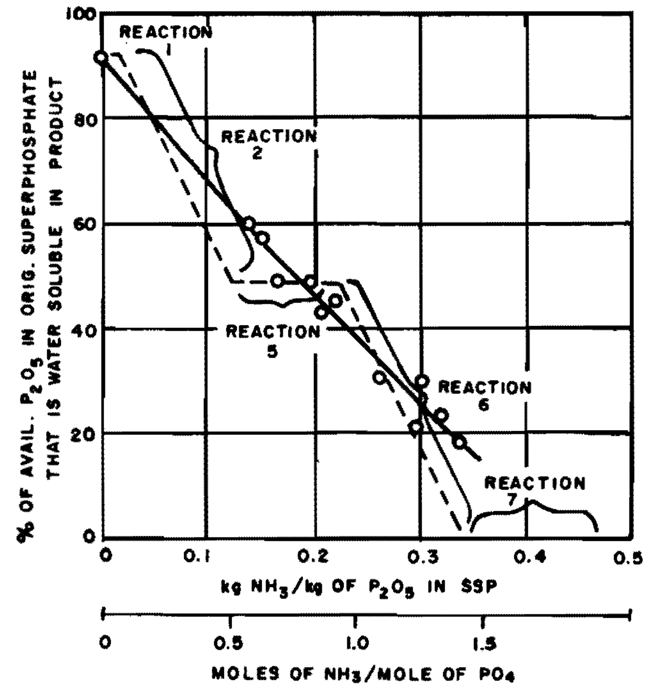

Figure 5. Effect of Ammoniation on Water Solubility of P_2O_5 in Single Superphosphate.

The development by TVA of a continuous ammoniator-granulator had a significant effect on the development of granulation processes in the United States. The continuous ammoniator originally was developed for more efficient ammoniation of superphosphate as compared with batch mixers that were in common use (8). However, it was found that granulation often occurred during ammoniation and could be controlled by addition of water or steam or by adjusting the formulation to provide sufficient chemical heat. Formulations were developed to provide enough heat of reaction to raise the temperature of the mixtures to a range of 80°-100°C to permit granulation with minimum moisture content (9). When the heat of the reactions involved in ammoniation of superphosphate was insufficient, sulfuric or phosphoric acid was added along with more ammonia to increase the total chemical heat. Granulation of two grades (6-12-12 and 10-20-20) was demonstrated in the TVA pilot plant in 1953; by 1962, 164 plants in the United States were known to be using the TVA process, probably about two-thirds of all U.S. granulation plants. Later the process was adapted to receive a slurry produced by reaction of ammonia or ammoniating solution with sulfuric or phosphoric acid for use with formulations in which the heat of reaction was too great for release in the ammoniator-granulator, and eventually all slurry processes were carried out in this type of equipment. The TVA ammoniator-granulator is described in U.S. Patent 2,729,554; a sketch of one of TVA's early pilot-plant units is shown in figure 6. A sketch of a large-scale unit used by TVA in a slurry granulation process is shown in figure 7. A diagram of a typical plant using a TVA ammoniator-granulator is shown in figure 8.

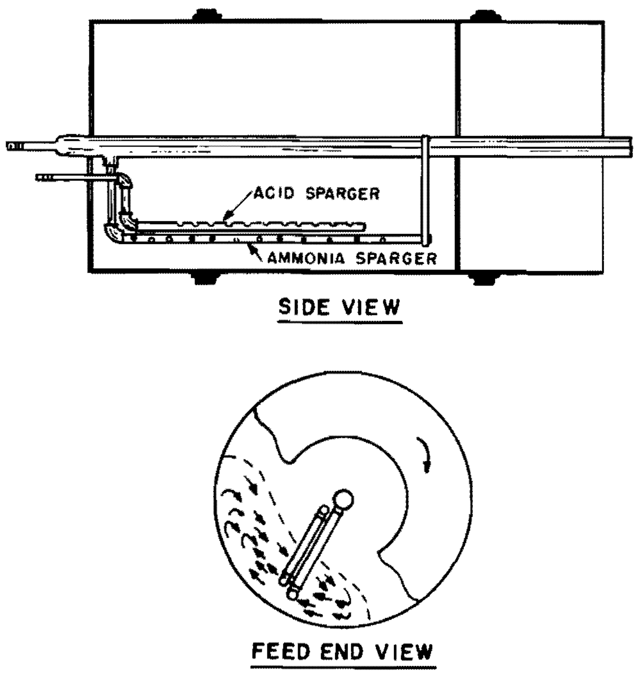

Figure 6. Sketch of TVA Pilot-Plant Ammoniator-Granulator.

During the past 15 years TVA has collected numerous ammoniation-granulation formulations that have provided excellent results during production runs in plants using a TVA ammoniator-granulator. These formulations have been used to calculate empirical liquid-phase factors that have been used to determine the total liquid phase in each formulation. These liquid-phase factors are shown in table 1. The total liquid phase is calculated by multiplying the weight of each material used in the formulation by its appropriate liquid-phase factor (table 1). The total heat in the formulation is calculated by multiplying the weight

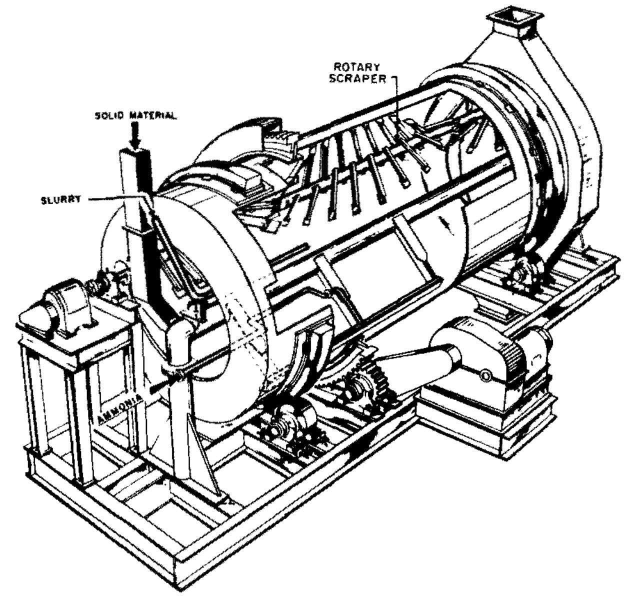

Figure 7. Cut-Away View of Large-Scale Ammoniator-Granulator.

of ammonia that reacts with each material by the appropriate heat of reaction shown in table 2. Experience has shown that usually good granulation occurs when the total amount of chemical heat used in the formulation is between 160,000 and 180,000 Btu/short ton of product (44,441-49,997 kcal/mt), provided the total liquid phase in the formulation is between 600 and 800 lb/short ton (300-400 kg/mt). All of these factors have been incorporated into a computer program which is used to determine least-cost formulations for these types of plants (10).

The principle of combining chemical reactions with granulation was utilized in various other processes. In some processes, ammoniation and granulation were carried out in a pugmill. In some plants that had drum-type batch mixers for preparing nongranular mixtures, the mixer was altered to serve as a combination mixer-ammoniator-granulator.

The number of compound fertilizer granulation plants in operation in the United States has decreased from a high of about 250 in 1962 to 118 in 1976; those remaining in operation are the larger ones. According to a 1976 estimate by Hargett and Sills, 58% of the compound fertilizer sold in the United States was bulk blends, 14% was fluids, and 28% was granular (chemically mixed) (11). Thus, bulk blending and liquid mixing have largely replaced granulation as a method for producing compound fertilizer.

In most other countries granulation is the principal method for producing compound fertilizers, but no data are available as to how this capacity is divided among various types of granulation processes.

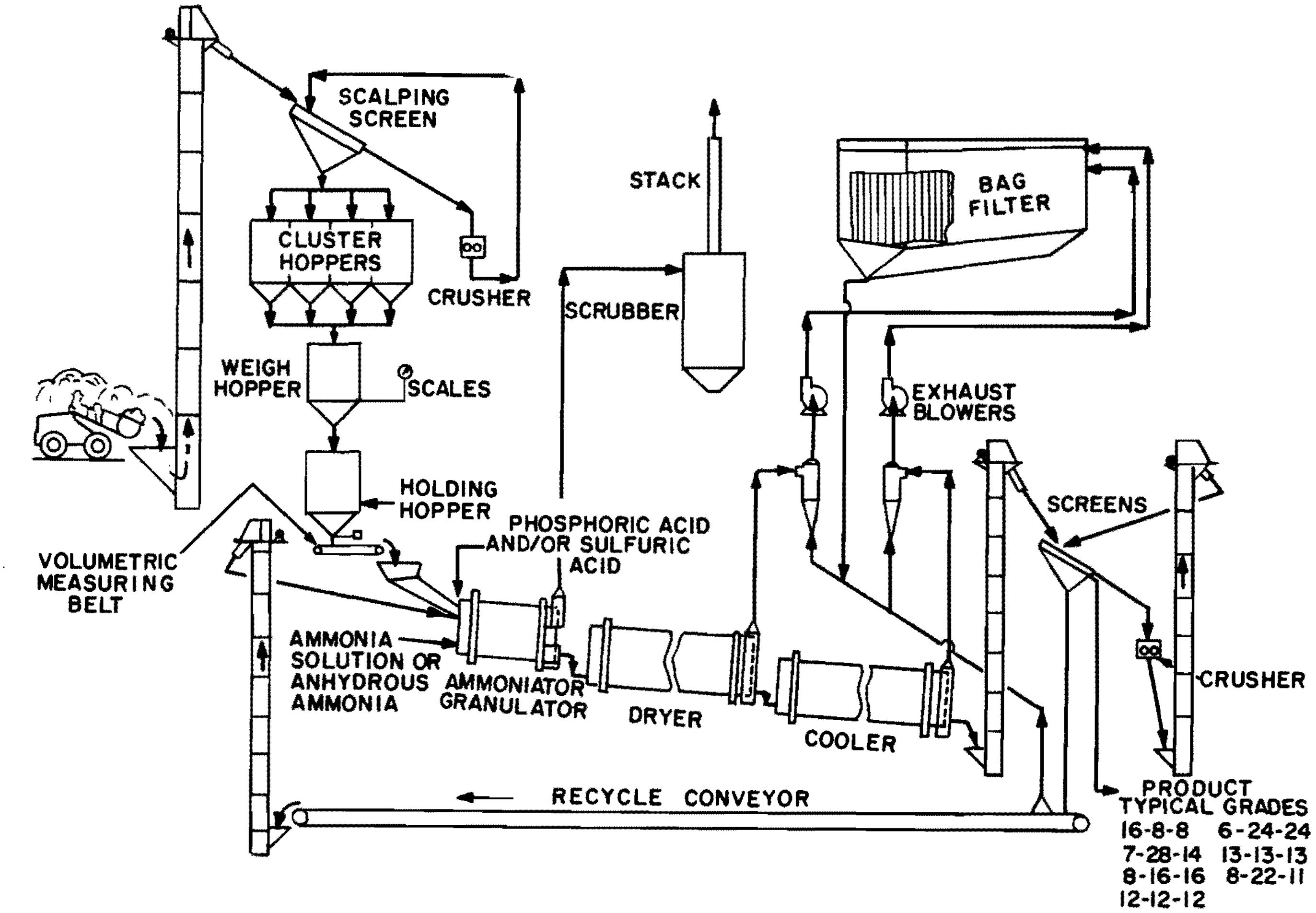

Figure 8. TVA-Type Ammoniation-Granulation Plant for NPK Mixtures.

Slurry Granulation

Slurry granulation processes may be defined as those processes in which all or most of the materials entering the granulation process are in the form of a slurry. The slurry usually is prepared by reaction of nitric, phosphoric, or sulfuric acid or some mixture of these acids with ammonia and (in some cases) phos-

TABLE 1. EMPIRICAL FACTORS FOR LIQUID PHASE IN A GRANULATION FORMULATION

Material	Liquid Phase, lb/lb of Material or kg/kg
Anhydrous ammonia	0.50
Ammoniating solution	1.00
Orthophosphoric or sulfuric acid	1.00
Superphosphoric acid	1.00
Water or steam	2.00
Ammonium sulfate	0.10
SSP	0.10
TSP	0.20
Granular KCl	0.30
Fine KCl	0.00
30-10-0 or 25-25-0	0.50
18-46-0	0.25
21-53-0	0.20
MAP	0.20

Multiply the weight of each raw material in the formula by the appropriate empirical factor to obtain the total weight of the liquid phase. This total weight should be about 600 lb/short ton (300 kg/mt) for good granulation, but it will be subject to judgment.

TABLE 2. HEAT OF REACTION OF AMMONIA WITH VARIOUS MATERIALS

Material	Btu/lb NH_3			kcal/kg NH_3		
	NH_3 Gas	NH_3 Liquid	NH_3 Solution[b]	NH_3 Gas	NH_3 Liquid	NH_3 Solution[b]
Phosphoric acid[a] (to MAP)	3,402	2,465	2,200	1,890	1,369	1,222
Phosphoric acid[a] (to DAP)	2,719	1,782	1,517	1,511	990	843
MAP to DAP	2,036	1,099	834	1,131	611	463
Triple superphosphate	2,845	1,908	1,643	1,581	1,060	913
Single superphosphate	2,630	1,693	1,428	1,461	941	793
Sulfuric acid	3,898	2,961	2,696	2,166	1,645	1,498

a. Phosphoric acid concentration about 54%; product (MAP or DAP) assumed to be in solid phase.
b. NH_3 in NH_3-NH_4NO_3-H_2O ammoniating solution.

phate rock. Such processes have been described in chapters XIV and XV under the headings "Ammonium Phosphates," "Ammonium Phosphate-Sulfates," "Ammonium Phosphate-Nitrates," "Urea-Ammonium Phosphates," and "Nitrophosphates." In each of these processes, solid materials such as potash salts may be added to the slurry before granulation or mixed with it in the granulator to produce a variety of NPK compound fertilizers. In some processes, part of the chemical reactions may be carried out in the granulator. The granulator is usually either a rotary drum or some type of pugmill or blunger. Recycled product is added, usually in the granulator, in sufficient proportions to decrease the liquid phase to the proper level for granulation.

The Spherodizer, a proprietary device developed by C&I Girdler, is a spray-drum granulator in which granulation and drying are combined. The "cold Spherodizer" for granulating and cooling melts of ammonium nitrate or urea has been described in chapter IX. The "hot Spherodizer" is used for granulating and drying slurries. It has become quite popular for nitrophosphate granulation and more recently for ammonium phosphate-nitrates. Also, urea-ammonium phosphate has been granulated and dried successfully (12). In the hot Spherodizer process, the neutralized slurry containing potash is sprayed against a falling curtain of solid particles in a rotary drum; flights in the drum lift the particles and cycle them through the spray. Heated air for drying is blown in concurrently to the spray. Typical inlet air temperature is 180°-200°C. Since the granules cycle through the spray many times before they leave the drum, a layering type of granulation and rapid evaporation of water are obtained. Most of the granules leaving the drum are on-size; only a small proportion is recycled. The process produces closely sized, well-rounded, hard granules which are generally considered to be of excellent quality. Granule size may be varied, but 2-4 mm is typical for European units.

One disadvantage of the Spherodizer is that large capacities require very large units or multiple units. Units 3.0-3.6 m in diameter have capacities of 250-300 tpd, units 4.25 m in diameter produce 500-700 tpd, and the largest unit, 4.50 m in diameter by 12.0 m long, operates at 600 tpd although the capacity may be greater. A unit 5.25 m in diameter was planned for capacities in the range of 1,000-1,300 tpd. Such large units are not easily transported to the plant site unless the site is accessible to waterways.

All of the Spherodizer feed must be in the form of a slurry, which could result in the need for adding water for grades of unusually high potash content.

Another example of drying during granulation is the Scottish Agricultural Industries' double-drum granulator with internal recycle. The outer drum of the granulator is 15 ft in diameter by 30 ft long (4.6 x 9.1 m), and the inner drum is 9 ft in diameter (2.7 m). The rate of rotation is 14 rpm (4).

Mixtures of nitric acid (65%-69% HNO_3) and phosphoric acid (28%-39% P_2O_5) are neutralized with ammonia in two stages to a pH in the range of 4.5-6.0. The heat of reaction evaporates much of the water; thus, the neutralized liquor contains only 10% water and its temperature is 140°-145°C. This liquor is injected into the granulator through a sparger under the rolling bed in the outer drum. The granules leaving the outer drum are elevated by means of internal buckets and discharged to the inner drum where potash salts and recycled material are added. The material from the inner drum discharges by gravity to the outer drum, thus maintaining a high rate of internal recycle estimated at 500 tph. Air, heated by combustion of fuel, is blown through the outer drum for drying. A portion of the product leaving the outer drum is drawn off for screening at 1.5-3.5 mm. The undersize and cracked oversize are recycled to the inner drum. The granules leaving the granulator-dryer have a moisture content of 0.3%-0.8% and a temperature of 75°-95°C depending on the grade. The onsize granules are cooled in a fluidized bed cooler to 35°C and then coated with oil and clay in a rotary drum. Product grades range from 15½-15½-21 to 27-7-7.

Another process that involves drying during granulation is the fluidized bed process developed by Montecatini and described by Arzani (13). In this process, neutralized ammonium phosphate-nitrate slurry is mixed with potash salts and recycled material and injected upwardly into a "spouted bed" conical granulator concurrently with a stream of hot gas. At the center of the bed where the gas velocity is highest, the granules travel upward; at the periphery of the bed, they travel downward, thus producing a circulating action. Each passage through the spray area adds a thin coating to the granules.

Further development of the spouted bed technique for granulation of fertilizers has been reported by Berquin (14). The feed material may be a solution or slurry with a stream of hot gas for drying or a melt with a stream of unheated air for cooling. In addition to compound fertilizers such as 17-17-17, various grades of ammonium phosphate and ammonium sulfate-phosphate have been granulated experimentally, as well as urea and other nitrogen fertilizers and triple superphosphate. The granules are well-rounded, hard, and closely sized. Recycle ratios of the order of 2:1 were reported. Ando reported in 1970 that a fluidized or spouted bed granulation process had been developed in Japan by Ube Industries and was in commercial use for granulating compound fertilizers (15).

The obvious advantage of combining granulation and drying is the elimination of one major piece of equipment. Also, heat for drying may be utilized more efficiently than it would be in a separate dryer with a high recycle ratio.

Melt Granulation Processes

Since the dryer usually is the largest and most expensive unit in a granulation plant, melt granulation processes have a strong advantage in eliminating the need for this unit. The saving in fuel for drying is a further advantage. Usually energy is required to evaporate water in some stage of the process by concentrating phosphoric acid or by evaporating water from solutions to produce a melt. Thus, the saving in fuel for drying the granular product is partially offset by the additional energy spent in producing the melt. However, energy is utilized more efficiently in evaporating water from solutions than in drying granular products; therefore, there is some net savings. Also, there are some combinations of processes in which the heat of reaction is sufficient to evaporate all of the water. For example, phosphoric acid can be produced at concentrations of 50% P_2O_5 or higher (chapter XIII), and nitric acid can be produced at concentrations in the range of 65%-75% HNO_3 without external heat. The heat of reaction of these acids with ammonia may be sufficient to evaporate their water content. The production of sulfuric acid creates excess energy as steam which can be used for concentrating other acids or solutions. Furthermore, the reaction of sulfuric acid with ammonia is highly exothermic. Mixtures of sulfuric acid with phosphoric and/or nitric acid often provide enough energy by reaction with ammonia to produce anhydrous melts.

Melt granulation processes for producing monoammonium phosphate, ammonium phosphate-nitrate (APN), or urea-ammonium phosphate (UAP) have been described in chapter XIV and (for nitrogen fertilizers) in chapter VIII. In these processes, potash salts and other solid materials can be added to produce NPK granular products. Methods for producing granules from melts include flaking (solidification on water-cooled surfaces of a drum or belt), prilling, pan granulation, spray-drum granulation, rotary drum granulation, and pugmill granulation.

The Fisons' melt granulation process is in commercial use in England (16). Early research by Fisons has shown that the eutectic mixture between ammonium nitrate and monoammonium phosphate melted at a temperature well below even that of ammonium nitrate (170°C). In practice the melt is produced by reacting wet-process phosphoric acid (50% P_2O_5) with the ammonia in stirred tanks with the addition of 92% ammonium nitrate solution. In this stage, the NH_3:PO_4 ratio is kept below that of monoammonium phosphate (MAP) to avoid ammonia loss. In a second stage, ammoniation is completed to MAP and the water evaporated by a countercurrent stream of hot air in a stripping column. The melt could be granulated by flaking or any common granulating equipment. In practice rotary drum granulators are used since they are available in conventional granulation plants.

The TVA pipe-reactor process has been in use for several years in various applications to produce ammonium polyphosphate (APP) melts or solutions. A demonstration-scale plant is in operation at Muscle Shoals, Alabama, which uses a pipe reactor to produce 16 tph of granular APP (11-55-0 to 11-57-0 or 28-28-0 (17). A flow diagram of the process is shown in figure 9. Phosphoric acid (54% P_2O_5) is partially preneutralized in a spray tower and then reacted with preheated, gaseous ammonia in a pipe reactor made of 316L stainless steel about 15 cm in diameter by 3 m long. The reaction temperature is 210°-230°C. The melt, which is foamy when using Florida black acid, goes to a vapor disengager and then to a pugmill for granulation with recycled, cooled fines. The product contains about 15%-25% of the P_2O_5 as polyphosphates, mainly pyrophosphate. The proportion of polyphosphate is controlled by the extent of preheating the ammonia and acid and by the concentration of the acid. For production of 28-28-0, urea melt is added to the recycled fines in the pugmill near the feed end.

In pilot-plant tests, a rotary-drum granulator has been used successfully, and potash has been added to produce several NPK grades. Urea can be added either as a melt or in solid form, or alternatively ammonium nitrate (melt or solid) may be used. The vapor disengager is not necessary in this arrangement because steam is flashed off from the melt in the granulator. Also, the preneutralizer can be omitted, and the small amount of ammonia in the vapor leaving the granulator can be recovered in a scrubber with phosphoric acid. The ammonium phosphate scrubber solution is returned to the granulator. There is sufficient heat in the hot granular material to evaporate the water in the scrubber solution. In some process modifications, more ammonia is added in the granulator. Figure 10 shows the pilot-plant granulator-pipe-reactor combination, and figure 11 shows a diagram of the entire pilot plant.

A further modification of the TVA melt-granulation process involves the use of the "pipe-cross reactor" in which sulfuric acid and phosphoric acid react with ammonia to form a melt which is sprayed into the rotary-drum granulator (18). The use of sulfuric acid increases the heat of reaction so that a melt can be produced with phosphoric acid concentrations below 54% P_2O_5 or without preheating the reactants. Alternatively, the additional heat may be used to generate more polyphosphate which improves granulation. Several commercial-scale granulation plants in the United States and some other countries are using this pipe-cross reactor process to make a variety of compound fertilizers, such as 12-48-0, 10-40-0, 6-24-24, and 13-13-13 (19, 20, 21). In some modifications, part of the phosphoric acid is added directly to the granulator together with ammonia to react with it. This arrangement gives better granulation of some grades (22). In other modifications, the pipe reactor is used to produce a low-moisture hot slurry rather than a melt when further ammoniation is carried out in the granulator.

A somewhat similar system is used by the firm S.A. Cros in Spain although, in this case, the pipe reactor is used to produce a slurry containing 5%-10% moisture which discharges into a pan granulator followed by a drum ammoniator-granulator (23). The

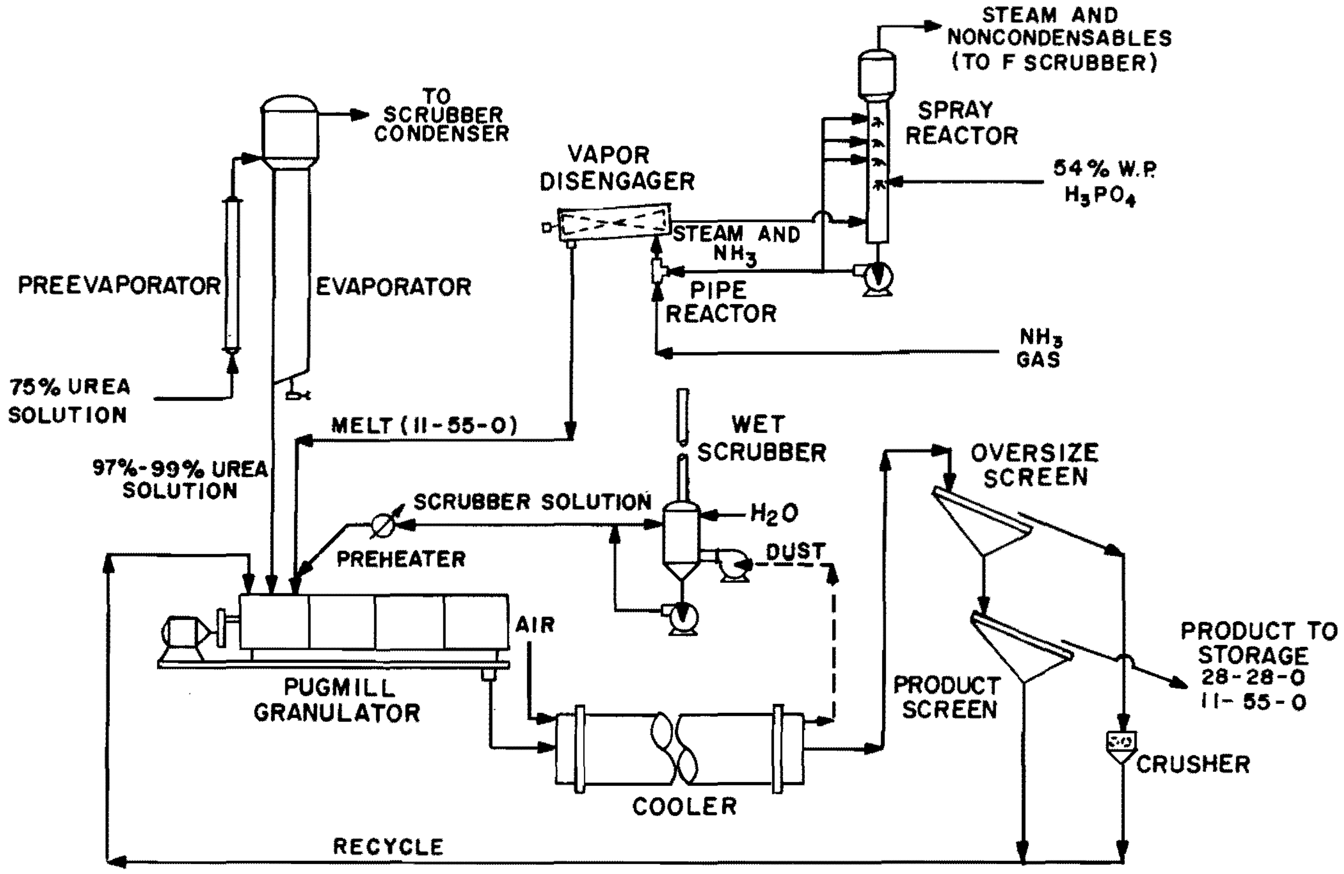

Figure 9. TVA Pipe Reactor–Pugmill Process for Production of Granular Urea–Ammonium Polyphosphate.

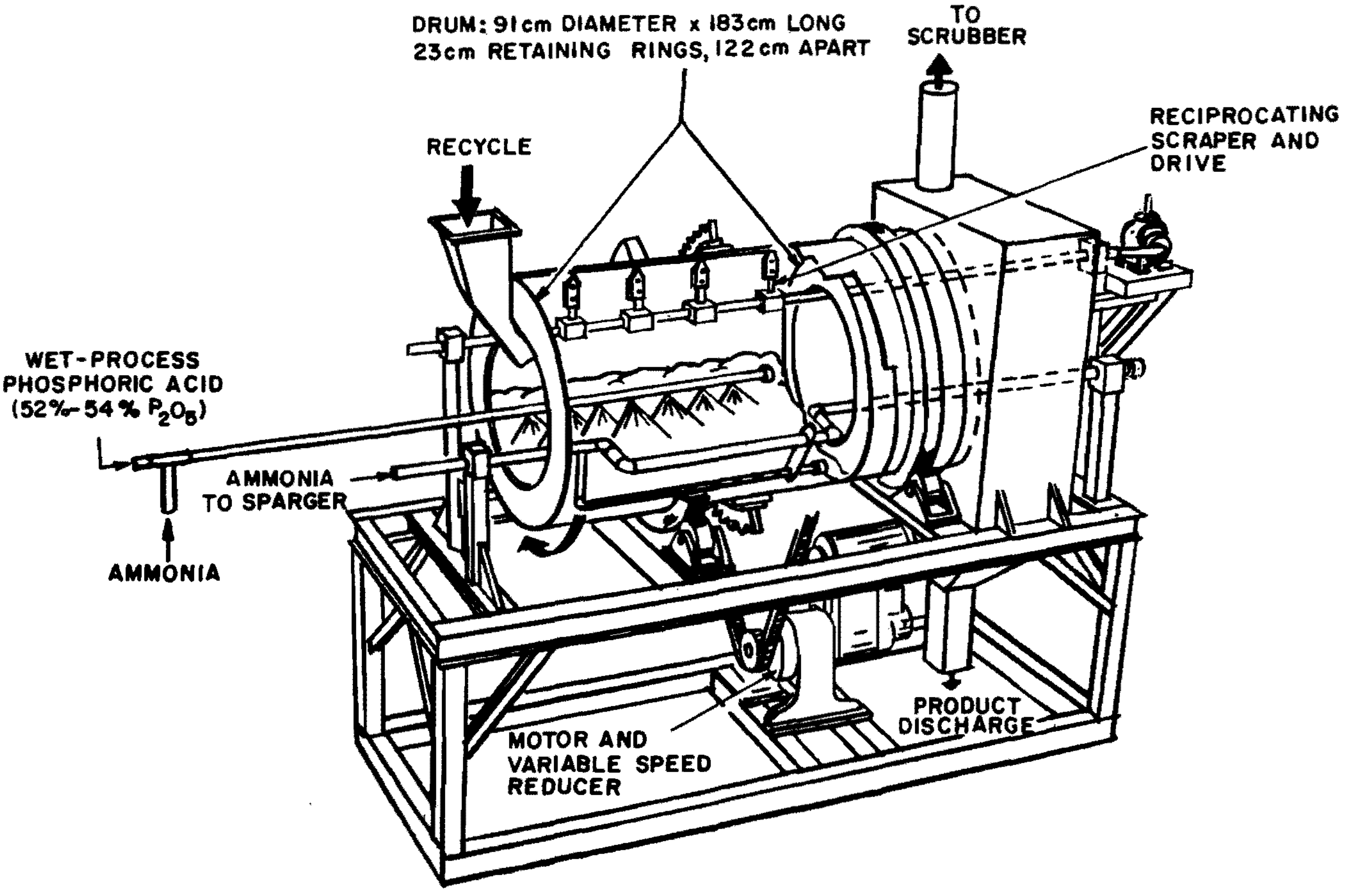

Figure 10. Sketch of Pipe Reactor and Rotary-Drum Granulator.

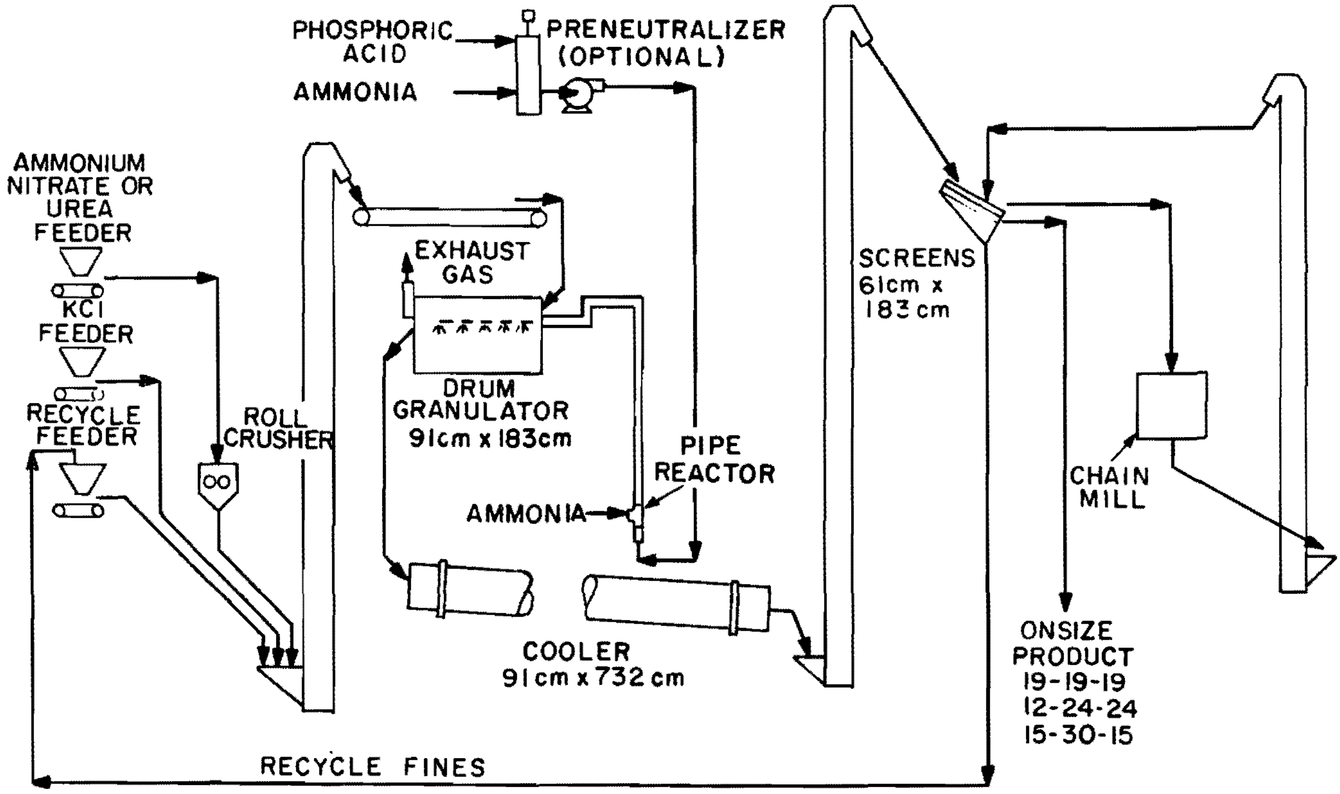

Figure 11. Flow Diagram of Granulation Pilot Plant Using Pipe-Reactor Process for NPK Fertilizers.

granules contain 2%-4% moisture and must be dried. A wide range of grades made with the addition of urea or ammonia in a ratio of 2:1 was reported. Diammonium phosphate can be produced by further ammoniation in the drum granulator (see chapter XIV).

Prilling Compound Fertilizers

Prilling may be viewed as a special type of melt granulation. It was one of the first methods for producing granular fertilizer; it was first applied to Chilean nitrate of soda about 1930. The nitrate of soda was melted at about 400°C and sprayed into a tower. The falling droplets were cooled by an ascending airstream which produced nearly spherical particles of about 10- to 20-mesh size.

Prilling has subsequently become a favored method for granulating ammonium nitrate, urea, and potassium nitrate. In these cases, the material to be prilled is a single chemical compound; it is sprayed into the prilling tower in the form of a melt or highly concentrated solution at a temperature somewhat higher than its melting point.

Prilling compound fertilizers containing two or more chemical compounds is a relatively new development. Mixtures of ammonium phosphate and ammonium nitrate (APN) form a fluid melt at temperatures even lower than the melting point of ammonium nitrate (170°C), and therefore they are relatively easy to prill. TVA reported prilling of APN mixtures in small-scale equipment in 1955 (24). Monsanto workers patented a method of prilling mixtures of monoammonium phosphate and ammonium nitrate in 1960 and produced limited quantities of 29-14-0 (25). Prilling NPK compounds involves more problems. Potassium chloride or sulfate has such a high fusion temperature that very little of it could be expected to dissolve in molten urea or ammonium nitrate at temperatures at which these materials are stable. However, melts containing up to 50% of solids in suspension can be pumped and sprayed provided suitable precautions are taken to prevent settling of solids and clogging of spraying equipment (26).

The preferred drop-forming equipment is a rotating, perforated cup with an internal scraper. This equipment is described in some detail by van den Berg and Hallie (27). The size of the droplets is controlled by the diameter of the holes in the cup, the rate of rotation, and the properties of the melt. One advantage of the prilling cup is that it is so compact that it can readily be removed for cleaning. In comparison, shower-head sprays are relatively more difficult to clean.

Prilling of NP and NPK compounds containing ammonium nitrate has been developed on a commercial scale by the Dutch State Mines (Stamicarbon process) and by Norsk Hydro (Norway). Both firms have licensed their processes to other manufacturers; the total number of commercial installations is not known. In both cases the prilling process was originally used for prilling nitrophosphate compounds which contain mainly ammonium nitrate, monoammonium phosphate, and dicalcium phosphate. However, Albright and Wilson have adapted the Stamicarbon process to a variety of ammonium phosphate-nitrate compounds with potash added as the chloride.

A brief description of the process as carried out by Albright and Wilson follows which is derived mainly from Proceedings of the Fertiliser Society (London) No. 141 (1974) (28):

Ammonium nitrate solution is produced by pressure neutralization of nitric acid with ammonia. The resulting solution is concentrated from 72% to 92%-94% in a vacuum evaporator using exhaust steam from the pressure neutralizer. The solution is then mixed with wet-process phosphoric acid which has been concentrated to 50% P_2O_5. The mixture is neutralized with ammonia to the monoammonium phosphate stage and concentrated in a vacuum evaporator to form a melt at 175°C which contains about 0.5% moisture. This melt is pumped to the top of the prilling tower where it is mixed with preheated, fine potassium chloride in a special mixer. The mixture discharges directly into a rotating prilling cup or "bucket."

The droplets cool and solidify as they fall through an ascending airstream in the prilling tower. The prills are collected at the bottom of the tower and cooled further in a rotary cooler. The product is screened between 1.2 and 4.0 mm; the oversize (mainly clusters of prills) is crushed; and fines, amounting to between 3% and 8% of the throughput, are recycled to the mixing vessel at the top of the prill tower. Some of the grades produced are 25-9-9, 22-11-11, 17-9-22, and 15-15-21.

One special requirement of the process is that the potash must be ground fine enough to prevent clogging of the holes in the prilling cup and preheated to a temperature sufficiently high to prevent chilling of the melt. The preferred particle size is smaller than 300 µm, and the preferred temperature range is 140°-160°C. However, very fine potash is undesirable because it is more difficult to mix with the melt in the mixer. The potash is prepared in a combination drying, grinding, and heating plant and pneumatically conveyed with hot air to a feed hopper at the top of the prill tower. Any trash such as wood splinter, paper, or tramp metal is removed by screening.

The mixing time must be very short since the chloride catalyzes a decomposition of ammonium nitrate. The retention time in the mixer that mixes the potash with the melt is less than 1 minute. In view of the short mixing time, the feed rates of melt and potash to the mixer must be accurate and steady to prevent excessive variations in composition of the mix.

The Norsk Hydro process, as described by Steen and Terjessen in a paper presented at the Second Interregional Fertilizer Symposium at Kiev (September 1971), seems to be generally similar to that described above insofar as the prilling operation is concerned. However, the ammonium phosphate-nitrate melt is prepared by a modification of the Odda nitrophosphate process in which up to 85% of the calcium is removed as calcium nitrate. Thus, the remaining solution, after neutralization, contains mainly monoammonium phosphate and ammonium nitrate, but it also contains some dicalcium phosphate. This solution is evaporated to a melt containing only 0.55% moisture at 180°C. The ratio of ammonium nitrate to ammonium phosphate can be controlled, within limits, by addition of ammonium nitrate solution obtained by conversion of the calcium nitrate. The melt is mixed with preheated potash salts in a special mixer at the top of the prill tower. Either potassium chloride or sulfate may be used. Norsk Hydro mentions the tendency of the viscosity of the melt to increase after mixing because potassium chloride reacts with ammonium nitrate to form ammonium chloride and potassium nitrate. This tendency is controlled by limiting the retention time of the mix and controlling the particle size of the potassium chloride. Some of the grades mentioned are 20-30-0, 23-23-0, 22-11-11, 17-17-17, and 15-20-15.

Compound fertilizers containing urea are prilled only in Japan so far as is known. There Mitsui Toatsu produces a prilled urea-KCl mixture. The potash is preheated and added to the urea melt just before prilling in a prill tower 40 m high (29). However, several organizations have produced prilled NP and NPK fertilizers based on urea on a pilot-plant scale.

In 1968 TVA demonstrated oil prilling of urea-ammonium polyphosphate mixtures (30). The use of oil rather than air as a cooling medium for prills was developed by Dutch States Mines and applied commercially for prilling calcium nitrate (27). In the TVA process, ammonium polyphosphate melt was premixed with urea melt in a trough which discharged into a rotating prilling cup. The temperature of the mixture was about 132°C. The droplets from the prill cup were quenched and collected in light oil which was maintained at about 38°C by cooling with water coils. The prills were separated from the oil by centrifuging and sized at 7- to 12-mesh. The ammonium polyphosphate melt was prepared from electric-furnace phosphoric acid and contained about 50% of the P_2O_5 in polyphosphate forms. Grades produced were 30-30-0, 36-18-0, and 39-13-0.

Further pilot-plant studies of oil-prilling urea-based compound fertilizer were reported by Hatakeyama (29). In this process, urea melt was mixed with dried and preheated monoammonium phosphate and (in some cases) potassium chloride and ammonium sulfate. The fluid mixture was prilled in a "prilling device" (details not disclosed) and collected in a low-viscosity oil. As in the TVA process, the prills were separated from the oil by centrifuging.

Hatakeyama stressed control of the temperature of the fluid mixture to be prilled. The optimum temperature for an 18.6-18.6-18.6 mix was 125°C. Some other grades mentioned were 18-21-17 and 28-28-0.

A short mixing time (about 4 minutes) was preferred; prolonged contact of urea melt with monoammonium phosphate causes decomposition of urea and formation of polyphosphate according to the reaction:

$$(NH_2)_2CO + 2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + CO_2 + 2NH_3 \qquad \text{(Equation 17)}$$

The reaction is undesirable because of foaming and possible loss of ammonia. (Some of the ammonia may be retained as diammonium orthophosphate or triammonium pyrophosphate).

More recently Norsk Hydro has developed an air-prilling process for compound fertilizers based on urea and monoammonium phosphate (MAP) (31). The MAP was produced as a melt from wet-process phosphoric acid in a pipe reactor of the type developed by TVA (22). The melt contains some polyphosphate, up to 30%. The presence of some polyphosphate is desirable because it lowers the melting point and improves the physical properties of the products. However, melts containing a high percentage of polyphosphate are slow to crystallize and may remain plastic too long for prilling.

Three methods of operation were described:

1. The MAP melt may be prilled without additives.
2. The MAP melt may be prilled with addition of preheated solid urea and KCl.
3. The MAP melt may be solidified, then preheated, and mixed with urea melt for prilling. Preheated KCl may also be added.

The third method has the advantage that a higher polyphosphate content can be tolerated since the polyphosphate in the solidified melt will have had time to crystallize before returning to the prilling process, and hence the plasticity or slow hardening characteristic of high-polyphosphate melts is avoided. As in other NPK prilling processes, close temperature control and rapid mixing with short retention time in the mixer are important.

The advantages and disadvantages of NPK prilling are many. The advantages are well known. A very high percentage of the product is "on-size," and hence there is little recycle. Usually there is little dust although there may be fume with some compositions. The moisture is removed more efficiently by evaporating solutions than by drying moist granules, particularly when the granulation process involves high recycle ratios. The near-spherical shape of the prills often is preferred to that of irregular-shaped granules. The capital and operating cost of a prilling plant is usually less than that of a granulation plant, particularly for large-scale operations.

A disadvantage is that formulations which can be prilled have some limitations since the mixture must be capable of forming a fluid melt. Also, formulations containing high percentages of ammonium sulfate, potash salts, and superphosphate might be difficult or impossible to prill. The particle size is not readily controllable within as wide a range as in granulation. However, most formulations will produce an acceptable particle size. Control of temperature, particle size, mixing time, and proportions is generally more critical than in most granulation processes. Since a prill tower must have some minimum height (commonly 40 m) a small-capacity unit tends to be nearly as expensive as a large one. Thus, prilling may be more expensive than granulation for small plants even though it is cheaper for large ones.

Diammonium phosphate is unstable at the high melt temperatures involved in prilling and in most melt granulation processes. Therefore, a disadvantage of melt processes in general is that full advantage cannot be taken of the capacity of phosphoric acid to fix ammonia. Since ammonia costs only about half as much as solid forms of nitrogen, diammonium phosphate has a substantial economic advantage, as pointed out in chapters XIV and XVII.

Bulk Blending

Bulk blending is a special form of dry mixing in which the materials to be mixed are all granular and about the same particle size. The mixtures may be distributed in bulk, or they may be bagged for marketing.

The materials to be blended may be either straight or compound fertilizers or some combination of the two. The most common materials are monoammonium and diammonium phosphate, triple superphosphate, potassium chloride, ammonium nitrate, urea, and ammonium sulfate. Table 3 shows the particle size and some physical properties of materials used for bulk blending in the United States. In most other countries, somewhat larger granules are preferred.

Bulk blending originated in the United States in the early 1950s and grew rapidly in popularity. In 1976 a joint survey by the Tennessee Valley Authority and the American Plant Food Control Officials showed that 58.5% of all compound fertilizers and 40.1% of all fertilizers sold in the United States were blends. The results of the survey are tabulated below:

	% of All "Mixed Fertilizers"
Blends	
Sold in bulk	49.2
Sold in bags	9.3
Total	58.5
Chemically granulated compounds	
Sold in bulk	14.4
Sold in bags	13.1
Total	27.5
Fluid mixtures	
Liquids and suspensions	14.0
Total	100.0

The total tonnage of bulk blends in 1976 was about 14 million mt. Official annual U.S. statistics do

TABLE 3. APPARENT SPECIFIC GRAVITY, PARTICLE SIZE DISTRIBUTION, AND PARTICLE SHAPE OF SOME GRANULAR FERTILIZER MATERIALS

	Apparent Specific Gravity	Grade	Tyler Screen Range, Wt. %					Particle Shape[a]
			+6	-6 +8	-8 +10	-10 +16	-16	
Ammonium nitrate								
Prills	1.29	33.5-0-0	0	6	65	25	4	WR
Prills (high density)	1.65	33.5-0-0	0	0	8	89	3	EWR
Granules	1.50	33.5-0-0	1	35	54	8	2	FWR
Flakes	1.63	33.5-0-0	0	25	43	28	4	B
Ammonium nitrate sulfate								
Granules	1.51	30-0-0	2	29	56	10	3	FWR-PR
Urea								
Prills, unconditioned	1.32	46-0-0	0	1	17	78	4	EWR
Prills, conditioned	1.31	45-0-0	0	0	1	94	5	EWR
Granules	-	46-0-0	1	90	9	<1	0	WR
Granules	-	46-0-0	3	80	17	<1	0	WR
Ammonium sulfate								
Compacted flakes	1.64	21-0-0	0	6	46	41	7	I
Crystals	1.75	21-0-0	0	2	38	51	9	R
	1.75	21-0-0	0	4	20	51	25	B
Ammonium phosphate nitrate								
Prill-like granules	1.27	30-10-0	0	5	63	31	1	WR
Granules	1.56	30-10-0	0	33	55	9	3	FWR
Diammonium phosphate								
Granules (from wet-process acid)	1.63	18-46-0	0	5	83	12	0	WR
	-	18-46-0	0	42	57	1	0	WR
Crystals (from furnace acid)	1.62	21-53-0	0	8	45	39	8	B
Triple superphosphate								
Granules	2.12	0-46-0	<1	29	56	14	<1	WR
	-	0-46-0	1	21	37	31	10	FWR
Potassium chloride								
Flotation product, granular[b]	1.97	0-0-60	2	36	52	10	0	B
Flotation product, coarse[b]	-	0-0-60	0	0	19	51	30	B
Solution-rounded crystals	1.93	0-0-62	0	5	29	58	8	WR
Compacted flakes	1.96	0-0-60	0	14	65	20	1	I
Filler								
Crushed limestone	2.53	0-0-0	0	9	60	26	5	I
	2.56	0-0-0	0	22	42	24	12	I

a. B = blocky, I = irregular, R = rounded (PR = poorly rounded, FWR = fairly well rounded, WR = well rounded, EWR = exceptionally well rounded).

b. "Granular" and "coarse" are terms used by the industry; "granular" usually is 6- to 20-mesh, and "coarse" is mainly 10- to 28-mesh.

not separate bulk blends from other dry "mixed fertilizers." Also, in several states blended materials are recorded as sales of straight materials for direct application. For instance, the farmer is invoiced for straight materials (TSP, KCl, and urea), and these materials are mixed by the retailer before delivery to the farmer. This situation makes it difficult to determine how much bulk blends are actually sold and used, but the survey mentioned above is believed to be the most reliable information available.

Bulk-blending systems are also in use in several other countries but not always as the same type of operation as in the United States. Three types of bulk-blending systems have emerged:

1. A small local distributor serving an area of perhaps 50 km in radius, usually in conjunction with other agricultural services.
2. A larger distributor located at a port or transportation center, often receiving materials by ship or barge.
3. An operation associated with manufacturing in which a few grades of granular compound or straight fertilizers are blended to produce a wider variety of compound fertilizers.

Type 1 (the local distributor) is the most common type in the United States. There are over 5,300 bulk-blending operations in the United States with a median annual output of about 2,500 mt of blends. Usually the distribution center also sells other types of fertilizers such as straight solid and fluid fertilizers and other agricultural supplies (pesticides, seeds, animal feeds, implements, etc.). The distribution center may also be a center for purchasing farm products such as grain for resale to food processors, exporters, or animal feed compounders. Fertilizers for blending are purchased in bulk and received usually by rail in covered, hopper-bottom railcars that are easily unloaded by gravity. The success of this type of operation depends on a reliable transportation system that can deliver bulk materials without loss by leakage or damage due to exposure to the weather. The fertilizer materials are stored in bins, mixed to the farmer's order, and delivered immediately to the farm or to the farmer's vehicle. Often the blend is taken immediately to the field and broadcast on the soil by a spreader truck, either by the farmer or by the blender (distribution center operator). Only 23% of the blenders in the United States have bagging facilities.

A common type of blending system is shown in figure 12. Many types of mixers are in use, but batch rotary-drum mixers seem to be the most common. Most mixers are capable of mixing at a rate of at least 15 tph or more. If operated 24 hours/day and 330 days/year, the annual output would be in excess of 100,000 tons. It follows that the typical blender operates his mixing system less than the equivalent of ten 24-hour days/year. Usually, all of the blending is done during peak seasons.

The main advantages of this local distributor system follow. First, the blender is also the retailer, thereby one step in the distribution system is eliminated. Second, since the fertilizers to be blended come from widely separated sources, there is some saving in transportation costs by shipping to local distribution centers rather than to a regional center.

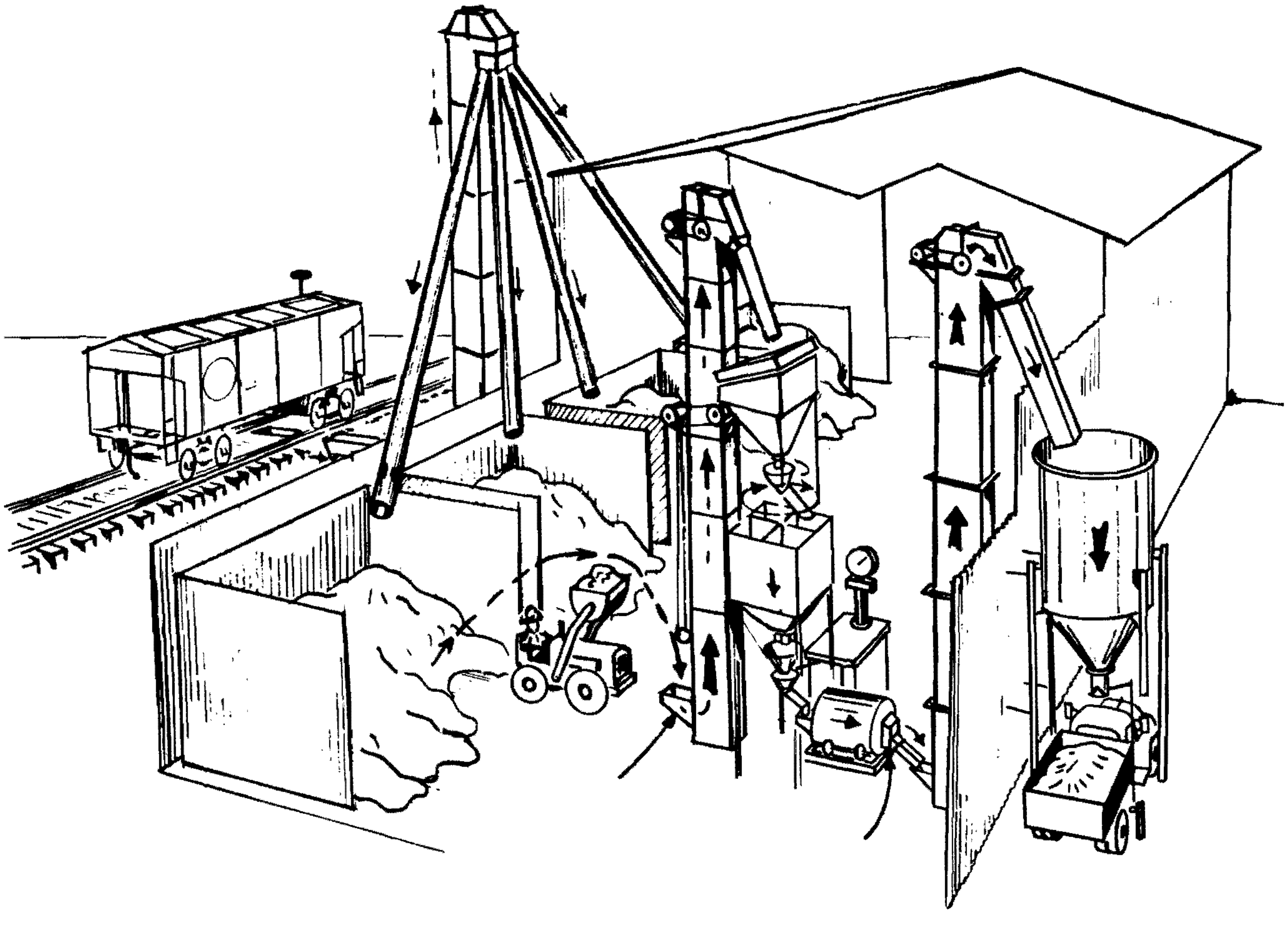

Figure 12. A Common Type of Bulk-Blending Plant.

Third, the blender is able to make any $N:P_2O_5:K_2O$ ratio desired; prescription mixes guided by soil analyses are popular. Secondary or micronutrients may be added.

The conditions that make bulk blending popular in the United States are often lacking in other countries. Poulton has described a bulk-blending plant of type 2 in the United Kingdom where blenders supplied 5.8% of the compound fertilizers used in England and Wales in 1975 (32). The bulk-blending operation described by Poulton receives materials in small ships carrying up to 1,500 tons, and this requires substantial storage space (a total of about 5,000 tons). The granular materials are purchased to a size specification. However, the materials are rescreened at 2-4 mm before being mixed, and the fines are sold to granulating plants. Mixing is done in a rotating drum, 5-ton batch mixer at a rate up to 50-60 tph. Several grades are produced to serve the needs of the area; some contain magnesium or boron. The mixing drum is equipped to coat the granules with micronutrient materials (such as boron) and/or clay using oil to ensure adherence of the fine powder to the granules. The blended material is rescreened before bagging or bulk storage. The products are distributed in 50-kg bags, in large bags of 1-ton capacity, or in bulk. The bags (large and small) are weatherproof and are often delivered to the farms in advance and stored in the open until needed. Some bagged material is also stored at the plant either in the open or under cover.

This type of bulk blending tends to be a much larger operation than the local distributor type; annual outputs in the range of 30,000-300,000 tons are typical. One such blending operation is The Andersons located in Maumee, Ohio (33). The location is near the port of Toledo, Ohio, which is well equipped to receive shipments from overseas (or Florida) locations through the St. Lawrence River. The plant has storage facilities for 200,000 short tons of fertilizer and produces more than 350,000 short tons per year of bulk-blended products. A few basic formulations are produced and sold either in bags or bulk. The company is also a grain dealer, and trucks bringing grain to the shipping terminal can transport fertilizer on the return trip. Only 20% of the output is sold directly to farmers; the remainder goes to retailers and cooperatives. Costs are minimized by buying in large quantities during the off-season and by automated handling, mixing, and loading for shipment by rail or truck.

A third type of bulk blending consists of blending a few grades of compound fertilizers to produce a wider variety of compounds. One example is in Korea where diammonium phosphate is produced with potash added during granulation. Examples of the grades produced include 14-37-12, 12-32-16, and 10-25-25. These products are blended with urea to produce other grades such as 22-22-11 and 18-18-18.

One large fertilizer producer in England produces a large number of grades by blending a few grades of N-P and N-K granular products. The advantage of this system is that numerous grades can be produced by blending without the expense and delays caused by frequent change in grade in a large granulating plant.

The technology of bulk blending is simple; yet, there are some basic principles that require attention to ensure satisfactory results. In the U.S. system where most of the blends are mixed and spread the same day, storage properties of the mix may be of little concern. In other countries where blends may be bagged and stored several weeks or months, storage properties are important.

All materials should be in the form of strong, well-dried granules of about the same size. The incoming bulk materials should be protected from moisture absorption during unloading and storage before mixing. In humid climates, dehumidified storage may be needed. If this is not possible, covering the piles with plastic sheets may suffice. For best results, the materials should be rescreened before they are mixed to eliminate any fines or lumps formed in shipment and handling. Also equipment for coating the granules after they are mixed is desirable.

Urea or compounds containing it must not be mixed with ammonium nitrate or any compound containing it. The mixture is extremely hygroscopic. Urea and single or triple superphosphate should not be used in the same blend if the blend is to be stored unless the superphosphate is exceptionally well dried. The monocalcium phosphate in superphosphates reacts with urea forming an adduct and releasing water of crystallization:

$$4CO(NH_2)_2 + Ca(H_2PO_4)_2 \cdot H_2O \rightarrow Ca(H_2PO_4)_2 \cdot 4CO\,(NH_2)_2 + H_2O \quad \text{(Equation 18)}$$

Hoffmeister reported tests of compatibility of five samples of TSP and two samples of SSP in blends with urea (34). Reactivity varied widely, but only one sample of TSP and none of the SSP produced blends with entirely satisfactory storage properties. The others became wet and sticky or severely caked in storage periods ranging from 1 day to 3 months. Reactivity was related to the hydrate water content rather than the free water content.

Further drying of the superphosphates rendered them compatible with urea in blends, but it seems unlikely that the blender can rely on receiving such thoroughly dried material. Therefore, unless the blender has his own drying facilities, it would be better to use ammonium phosphates (DAP or MAP) rather than superphosphates in blends with urea.

Superphosphates will react with diammonium phosphate according to the equation:

$$(NH_4)_2HPO_4 + Ca(H_2PO_4)_2 \cdot H_2O \rightarrow CaHPO_4 + 2NH_4H_2PO_4 + H_2O \quad \text{(Equation 19)}$$

This reaction will cause caking in storage; thus, the combination should be avoided in blends that are to be stored.

Segregation of the materials after they are mixed can be serious. For instance, if a blend is bagged from a hopper, successive bags may have widely differing compositions (35). The segregation is caused by difference in particle size of raw materials and can be prevented by exact size matching of the materials. Since exact size matching is seldom possible, additional precautions usually are necessary. Suitable precautions have been described by Hoffmeister (36), Silverberg and Hoffmeister (37), and Poulton (32).

A UNIDO publication (Fertilizer Industry Series, Monograph No. 8, 1976) describes specifications for a bulk-blending and bagging plant in a developing country with an annual capacity of 30,000 or 50,000 tons. The estimated cost is $440,000 or $550,000. Much of the cost is in storage buildings and materials handling equipment which would be required for importation and distribution of fertilizers in any case.

A bulk-blending plant may be a good choice for a developing country that imports its fertilizer requirements when the annual requirements are too small to justify a granulation plant. For developing countries that produce some or all of their fertilizer requirements, some type of bulk blending may be useful, but alternatives should be considered (see chapter XXIV).

Use of bulk blending in small local distribution centers requires a well-developed infrastructure capable of timely delivery of bulk materials without loss or deterioration in quality; such conditions are often lacking in developing countries.

Production of Fluid Compound Fertilizers

Two types of fluid compound fertilizers are recognized--liquids in which all ingredients are in solution and suspensions which are liquids containing solids which are held in suspension by an addition of a gelatinous material such as certain types of clay which increases the viscosity and delays settling. The solids in suspensions are often soluble salts in their saturated solution but may also be insoluble materials. A third type that sometimes is recognized is "slurry fertilizers" which are fluid fertilizers containing solids that settle rapidly unless continuously agitated. This type is not very popular and will not be described here. The first part of this section will deal with solutions or "clear liquids", followed by a brief description of suspension fertilizer technology.

Fluid fertilizers are not a new development; several references to production and use of liquid fertilizers in the early part of the nineteenth century are found in the literature. However, the manufacture and use of liquid fertilizers did not become popular until quite recently. Their popularity has grown rapidly in the United States where liquid compound fertilizers (including suspensions) now constitute 15% of all compound fertilizers. Straight nitrogen liquid fertilizers (see Chapter X) are even more popular. About 30% of all fertilizer sold in the United States is fluids, including anhydrous ammonia. Liquid fertilizers also have found substantial use in England, France, Belgium, Mexico, Colombia, and perhaps other countries for which data are not available.

Clear Liquid Fertilizers

Some advantages of clear liquid fertilizers are:

1. Energy requirements are lower, and no evaporation or drying is required.
2. There are no problems of dust or fume in manufacture or use of liquids.
3. Problems of physical properties such as hygroscopicity and caking are absent.
4. Storage, handling, and loading for shipment are less expensive and require less labor than for solids.
5. Application of liquids is convenient and rapid, given the proper equipment. Even distribution or precise placement is easier with liquids than with solids.
6. Liquid fertilizer can be applied in irrigation water, particularly with spray or drip-type irrigation.
7. Liquid fertilizers are adaptable to foliar application (when properly diluted) which is sometimes more efficient than soil fertilization. When spraying with pesticides is necessary (as in some tree crops), foliar fertilization can be combined with the spraying operation.
8. Transplanting solutions are popular for use with some crops, particularly vegetable crops such as tomatoes.
9. Equipment for producing liquid compound fertilizers is simple and inexpensive, provided suitable materials are available from manufacturers of primary materials.
10. In some cases liquid fertilizers may have a higher agronomic efficiency. This is a debatable point (38).

Some disadvantages are:

1. Materials for liquids must be water soluble; thus, the choice is limited. Some of the materials are more expensive or less readily available.
2. Liquid compound fertilizers are less concentrated than solids; therefore, shipping costs are increased.
3. When solutions are cooled, crystals may form and settle. To guard against this, liquids should be formulated to withstand the lowest temperature that is likely to be encountered. Thus, warm climates permit marketing of more concentrated solutions. However, in any case solutions are less concentrated than solids, thereby transport cost is increased.
4. Specialized equipment is needed for storage and transport of liquids--tanks, barrels, and rail or road tankers. Ships, barges, and pipelines also are used. The equipment is not necessarily more expensive than that for solids but may not be available in some countries. On the other hand, bags are not required.
5. It is often stated that expensive, sophisticated equipment is required for application of liquids. This is true of anhydrous or strong aqua ammonia, but it is not true of liquid compound fertilizers. While expensive equipment is used in the United States to save labor, equally expensive equipment is used for solids. Primitive equipment can be used (such as a bucket and a ladle). The feasibility of distribution and application of liquids with primitive equipment has been demonstrated by the use of night soil in some countries, the use of low concentration ammonia solutions in China, and the use by small farmers of liquid compound fertilizers in Colombia (39).

The principal materials for liquid compound fertilizers are urea or urea-ammonium nitrate (UAN) solution, ammonium ortho or polyphosphate, and potassium chloride. UAN solution usually is less expensive than solid nitrogen. Fully soluble potassium chloride is slightly more expensive than grades containing insoluble impurities but cheaper than granular grades. It is available from potash producers in Canada, United States, England, and Israel that use solution mining, recrystallization refining, or recovery from salt lakes. The ammonium phosphate is a key ingredient; its cost, availability, and technology for producing it vary widely as discussed later.

For some special uses such as foliar application, potassium phosphates, potassium sulfate, and other more expensive materials may be used. In some sulfur-deficient areas, ammonium thiosulfate solution or ammonium sulfite-bisulfite is used. Various micronutrient materials also are used.

The most important source of phosphate is ammonium polyphosphate solution. In early practice pure crystalline diammonium phosphate was an important material; it was made from furnace acid or from wet-process acid by a special process that eliminated insoluble impurities. Some relative minor use is still made of the crystalline material. Later, ammonium orthophosphate solutions were made from furnace acid, and still later ammonium polyphosphate solutions were produced at first from furnace superphosphoric acid and later from wet-process superphosphoric acid. The most recent development is production of ammonium polyphosphate solution directly from wet-process orthophosphoric acid (38).

Ammonium polyphosphate solution has two important advantages for liquid fertilizers; it is more soluble than the orthophosphate, and it sequesters (holds in solution) most of the common impurities in wet-process acid, as well as some micronutrient materials that may be added.

Figure 13 shows the effect of $N:P_2O_5$ ratio and polyphosphate content on the solubility of pure ammonium phosphate solutions at 0°C. The solubility of

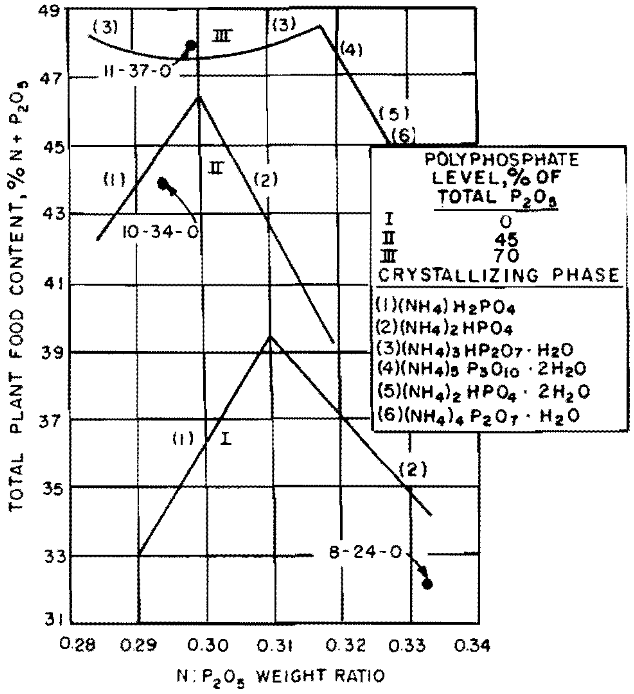

Figure 13. Effect of Polyphosphate Level and N:P_2O_5 Weight Ratio on Solubility of Ammonium Polyphosphates at 0°C.

impure solutions made from wet-process acid depends on the impurities, but 10-34-0 is the most popular grade. It may have a salting-out temperature far below 0°C.

Most of the ammonium polyphosphate solution produced in the United States is made from wet-process superphosphoric acid. Superphosphoric acid is produced in 11 plants in the United States. The production capacity totals 0.91 million mt of P_2O_5 (40). Most of the acid is used to make liquid fertilizers.

Two methods are used to convert superphosphoric acid to ammonium polyphosphate (APP) solution. In the first method the superphosphoric acid, ammonia, and water are metered into a stirred reactor vessel where the pH is controlled at about 6.0 to 6.5. The temperature is controlled at about 75°C by circulation through a cooler, and the product is further cooled to about 35°C to minimize the rate of hydrolysis in storage. In this method, the polyphosphate level in the product, expressed as a percentage of total P_2O_5, is about the same as that in the acid or slightly less.

In the second method superphosphoric acid and ammonia react in a pipe reactor at temperatures ranging from 340° to 390°C (see figure 14). The reaction products, melt and steam, are quenched in the cooled solution which is adjusted to the desired pH, 6.0 to 6.5, by additional ammonia. By this method the polyphosphate level is increased as a result of dehydration and polymerization in the pipe reactor. For instance, "low-poly" acid containing only 10%-20% of the P_2O_5 as polyphosphate can be used to make solutions with polyphosphate levels above 50% and often as high as 75% (22). This method has become popular because the "low-poly" superphosphoric acid is much easier to produce than "high-poly" (above 50%) and is less viscous and therefore easier to pump.

The quality of the APP solution depends on the impurities in the acid. The most troublesome impurities are carbonaceous matter and magnesium. Carbonaceous matter forms a black, flocculent precipitate in the solution, rendering it opaque. This is objectionable mainly because farmers expect a "clear" solution to be actually clear. Magnesium causes delayed or continued slow precipitation of compounds such as $MgNH_4PO_4 \cdot 6H_2O$, $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$, and $MgAl(NH_4)_5(P_2O_7)_2F_2 \cdot 6H_2O$ depending on the composition and polyphosphate level of the solution (41). These crystalline precipitates grow to such size as to cause clogging of spray nozzles. The amount of magnesium that can be tolerated in superphosphoric acid is somewhat indefinite, but 0.8% MgO is probably a maximum. Some producers of superphosphoric acid have developed methods of removing magnesium. Satisfactory quality superphosphoric acid has been produced from Kola apatite, some grades of Moroccan rock, calcined North Carolina and Western U.S. rock, and some Florida rocks (calcined or raw). Some partially purified acid made from Florida rock is imported into the United States from Mexico for liquid fertilizer production.

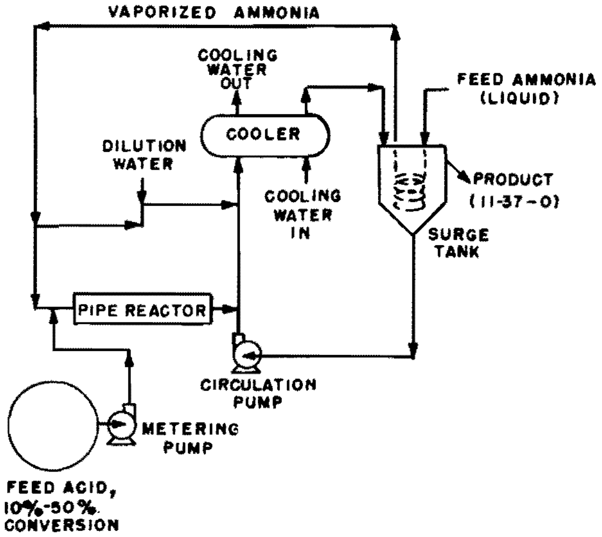

Figure 14. Production of High-Polyphosphate Liquid Fertilizer from Wet-Process Superphosphoric Acid.

APP solution may be made from orthophosphoric wet-process acid (54% P_2O_5), as described previously under "Melt Granulation." A process of this type is in use in France (42). To attain a polyphosphate level of 50% or more, it is necessary to preheat the acid and ammonia when the acid concentration is about 54%; at concentrations above about 60% P_2O_5, preheating may not be necessary. For production of satisfactory clear liquids by this process, the phosphoric acid should be unusually low in impurities; acid made from Kola rock is suitable, but acids made from most Florida rocks have not produced sludge-free solutions.

APP solutions are stored and transported in mild steel tanks. The polyphosphates hydrolyze during storage at a rate dependent on temperature. At 15°C or below, the rate is very slow. It is still moderate at 27°C, but in the range of 30°-40°C, the rate may be so rapid as to cause serious deterioration in 2-3 months. Thus, in tropical areas, APP solutions may have to be cooled by refrigeration or used soon after production.

Production of compound fertilizers from water, UAN solution or urea, APP solution, and potassium chloride is a simple mixing process, often carried out batchwise. The water used should be reasonably pure; high concentrations of calcium or magnesium will cause formation of insoluble phosphate precipitates. If the APP solution is manufactured onsite, it can be used while hot to dissolve solids, such as potassium chloride or prilled urea. The solids have a negative heat of solution and may be slow to dissolve in cold water. Also, the negative heat of solution helps cool the APP solution to slow the rate of hydrolysis.

The choice between urea and UAN solution may depend on which is available. Higher concentrations are possible with UAN solutions for NP grades while, with most NPK grades, straight urea gives a higher concentration. This is because ammonium nitrate reacts with potassium chloride in solution, producing ammonium chloride and potassium nitrate. Potassium nitrate has a low solubility at low temperatures. If the plant is near a urea production unit, urea solution may be used as the source of supplemental nitrogen; if immediately adjacent to it, the hot urea solution which usually contains about 75% urea can be used. For shipment the solution should be diluted to 40%-50% depending on the ambient temperature.

As mentioned previously an important property of liquid compound fertilizers is the temperature at which crystals appear, commonly known as the "salting-out point." Slack has given empirical methods for predicting salting-out temperatures for mixtures of KCl, urea or UAN solution, and APP solution of standard composition (43). The predictions are only approximate since the APP solution is of variable composition. The predicted (calculated) and measured salting-out temperatures for some KCl-UAN-APP formulations are given in table 4. Most of these formulations have salting-out temperatures of 0°C or lower which is desirable in temperate climates. Higher grades would be possible in tropical areas where the minimum temperature expected is higher than 0°C. This is particularly true of potash-containing grades in which the crystallizing phase is KNO_3, which has a high temperature coefficient.

The formulations shown in table 4 could be modified by substituting an equivalent amount of nitrogen in the form of urea (solid or solution) for UAN solution. This would change the salting-out temperature; most potash-containing grades would have a lower salting-out temperature, while nonpotash grades would have a higher salting-out temperature. The maximum grade that could be produced at any given temperature could be estimated with the help of charts and formulas given by Slack, *et al.*, but it is usually preferable to determine it experimentally, using the actual materials that are available for formulation of the mixtures (43). Table 5 shows some formulations for liquid fertilizers made from urea, 10-34-0, and KCl and their estimated salting-out temperatures.

TABLE 4. FORMULATIONS FOR LIQUID FERTILIZERS USING 10-34-0, UAN SOLUTION, AND KCl

	Formulation, kg/ton				Salting-Out Temp., °C	
Grade	10-34-0	UAN, 32% N	KCl, 62% K_2O	H_2O	Calculation	Determination
16-16-0	470	353	-	177	-3.3	-3.3
13-26-0	765	167	-	68	-7.8	-
10-30-0	883	36	-	81	-17.8	-
8-8-8	236	126	129	459	+5.0	+0.6
8-16-8	471	102	129	298	+2.8	-10.0
7-21-7	618	25	113	244	-11.1	-11.1
5-5-10	147	111	161	581	-6.7	-
5-10-10	294	65	162	479	-7.8	-
5-15-10	441	19	162	378	+6.7	+2.2
4-4-12	117	89	194	600	-6.7	-
4-8-12	236	51	193	520	0.0	+6.1
3-9-9	264	11	145	580	<-18.0	-
20-10-0	294	533	-	173	<-18.0	-
10-5-5	147	266	80	507	0.0	-
10-15-5	441	175	80	304	-5.0	-
10-20-5	588	130	80	202	+1.7	-
6-3-6	88	161	97	654	-7.8	-
8-12-8	353	140	129	378	0.0	-
6-3-9	88	161	145	606	-2.8	-
6-6-9	176	133	145	546	0.0	-
6-9-9	265	106	145	484	0.0	-
21-7-0	206	592	-	202	<-18.0	-
18-12-0	353	453	-	194	<-18.0	-
12-4-4	118	339	64	479	-2.2	-
12-8-4	235	302	64	399	0.0	-
12-12-4	353	266	64	307	0.0	-
12-16-4	471	228	64	237	0.0	-
9-3-6	88	254	97	561	0.0	-
9-6-6	176	227	97	500	+2.2	-
9-9-6	264	200	97	439	+2.2	-
6-2-6	59	169	97	675	-7.8	-
6-4-6	117	152	97	634	-7.8	-
24-6-0	177	695	-	128	-6.7	-
12-3-3	88	349	48	515	-7.8	-
12-6-3	176	321	48	455	-7.8	-
12-9-3	265	292	48	395	-7.8	-
12-12-3	353	266	48	333	-5.0	-
8-2-4	59	232	64	645	-10.0	-
8-6-4	176	196	64	564	-12.8	-
8-2-6	59	231	97	613	0.0	-
8-4-6	117	214	97	572	0.0	-
8-6-6	176	196	97	531	-2.2	-
8-8-6	236	176	97	491	-2.2	-
8-6-8	176	196	129	499	+4.4	-

TABLE 5. FORMULATIONS FOR LIQUID FERTILIZERS USING UREA, 10-34-0, AND KCl[a]

Grade	Formulation, kg/ton				Salting-Out Temp., °C (calc.)
	Urea, 46% N	10-34-0	KCl, 62% K_2O	H_2O	
18-6-0	353	177	0	470	-3
16-8-4	296	236	65	403	-2
15-10-4	262	294	65	379	-1
15-5-5	294	147	81	470	-9
14-7-7	260	206	113	421	-1
12-12-6	184	353	97	366	-3
10-20-0	90	588	0	322	-17
9-9-9	138	265	145	452	-8
8-24-0	20	706	0	274	-17
7-14-7	63	412	113	412	-13
6-18-6	16	530	97	358	-17
5-10-10	45	294	162	500	-13

a. Includes only grades with salting-out temperatures below 0°C.

Formulations for foliar application can, in general, be made from any soluble fertilizer material if diluted sufficiently to avoid leaf burn. The required dilution varies widely depending on the materials, the type of crop, moisture conditions, etc. The "salt index" is a general guide to selection of materials; a low salt index is desirable because it indicates that higher concentrations can be tolerated. Salt indexes for common fertilizer materials are given in chapter XXII. Among straight nitrogen materials, urea has the lowest salt index per unit of N and is generally favored for foliar application. Some crops are sensitive to biuret in urea, but commercial urea containing up to 1.5% biuret has been used on grain crops without deleterious effects (44). Salt indexes are not available for polyphosphates, but experimental work has demonstrated that leaves are less sensitive to polyphosphate (pyro and tripoly) than orthophosphate. Also, polyphosphate gives better responses in experiments with grain. Potassium sulfate has a lower salt index than potassium chloride, and monopotassium phosphate has a very low index.

A promising practice, still in the experimental stage, is foliar fertilization of soybeans and other grain crops during the seed-forming stage. Widespread experiments in the United States and Brazil have been carried out mainly by Allied Chemical Corporation and Iowa State University since 1974.

Allied Chemical has developed several formulations trade-marked "Folian" which are composed of urea, polyphosphate, and potassium sulfate. The exact formulation has not been published, but a 1971 patent mentions ammonium polyphosphate. Since potassium sulfate is not very soluble, it is likely that some of the potassium is in the form of potassium ortho- or polyphosphate. In the most recently reported tests, the solution grade was 12-6.0-6.0-0.5S. Five field experiments with four replications were made in Brazil with soybeans. The best treatment was a single spray application of 112 kg/ha (100 lb/acre) at a growth stage of between early-pod and mid-pod. This treatment gave a 22% increase in yield (about 442 kg/ha) as compared with no foliar application (45). The foliar application was supplemental to soil fertilization, not a substitute for it.

Formulations used by Iowa State University were made from urea, potassium polyphosphate, and potassium sulfate. A solution grade of 10-2.4-4-0.6S was used for soybeans in some tests. Gray has reviewed these and other tests (44). The results were very encouraging in some cases and disappointing in other cases. Evidently, much further research will be required to provide predictable results. The high cost of potassium polyphosphate made from potassium hydroxide and superphosphoric acid is a drawback. Less expensive potassium phosphates or other less expensive formulations are likely to be needed for economically favorable results on grain crops.

Suspension Fertilizers--Formulations and practices for production of suspension fertilizers are so diverse that no attempt will be made to describe them completely. The most popular type uses techniques and materials similar to those used for clear liquids except that the concentration is limited by fluidity rather than solubility. Ammonium orthophosphate suspensions made from wet-process acid and containing insoluble impurities can be used, but ammonium polyphosphate gives better quality products. UAN solution is the usual source of supplemental nitrogen, and fine potassium chloride, not necessarily fully water soluble, is the usual source of potash. Insoluble materials, or materials which form insoluble precipitates, may be added to supply secondary or micronutrients. In fact, suspensions of entirely insoluble materials such as ground limestone or phosphate rock can be produced and applied with the advantage of eliminating dust problems.

The most common suspending agent is attapulgite clay, which forms a gel on vigorous agitation with water or aqueous solutions. The usual amount is 1%-2% which is enough to provide a suspension viscosity in the preferred range of 300-700 centipoises. This viscosity range prevents rapid settling of solids but does not cause difficulty in pumping or spraying if the proper equipment is used.

Suspensions may be stored for several weeks or months by using periodic agitation, but the general tendency is to limit storage since crystals may grow to such size as to cause problems.

Balay and Salladay have described the practice of making suspensions from solid materials (46). It seems evident that suspensions could have an economic advantage over bulk blends for the following reasons:

1. Powder MAP or DAP can be used which is cheaper than granular ammonium phosphates.
2. Supplemental nitrogen could be urea solution which would be less expensive than solid urea if near the source. Otherwise solid urea in any form can be used. Byproduct ammonium sulfate might be an economical material in some locations.
3. Fine potash should be used which is cheaper than granular potash.

The application of suspension fertilizers requires specialized equipment and techniques. For this reason suspensions are usually distributed by custom application services rather than by the farmer. However, in countries where labor is abundant and inexpensive, manual application would be feasible.

Economics of Production of Compound Fertilizers

Capital and operating costs for production of compound fertilizers will vary widely depending on whether the operations start with basic raw materials, intermediates, or finished products. Comments in this section refer exclusively to the capital and operating cost of producing compound fertilizers and do not include marketing and distribution. In choosing a production process, the aim should be to achieve the lowest delivered cost of the most suitable products. Because of the diversity of marketing systems, raw material availability, and agricultural needs, no attempt will be made to define the least-cost production-marketing system for any specific situation, but some guidelines will be given in chapter XXIV.

Blending is one of the least expensive processes, but its success depends on tight specifications and selective purchase of the granular materials to be blended, which cannot always be accomplished satisfactorily. Also, the materials are more expensive than nongranular materials or intermediates. As noted previously, Monograph No. 8 of UNIDO's Fertilizer Industry Series gives a detailed description of fertilizer bulk-blending and bagging plants with throughputs of 30,000 or 50,000 tpy. The estimated capital costs are $443,300 and $565,300, respectively. Much of the capital cost would also be required for receiving bulk fertilizer and bagging it and for storage of incoming bulk material and outgoing bagged material. Smaller bulk-blending facilities for annual sales of 3,000-5,000 tons have been built in developed countries for as little as $100,000, usually without bagging facilities or storage of blended products.

Facilities for producing liquid compound fertilizers likewise can be quite inexpensive if the ingredients of the required quality can be obtained from basic suppliers, which would be difficult in many countries. Production of ammonium polyphosphate solution from ammonia and phosphoric acid is much less expensive in capital and operating cost than the production of granular ammonium phosphate, but it requires phosphoric acid of a higher concentration and more rigid specification of composition. Such acid is not readily available in some countries. Urea solution or UAN solution, if available from a nearby source, should be less expensive than solid urea. Energy requirements for solutions are less than for solids since fuel for evaporation or drying is not necessary.

Illustrative estimates for production of granular ammonium phosphates and nitrophosphates are given in chapters XIV, XV, and XXV. The addition of potash salts in these processes requires very little additional investment or operating cost. In slurry granulation processes, potash addition usually decreases the recycle ratio; thus, for a given size of granulation equipment, a larger output of (for example) 10-25-25 than 18-46-0 would be expected. However, addition of ammonium nitrate or urea may not decrease the recycle ratio; therefore, the size and cost of the granulation plant would need to be increased in proportion to the throughput as explained in chapter XIV. Little information is available about the cost of melt granulation or prilling of compound fertilizer except for a few grades as discussed in chapter XIV. A comparison of the cost of prilling versus melt granulation for urea or ammonium nitrate has been given by Ruskan (47). Possibly this comparison may be valid for prilling versus melt granulation of such compound fertilizers as are adaptable to these processes.

Some information on steam granulation of dry mixtures of fertilizer has been supplied by Fisons, Ltd., which offers standardized "Granupak" plants in various sizes (48). The basic plant consists of raw-material hoppers and feeders, a raw-material crusher, a granulator equipped for steam injection and spray water addition, a dryer, a cooler, dry dust collectors, screens, oversize crusher, and equipment for coating the finished product, together with necessary conveyors and instruments. The order-of-magnitude costs of battery-limits basic granulation plants, not including storage of raw materials or products, based on prices prevailing in England on July 1, 1977, are:

	Tons/Hour		Cost of Basic Plant (Approx.)	
Type	Output	Throughput	£	$ Equivalent[a]
I	5 to 10	15	906,000	1,540,000
II	7 to 15	22	1,196,000	2,033,000
III	10 to 20	35	1,696,000	2,883,000
IV	15 to 30	55	2,161,000	3,673,000

a. Assuming exchange rate of 1£ = US $1.70.

Optional additional equipment can be included at the following approximate costs:

1.	Package steam boiler for granulation	£21,500
2.	Wet gas scrubber	£39,750
3.	Phosphoric acid preneutralizer system	£55,250
4.	Ammonium nitrate solution addition	£17,500

The Fisons' brochure gives the following range of utility requirements for granulation of a wide range of NP, NPK, and PK fertilizers:

	Requirement per Ton of Product	
Steam (3 kg/cm^2, min)	20-80	kg
Water (3 kg/cm^2, min)	0.05	m^3
Fuel	60,000-150,000	kcal
Electricity	15-25	kWh

These data could be used to estimate roughly the cost of granulation of compound fertilizer using dry materials. Naturally, allowance should be made for storage of raw materials and products; bagging facilities (if required) and various offsite, auxiliary facilities; and any additional costs associated with the particular location. The operating cost per ton of product will obviously depend on the recycle ratio since this ratio determines the production rate for a given size plant. The recycle ratio depends on the formulation and the accuracy of control of operating variables as pointed out previously in this chapter.

Figure 15 shows estimated capital costs for battery-limits granulation plants of various types for an industrial location in the United States or western Europe. The cost does not include storage of raw materials or products or any auxiliary or supporting facilities, except as noted below.

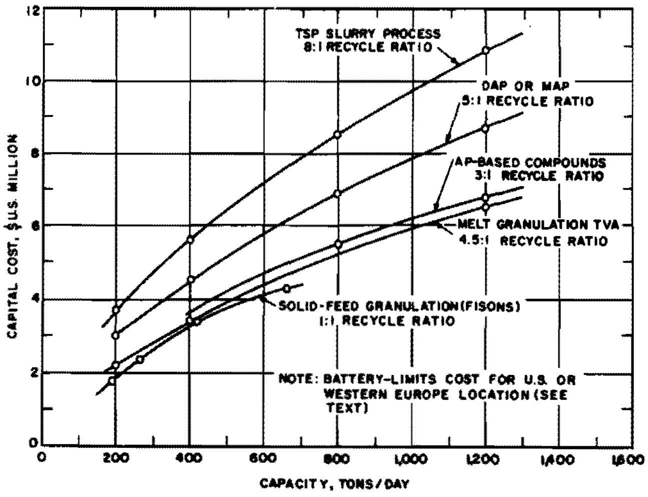

Figure 15. Capital Cost of Granulation Plants Versus Capacity.

The TSP curve includes rock grinding and slurry acidulation facilities (see chapter XIV, table 2).

The curve for DAP and MAP is for the conventional TVA-type process, including preneutralization and ammonia recovery, and would apply approximately for any ammonium phosphate-based compound fertilizer with a recycle ratio of about 5:1.

The curve for AP-based compound fertilizers would apply to any NP or NPK compound fertilizer based on phosphoric acid and ammonia made by a slurry-type process with a recycle ratio of about 3:1. It would also apply to straight diammonium phosphate produced by a pipe-reactor process such as the TVA or S.A. Cros system in which the recycle rate is reported to be 3:1 (see chapter XIV).

The curve for melt granulation applies primarily to ammonium phosphate or phosphate-sulfate compound fertilizers made by use of the TVA pipe reactor or pipe-cross reactor. This process would not require a dryer, and a recycle ratio of about 4.5:1.0 would be used. It should also apply approximately to other NP or NPK compounds produced by similar processes by addition of anhydrous solid materials or melts, provided the recycle ratio is about the same. The steam granulation curve is based on data supplied by Fisons, Ltd., for "Granupak" plants, assuming the recycle ratio is 1:1. The cost includes a packaged steam boiler and facilities for preneutralizing phosphoric acid, if desired. However, the process is basically designed for granulation of dry material (see previous description in this chapter).

It should be noted that a granulation plant is usually designed for a specific throughput capacity (recycle plus product), and this throughput capacity is a principal factor in its cost (see figure 13, chapter XIV). Once the plant is built, its production capacity depends on the recycle ratio. Thus, accurate estimation of the recycle ratio for intended products is important in plant design.

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XX Secondary and Micronutrients

In recent decades there has been a growing need for the inclusion in fertilizers of nutrients other than the primary elements, nitrogen, phosphorus, and potassium. There are several reasons for this. The grades of fertilizers have been increased to decrease handling and shipping costs, with the result that there is less room for the secondary and micronutrients that formerly were included incidentally because they were present in the original raw materials. Furthermore, the problem of supplying micronutrients is expected to become increasingly important as the natural supply in the soil becomes depleted. Needs have developed in some areas and for some crops for specific micronutrients in fairly large amounts--larger than would be supplied even by unpurified raw materials. More instances of need for micronutrient elements are being discovered also by research and by improved methods for identifying deficiencies.

The need for including additives in fertilizers has introduced several problems in production. In making solid mixes, it is difficult to get good mixing of the small amount of additives with the other materials and, once mixed, segregation may take place in handling. Moreover, some of the additives may not be chemically compatible with the main constituents of the mixture. In the production of liquid fertilizers--liquid mixed and nitrogen liquids--the problem of incorporating the additive thoroughly is often simplified but, unfortunately, many of the additive materials needed are not very soluble in the usual types of such liquids.

This chapter covers methods for incorporating secondary nutrients (calcium, magnesium, and sulfur) and micronutrients (boron, copper, iron, manganese, molybdenum, and zinc) in the solid, liquid, and suspension types of fertilizers. These nutrients are just as essential to proper plant growth as the primary nutrients. Chlorine is also an essential micronutrient but deficiencies seldom occur (1).

Secondary Nutrients

The importance of the secondary nutrients, calcium, magnesium, and sulfur, in agriculture has been realized for some time, and the addition of sources of these elements to soils is commonly practiced in areas where modern fertilizer technology is applied. In addition to serving important functions as plant nutrients, they are also used extensively as soil amendments to correct undesirable soil conditions. Maintenance of the proper soil pH, generally 6-7, is most important in order to obtain efficient utilization of nutrients by the plants.

Certain soils are naturally productive; however, to retain their high productivity, the addition of the amendments is necessary. In soils that are naturally unproductive because of excessive acidity or alkalinity, these conditions must be corrected before the soils can become economically productive. Furthermore, many soils which are currently considered unsuitable for agricultural purposes could quite possibly be amended economically and used satisfactorily.

Calcium and Magnesium

Calcium and, to a lesser extent, magnesium are present in many of the commonly used fertilizers (table 1). However, calcium and magnesium compounds are often applied separately for correction of soil acidity.

Calcium and magnesium are important constituents of plants, and symptoms of deficiencies in these nutrients are shown in table 2. However, the sources of calcium and magnesium are often supplied in amounts required to adjust the soil pH, rather than in response to an indicated plant deficiency. The usual materials

TABLE 1. COMMON FERTILIZER MATERIALS WHICH ALSO CONTAIN SECONDARY NUTRIENTS

Fertilizer	Formula of Principal Compound Present	Analysis (Percentage by Weight)					
		N	P_2O_5	K_2O	CaO	MgO	S
Ammonium nitrate-limestone[a]	$NH_4NO_3 + CaCO_3 + MgCO_3$	21-26	-	-	10-22	0-7	-
Ammonium phosphate sulfate	$NH_4H_2PO_4 + (NH_4)_2SO_4$	16	20	-	-	-	15
Ammonium sulfate	$(NH_4)_2SO_4$	21	-	-	-	-	23
Ammonium sulfate nitrate	$(NH_4)_2SO_4 \cdot NH_4NO_3$	26	-	-	-	-	12
Calcium cyanamide	$CaCN_2$	21	-	-	70	-	-
Calcium nitrate	$Ca(NO_3)_2$	15	-	-	27	2	-
Phosphate rock	$3Ca_3(PO_4)_2 \cdot CaF_2$	-	30-36	-	45-50	0.1-1	-
Potassium magnesium sulfate (langbeinite)	$K_2SO_4 \cdot 2MgSO_4$	-	-	21	-	19	22
Potassium sulfate	K_2SO_4	-	-	50	-	-	17
Ordinary superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4$	-	20	-	28	-	13
Triple superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	-	46	-	19	-	1
Fused calcium magnesium phosphate	indefinite	-	20	-	32	18	-
Basic slag	indefinite	-	15-20	-	42-50	2-8	-

a. Also known as calcium ammonium nitrate.

TABLE 2. SYMPTOMS OF CALCIUM, MAGNESIUM, AND SULFUR DEFICIENCIES IN PLANTS

Secondary Nutrient	Symptoms of Deficiency
Calcium	In most plants, root growth is reduced, root rotting frequently occurs, and the roots are affected before the tops have shown any symptoms. In moderate stages of deficiency, the young leaves become distorted, fail to grow, and show spotting or necrotic areas. In the acute stage, there is a general collapse of growing points and a die-back of the terminal buds.
Magnesium	Deficiency symptoms are frequently found on lower leaves of plants. In cotton, a reddening of the lower leaves occurs; while in potatoes, an orange-yellow coloration appears on the lower leaves and along the veins. In corn, there is a striping or chlorosis between the veins, and if the deficiency is severe, a crimson-red color frequently appears on the lower leaves.
Sulfur	Sulfur deficiency symptoms tend to resemble those of nitrogen deficiency. Under a continuous low supply of either element, plant appearance does not provide an ensured means of differentiating between deficiencies of sulfur or nitrogen. With a diminishing supply, however, a distinction may be observed. With nitrogen deficiency, the plant may become a yellowish-green color; and with some plants, the lower leaves may turn yellow and fall from the plant. With sulfur deficiency, the older leaves remain green, and the younger leaves become yellow-green and, in severe cases, chlorotic.

Source: K. C. Berger, and P. F. Pratt. 1963. "Advances in Secondary and Micronutrient Fertilization," IN *Fertilizer Technology and Usage*, p. 287-340, M. H. McVickar, G. L. Bridger, and L. B. Nelson, eds., Soil Science Society of America, Madison, Wisconsin.

are finely ground agricultural limestone (principally calcium carbonate), dolomite (a double carbonate of calcium and magnesium), or dolomitic limestones which are mixtures of the two minerals. Other sources include burned or hydrated limes, marl, and such calcareous wastes as oyster shells, sludges, or slags. The material used depends principally upon local availability and economic considerations. The relative neutralizing values of pure materials are shown in table 3.

TABLE 3. RELATIVE NEUTRALIZING VALUES OF PURE LIMING MATERIALS

Liming Materials	Relative Neutralizing Values	Kilograms of Liming Materials Equivalent to 1 mt	
		Calcium Carbonate	Calcium Oxide
Calcium carbonate	100	1,000	1,785
Magnesium carbonate	119	840	1,500
Calcium oxide	178	560	1,000
Magnesium oxide	250	400	715
Calcium hydrate	135	740	1,320
Magnesium hydrate	172	580	1,035
Dolomite	108	925	1,665
Dolomitic hydrate	175	572	1,020

Source: R. S. Boynton. 1960. "Calcium and Magnesium in Mixed Fertilizer," IN *Chemistry and Technology of Fertilizers*, p. 447, Vincent Sauchelli, ed., Reinhold Publishing Corporation, New York; Chapman & Hall, London.

The fineness of limestones used for this direct application, called liming, varies widely and ranges from limestone "meal" passing an 8-mesh screen to limestone "flour" of 100-mesh or smaller size. The finer a liming material is ground, the more quickly it becomes effective. A particle size such that about 50% passes an 80-mesh screen may be a good compromise.

The application of these calcium and magnesium compounds to many soils results in striking increases in plant growth beyond that expected from a simple response to the deficient nutrient element (2). The benefits follow.

Improved Phosphorus Availability--With low pH soils and soils high in aluminum and iron oxide content, phosphates are made less available because of their reaction with these compounds. Liming to a pH of 6-7 increases phosphate availability because of the precipitation of the iron and aluminum in forms other than the phosphate. At higher pHs, the availability is decreased, however, because of the precipitation of calcium or magnesium phosphates.

Nitrification--Most of the organisms responsible for conversion of ammonia to nitrates require calcium.

Nitrogen Fixation--This process is favored by the addition of liming agents.

Optimization of Micronutrient Uptake--Although small amounts of micronutrients are required for healthy plant growth, whenever any micronutrient is present in the available form in too large a concentration, it becomes toxic and produces an adverse effect on the plants. Liming materials can be added to regulate the micronutrient uptake. Except for molybdenum, the availability of the micronutrients decreases with an increase in the pH of the soil. Depending upon the soil, a pH of 6-7 is usually most satisfactory from the standpoints of nutrient availability and toxicity. Molybdenum deficiency generally decreases with an increase in soil pH, and a pH greater than 7 is preferred; however, liming soil to this high pH is discouraged because of previously stated reasons.

Physical Condition of Soil--Liming improves the structure of fine-textured soils.

Sulfur

The use of sulfur compounds as soil amendments to correct alkalinity or salinity in soils (presence of excess sodium salts, particularly sodium chloride and carbonates) is commonly practiced. Large tonnages of calcium sulfate (gypsum) are used for this purpose in areas where these conditions exist (3). Elemental sulfur also is used. Gypsum is also useful for reclaiming soil that has been inundated with seawater. The successful use of pyrites (FeS_2) for reclaiming alkaline soils in India has been reported (4). Thousands of hectares have been reclaimed by application of 7 tons or more of this mineral per hectare. Application of pyrites is also useful in decreasing the pH of calcareous soils.

Until comparatively recently, the essential role of sulfur in plant nutrition had not been given much publicity, nor had it required much attention. From its very beginning, fertilizer manufacture has relied heavily on sulfuric acid as a reagent to free phosphate from the ore--as in the production of superphosphate--and to fix ammonia in a solid form--as in ammonium sulfate. Much of the sulfur in the air as sulfur dioxide is brought down and made available for plant nutrition by rainfall. The amounts vary from perhaps 4 to 44 kg/ha/year, depending largely on the proximity of areas where sulfur-containing fuels are used. Sulfur also occurs naturally in some soils in ample amounts.

Changes in recent years have tended to decrease these sources, and attention is now focused on how best to supply sulfur to many of the crops being grown. One of these changes is the trend toward higher analysis fertilizers. Another is that the amount of sulfur available from the atmosphere is decreasing. Greater emphasis is being placed on the control of atmospheric pollutants, sulfur dioxide included, and the use of low-sulfur or sulfur-free fuels is increasing. Combustion of coal in power-generating plants releases large quantities of sulfur into the atmosphere, but this source will diminish because of more stringent pollution control regulation and increased use of atomic power.

Symptoms of sulfur deficiencies in plants are given in table 2. A deficiency is corrected either by adding a sulfur-containing fertilizer or by separate application of a sulfur compound, depending generally on economic considerations (5). A usual range of application rate is 10-50 kg/ha. The analyses of many of the common sulfur-containing fertilizers are given in table 1.

Incorporation of Secondary Nutrients in Granular Fertilizers

Even though significant quantities of calcium are present in many of the common fertilizer materials (superphosphates, nitrophosphates, calcium cyanamide, and calcium nitrate), calcium is commonly applied directly to the soil in the form of ground limestone or dolomite, which also is the common source of magnesium. On some soils, however, magnesium is needed, and dolomite addition is undesirable because the soil pH is already high. Magnesium sulfate or magnesium potassium sulfate is incorporated in the fertilizer for these soils (6); generally 20-60 kg of magnesium is supplied per hectare. Ground magnesium silicate minerals such as serpentine have also been used for this purpose.

In some European countries, the addition of magnesium to fertilizers is quite common. Kieserite ($MgSO_4 \cdot H_2O$) is the usual form. With heavy applications of nitrogen on grassland, the magnesium need becomes acute in some areas. The need for supplying magnesium in fertilizer in other countries probably will increase as fertilization rates approach those in European countries.

Several methods for incorporating sulfur compounds in granular fertilizers have been developed (6, 7). Elemental sulfur has been incorporated successfully in concentrated superphosphate by granulating the superphosphate and sulfur with steam and water in a rotating drum. Commercial-scale production of granular high-analysis fertilizer with added elemental sulfur has been reported. Furthermore, a prilled mixture of urea and sulfur (40% N and 10% S) is a relatively new material now being produced in the western part of the United States of America.

Ammonium nitrate, or any other undiluted nitrate fertilizer, should not be combined with elemental sulfur (8). The sulfur is an oxidizable material, and in such mixes it constitutes a potential explosion hazard. Nitrates can be combined safely with sulfates, however, and one such product, ammonium sulfate nitrate (26% N and 12% S), is commercially produced. Care should be exercised also if elemental sulfur is dry mixed with granular fertilizers. To avoid the possibilities of explosions, it is essential that dusting in enclosed areas be minimized and that any possible source of ignition in the vicinity be avoided. Adequate ventilation must be provided. Some operators have found that the use of steam or water fog is helpful in minimizing dusting and the development of static electric charges (3).

Sulfur is commonly added to granular compound fertilizers or bulk-blended fertilizers in the form of ammonium sulfate, single superphosphate, or calcium sulfate. Use of sulfuric acid and ammonia in granulation processes forms ammonium sulfate in situ (see chapter XIX). In some plants, part of the phosphoric acid-gypsum slurry from a phosphoric acid plant is drawn off before filtration for direct use in production of granular compound fertilizers in such proportions as to supply the desired amount of sulfur in the product.

In some countries, enriched superphosphate with a sulfur content between that of ordinary and triple superphosphates is used. In Australia and New Zealand, ordinary superphosphate is fortified with elemental sulfur to give mixtures of 18%-36% sulfur content. The materials can be simply mixed; however, in most cases, the sulfur is added during the acidulation step.

Materials for Bulk Blending or Direct Application--Some secondary element-containing materials available in granular form that would be suitable for direct application or bulk blending are:

- Single and enriched superphosphate
- Ammonium nitrate-limestone (calcium ammonium nitrate)
- Ammonium sulfate
- Ammonium sulfate-nitrate
- Gypsum
- Langbeinite
- Urea ammonium sulfate
- Urea-sulfur
- Elemental sulfur
- Potassium sulfate

"Granular" in this context is used to include any material of a suitable size whether produced by prilling, compaction, crushing and screening, or conventional granulation. Typical analyses of some of these materials are given in table 1. Some examples of composition of commercial products not given in table 1 are: urea-sulfur--40% N and 10% S, urea ammonium sulfate--40% N and 6% S, and gypsum--32% CaO and 18% S.

Secondary-Nutrient Addition to Liquid Fertilizers

Of the secondary elements, calcium and sulfur are the ones most often added to liquid fertilizers (9). The addition of calcium is restricted mainly to the western United States where it is used in the form of calcium nitrate in ammonium nitrate solution. The solution produced there commercially contains 26% calcium nitrate and 30% ammonium nitrate, with a total of 17% nitrogen. The solution is applied directly rather than being mixed with other solutions.

Calcium is not compatible with the usual type of liquid compound fertilizers containing phosphates, since it precipitates as the phosphate. There appears to be little need for adding it to mixed liquids, however, because the direct application of limestone from local sources generally is more economical.

Very little magnesium is used in liquid fertilizers. Like calcium, it precipitates as phosphates from the liquid-mixed fertilizers containing phosphate.

Sulfur is added to nitrogen solutions and to liquid-mixed fertilizers in three forms, as ammonium polysulfide, as ammonium bisulfite, and as ammonium thiosulfate solutions. The ammonium polysulfide solution is compatible with anhydrous or aqua ammonia, but it is not soluble to any useful extent in mixed liquids containing phosphate. The ammonium bisulfite solution (8.5% nitrogen and 17% sulfur) can be mixed with any of the fertilizer solutions. Typical grades with ammonium nitrate solution are 18-0-0-2 (N-P_2O_5-K_2O-S) and 14-0-0-7. With mixed liquids, such grades as 10-10-0-3, 8-8-0-8, and 15-5-0-1 are reported.

Addition of the ammonium bisulfite solution to a 10-34-0 grade ammonium polyphosphate liquid fertilizer gave liquid products with such grades as 10-30-0-3 and 10-26-0-5. As is discussed below in the micronutrient section, this 10-34-0 grade liquid, which contains about half of its phosphate as orthophosphate and half as polyphosphate, is an effective sequestering agent. Its use in the liquid fertilizer industry is increasing rapidly. Ammonium sulfate and ammonium sulfite are somewhat less soluble in such solution.

Ammonium thiosulfate is used as a 60% aqueous solution which contains 12% nitrogen and 26% sulfur. The solution is compatible in any proportion with neutral or alkaline phosphate-containing solutions, as well as with aqueous ammonia and nitrogen solutions. Addition of this solution to 8-24-0 grade orthophosphate solution or 10-34-0 grade polyphosphate solution gives such grades as 10-12-0-13 and 11-17-0-13.

Ammonium or potassium sulfate is also used to supply sulfur in liquid fertilizers, but the relatively low solubility of these materials limits the percentage that can be used.

Secondary-Nutrient Addition to Suspension Fertilizers

The best method for incorporating magnesium and other insoluble materials in liquid products probably is the recently developed suspension technique (10). The insoluble material, in fine particle size, is combined with a suspending agent to give a stable, nonsettling suspension.

A recent development is the practice of applying finely ground limestone or dolomite as a suspension. It has the advantage of avoiding the dusty conditions involved in applying the dry material. Suspensions containing up to 60% by weight of limestone in water are practical.

Sulfur may be added to suspensions as fine elemental sulfur, ammonium sulfate, or ground gypsum.

Micronutrients

The micronutrient elements--boron, copper, iron, manganese, molybdenum, and zinc--are just as essential to plant growth as are the primary elements (nitrogen, phosphorus, and potassium) and the secondary elements (calcium, magnesium, and sulfur). As crop yields are pushed upwards by more adequate fertilization with primary nutrients, the need for one or more of these micronutrients often becomes the limiting factor. Each year more cases of economically significant response to added micronutrients are found, often in areas where deficiencies were previously unsuspected.

Progressive farmers who learn of crop increases deriving from micronutrient additions are eager to reap these benefits, but the job of determining which micronutrients are needed for each crop and each farm is formidable. Even if this information were obtained, there is no guarantee that it would hold good for succeeding years. Micronutrient needs are likely to appear for a variety of reasons: exhaustion of soil supply, change in soil pH, repression of availability by interactions with other nutrients, and removal of other yield limitations.

Generally, the micronutrients are combined with standard chemical fertilizers and added to the soil in the normal fertilization programs. In some special cases, however, they are applied directly to the soil or used in foliar sprays. Many manufacturers mix the micronutrients with the fertilizer at the time of shipment. Others incorporate the micronutrients during manufacture of the fertilizer to give "premium" fertilizers, which supply moderate quantities of several micronutrients. Some agronomists object to this approach, however, because the use of unneeded elements wastes the farmer's money, and the indiscriminate use of micronutrients may cause adverse effects. The first point is an economic question of whether the insurance is worth what it costs. Failure to supply needed micronutrients also wastes the farmer's money, and determination of micronutrient needs is often expensive, cumbersome, and uncertain. As to the second point, adverse effects are unlikely when the premium fertilizer supplies approximately the amount of micronutrients that will be removed by the crops.

When micronutrients are combined with fertilizers, however, chemical reactions may occur, forming new compounds. As a result, the solubility of the micronutrients and, hence, their agronomical effectiveness may be altered--for better or worse. Use of a water-soluble micronutrient carrier does not necessarily mean that the element will be water soluble in the mixture. Conversely, when insoluble micronutrient carriers are incorporated in mixtures, the micronutrient may become soluble.

There is not much information available to answer the question of whether water solubility of the several micronutrient elements is agronomically important. However, it is likely that micronutrients in granular fertilizers will be more effective if they are at least partly water soluble as this is usually true of the primary elements. Some insoluble compounds are known to be effective micronutrient sources when finely ground and mixed with the soil, but when supplied in granular form, they usually are less effective.

The principal sources of micronutrients now commonly used are borax (sodium tetraborate decahydrate), sodium molybdate, and the soluble sulfate salts of the metallic elements. Other materials that are used include: (a) oxide and carbonate salts; (b) frits, prepared by fusing micronutrient salts and silica into a glass or slag; and (c) chelates, complexes of micronutrients and organic compounds, e.g., ethylenediaminetetraacetic acid. Some micronutrient sources and their nutrient content are shown in table 4. In addition to these refined materials, there are numerous

TABLE 4. MICRONUTRIENT CONTENT OF SOME MICRONUTRIENT SOURCES

Material	Formula of Principal Compound Present	Micronutrient Content (Percentage by Weight of Element)
Sources of boron		
Sodium tetraborate decahydrate (borax)	$Na_2B_4O_7 \cdot 10H_2O$	11
Sodium tetraborate pentahydrate	$Na_2B_4O_7 \cdot 5H_2O$	14
Sodium tetraborate-pentaborate	-	20
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	16
Sources of copper		
Cupric oxide	CuO	79
Cuprous oxide	Cu_2O	86
Cupric sulfate monohydrate	$CuSO_4 \cdot H_2O$	35
Cupric sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	25
Sources of iron		
Ferric sulfate nonahydrate	$Fe_2(SO_4)_3 \cdot 9H_2O$	20
Ferrous sulfate heptahydrate	$FeSO_4 \cdot 7H_2O$	20
Sources of manganese		
Manganous carbonate	$MnCO_3$	46
Manganous oxide (impure)	MnO	48
Manganous-manganic oxide	Mn_3O_4	69
Manganous sulfate monohydrate	$MnSO_4 \cdot H_2O$	24
Sources of molybdenum		
Ammonium molybdate	$(NH_4)_2MoO_4$	49
Sodium molybdate (anhydrous)	Na_2MoO_4	46
Molybic oxide (technical grade)	MoO_3	58-62
Sources of zinc		
Calcined zinc concentrate (impure ZnO)	ZnO	74
Zinc carbonate (byproduct)	$ZnCO_3$	56
Zinc oxide	ZnO	80
Zinc sulfate monohydrate	$ZnSO_4 \cdot H_2O$	36

byproducts from mineral and metal refining industries that are sold and used for their micronutrient content.

The amounts of micronutrients supplied in actual practice are quite variable, depending upon soil conditions and the crop to be fertilized. Typical application rates recommended for correction of deficiencies are tabulated below:

Micronutrient	Micronutrient Applied, (B, Cu, Fe, Mn, Mo, Zn), kg/ha
Boron	0.1-1.1
Copper	5-22
Iron	3-11
Manganese	5-22
Molybdenum	0.01 to 0.07
Zinc	5-11

In the United States of America, in 1964, fertilizers enriched with boron, copper, iron, manganese, and zinc contained, on the average, 0.09% B, 0.36% Cu, 0.46% Fe, 0.63% Mn, and 0.39% Zn (11). Micronutrient deficiency symptoms in plants are shown in table 5.

Micronutrient Addition to Granular Fertilizers

Several methods are available for combining micronutrients with granular fertilizers. These are: (a) dry mixing with product granules; (b) coating on product granules; and (c) incorporation during manufacture of the fertilizer. In methods (a) and (b), the micronutrient may be combined with the fertilizer granule at the time of its manufacture or later at a bulk-blending plant. The advantages and disadvantages of each method are discussed below. A more complete discussion of this subject has been given by Achorn and Mortvedt (12).

Addition at Time of Shipment--Micronutrients are sometimes mixed with granular fertilizers when the fertilizer is removed from the manufacturer's storage pile for shipment. Such a method provides wide flexibility in types and proportions of micronutrients for various customers. The chief problem with such a procedure, however, is that of providing a nonsegregating mixture of the powdered micronutrient and granular fertilizer. If segregation of micronutrients occurs during handling or application of the fertilizer, crop responses may be spotty. In the case of some micronutrients, overdosages are toxic; therefore, it is possible that nonuniform application on the field will result in poor yields in spots where the supply of micronutrient is excessive, as well as in spots where the supply is inadequate.

One way of obtaining a nonsegregating mixture of micronutrient with granular fertilizer is to furnish the micronutrient in granular form with the particle size matching that of the fertilizer; some micronutrient manufacturers are now producing their materials in such a form. This method, however, may not be entirely satisfactory from an agronomical standpoint. The proportions of micronutrients usually added to fertilizers are so small that only a relatively small number of granules would be added; thus, the distances between granules of micronutrient on the field could be excessive. For example, use of a micronutrient as 8-mesh granules at the rate of 1 kg/ha would result in the application of about 1 granule per 1,000 cm^2 of field surface.

An alternate method of producing nonsegregating mixtures is to coat the fertilizer granules with micro-

TABLE 5. SYMPTOMS OF MICRONUTRIENT DEFICIENCIES IN PLANTS

Micronutrient	Symptoms of Deficiency
Boron	Stunted growth of the younger parts of plants, frequently combined with a red or yellow coloration. Common symptoms are disintegration and decomposition of tissues in root crops and in stalks of members of the cabbage family.
Copper	Wilting and eventual death of leaf tips.
Iron	In early stages, leaves are pale without veinal patterns. The next stage consists of an interveinal chlorosis in the leaves. In the most severe stage of deficiency, the veins are yellow.
Manganese	Plants with net-veined leaves develop chlorosis in interveinal tissues, while veins remain green. Plants with parallel veins develop a general chlorosis condition and such secondary symptoms as grey specks on cereals.
Molybdenum	Foliage is yellow or greenish yellow, similar to nitrogen deficiency symptoms. Leaf blades fail to expand.
Zinc	In most plants there is a decrease in the rate of terminal growth with a decrease in stem length accompanied by a rosetting or whorling of the leaves.

Sources: "The Use of Additives is Theme of Liquid Fertilizer Meeting." 1964. Agricultural Chemicals, 19(12): 46, 48, 50; and Berger, K. C., and P. F. Pratt. 1963. "Advances in Secondary and Micronutrient Fertilization," IN Fertilizer Technology and Usage, p. 287-340, M. H. McVickar, G. L. Bridger, and L. B. Nelson, eds., Soil Science Society of America, Madison, Wisconsin.

nutrient in finely divided form (13). Since each granule of fertilizer has a coating of micronutrient, the density of distribution of micronutrient on the field is as uniform as that of the fertilizer. In most cases, a binder is required to promote adherence of the micronutrient material to the granule. In work at TVA, micronutrient materials were blended with granular fertilizers for 1 minute in a small rotary mixer; then oil (usually waste motor oil) or water was added and the mixing was continued. (This procedure was better than adding the binder before adding the micronutrient). Over 90% adherence of various micronutrient sources (salts, oxides, or frits) was obtained by the use of small amounts of oil (1.5%-3% by weight) or water (1.5%-2%). The proportions of micronutrient materials ranged from 2% to 12.5% by weight of the fertilizer. Fertilizer solutions have been used instead of water as the binder.

The treated products were dry in appearance and were free flowing. When treated with oil, no loss of adherence of the micronutrient was noted after 1 month's storage. However, in some cases, the bags were discolored and weakened. While the treatment with water promoted adherence with many combinations, the water treatment lost most of its effectiveness after 1 week of storage. Also, it caused some mixtures to cake in storage. This treatment should be useful, however, when the materials are spread immediately after being mixed. Coating bulk blends with micronutrient, oil, and clay has been reported to be a practice used in England (14).

Since micronutrient requirements vary widely in different areas and with different crops, provision of the proper micronutrients fits in well with the custom formulation service that bulk blenders usually offer (14). The addition of micronutrient materials during blending offers the blender the greatest flexibility in formulation and does not require additional storage for fertilizer.

Incorporation in Granules During Manufacture--Incorporation of micronutrients in granular fertilizers during manufacture eliminates the problem of segregation of the micronutrients from the fertilizer granules. The method also probably has economic advantage in the production of large quantities of fertilizer containing micronutrients. Disadvantages arise from the inflexibility of the method. Manufacturers cannot economically make and store small lots of special products containing various kinds and proportions of micronutrients. However, the method is useful in many cases when a regional deficiency of a micronutrient has been identified.

Micronutrient Addition to Liquid Fertilizers

Foliar application of soluble micronutrient sources is another method of combating micronutrient deficiency. This method has the advantage of fast crop response. Furthermore, with some soils, foliar application is often the most effective way to supply the micronutrient. The major disadvantage is that with some nutrients an excessively large number of dilute applications are required to supply sufficient amounts of the micronutrients.

Addition to Liquid Compound Fertilizers--The incorporation of micronutrients in liquid compound fertilizers would be advantageous since little difficulty would be encountered in homogeneously supplying the small amounts required. However, only sodium borates and sodium molybdate have adequate solubility in liquid fertilizers made from orthophosphoric acid to supply agronomical needs. The solubilities of copper, iron, manganese, and zinc salts in such liquids are practically nil.

One method of incorporating these micronutrients is through the use of a sequestering agent, which forms complexes with the nutrients and makes them resistant to precipitation by the phosphate. Organic sequestering agents have been used to some extent; however, their cost is quite high. An inorganic sequestering agent, e.g., ammonium polyphosphate liquid fertilizer of 10-34-0 or 11-37-0 grade, appears to be a better choice because of its relatively low cost. Such solutions contain about 50% and 70%, respectively, of their P_2O_5 as polyphosphates (the remainder is present as orthophosphates). Production of these solutions has been described in chapter XIX. Studies by TVA have shown that the solutions are effective sequestrants for the metallic trace elements, with the exception of manganese (15). The solubilities at 27°C of several of the micronutrient salts in ammonium polyphosphate solution of 11-37-0 grade and in ammonium orthophosphate solutions of 8-24-0 grade are tabulated below:

	Solubility, % by Weight of Element: B, Cu, Fe, Mn, Mo, Zn	
Micronutrient Source Added	In 11-37-0 Ammonium Polyphosphate Solution	In 8-24-0 Ammonium Orthophosphate Solution
Sodium tetraborate decahydrate	0.9[a]	0.9[a]
Cupric oxide (CuO)	0.7	0.03
Cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)	1.5	0.13
Ferric sulfate nonahydrate [$Fe_2(SO_4)_3 \cdot 9H_2O$]	1.0	0.08
Manganous-manganic oxide (Mn_3O_4)	0.2	<0.02
Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$)	0.5[a]	0.5[a]
Zinc carbonate ($ZnCO_3$)	3.0	0.05
Zinc oxide (ZnO)	3.0	0.05
Zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$)	2.0	0.05

a. Largest amount tested. Maximum solubility not determined because only small amounts of molybdenum and boron are required for plant growth, and the amount solubilized was adequate.

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), ferric oxide (Fe_2O_3), manganese dioxide (MnO_2), manganese sulfate ($MnSO_4 \cdot H_2O$), and manganese carbonate ($MnCO_3$) were much less soluble in the 11-37-0.

Use of the sequestering effect of ammonium polyphosphate solutions to incorporate micronutrients in liquid fertilizers appears to be attractive. Aside from the sequestering effect, its use is advantageous because the grade of the product is increased. Thus, the sequestering effect is an incidental advantage, without extra cost for a sequestering agent. The incorporation of trace elements by sequestration has the advantages, in comparison with solid mixes, that good mixing can be obtained easily and that segregation cannot occur after mixing. Moreover, there are no undesirable reactions among the trace elements and other constituents of the fertilizer, as sometimes occur in solid mixes. One disadvantage is that the amount of trace element which can be dissolved may not give the amount per hectare desired in some cases. Practice is so varied in regard to application rate that this disadvantage is difficult to evaluate.

Some of the metallic micronutrients are soluble in nitrogen solutions containing free ammonia and in aqua ammonia.

Addition to Suspension Fertilizers--The suspension type of technique discussed earlier appears to be especially applicable for use with micronutrients, since the solubility of the micronutrient carrier is immaterial except insofar as it affects the agronomical properties (10). If insoluble, the micronutrient should be fine enough that it will not settle rapidly or clog spray nozzles. The only restriction to the amount that can be added is the viscosity of the final product, as limited by the type of application equipment used.

Experimental NPK suspensions have been made with micronutrient additions from fritted trace elements--copper sulfate, zinc sulfate, manganese sulfate, or iron sulfate. In general, these materials had no important effect on the physical properties of the suspensions when the amount added was about 5%.

Suspensions applied soon after preparation present no difficult problems of settling and crystal growth. They can be applied with some types of standard liquid fertilizer equipment, although larger nozzles usually are required. If suspensions are stored for days or weeks, provision should be made for agitation. Crystal growth may be troublesome in long storage.

Other Useful Elements

"Essential" elements are those which have been demonstrated to be essential in the sense that plants cannot grow to maturity when the element in question is absent. Some elements or compounds that have not been demonstrated to be essential have been shown to increase yields substantially under certain conditions or to increase the nutritive value of the crop.

Large amounts of silica are taken up by the plants, and from the time of Liebig (1840) there has been speculation as to the role of silica in plant growth. Silicon has not been proven to be essential to plant growth, but it has been shown to be essential for maximum yields of some crops. In Hawaii on soils with low extractable silica, application of calcium silicate slag increased the yield of sugarcane by 8-10 tons/ha. On the same soil, application of calcium carbonate did not increase yields (16). Subsequent studies showed that several slags and silicate minerals were useful in increasing yields of sugarcane or sudan grass, but calcium metasilicate ($CaSiO_3$) was the most effective (17). Sodium metasilicate was also effective. Portland cement (which contains di- and tricalcium silicate) was effective. Calcium metasilicate is now produced commercially for agricultural use in Hawaii by sintering a mixture of silica sand and coral limestone in a cement kiln.

Silicate applications have given large yield increases of rice in Japan, and application of silica in the form of slags or hearth ashes has become a standard practice (18). Consumption of calcium silicate fertilizers in Japan in 1977 amounted to 789,000 tons, not including fused calcium-magnesium phosphate (515,000 tons), which also contains soil-soluble silica (19).

Elsewhere in the world the deliberate addition of silicate materials is rare, although there is extensive use of various types of slags containing silicates for their calcium, phosphorus, or micronutrient content. As noted previously, fused calcium magnesium phosphate contains 20%-30% SiO_2 while Rhenania phosphate and basic slag contain smaller percentages. Production of iron in the blast furnace yields slags containing 30% SiO_2 or more, and production of elemental phosphorus in the electric furnace yields a calcium silicate slag containing 35%-40% SiO_2. These materials are occasionally used as liming materials. The usefulness of their silica content sometimes has been mentioned speculatively but seldom studied systematically.

Sodium sometimes increases the yield of asparagus or some root crops and is sometimes added to fertilizers for that purpose, usually as sodium chloride.

Cobalt has been applied to rangeland in Australia in small amounts, mainly to improve the health of sheep that graze there. Cobalt is essential for animal nutrition, but it has not been established as essential to plant growth. The more common practice is to supply cobalt-containing materials directly to the animals, when needed. However, cobalt plays an essential role in fixation of nitrogen by legumes and, hence, is helpful to growth of such crops.

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XXI Controlled-Release Fertilizers

Fertilizers that release plant nutrients slowly throughout the growing season or even several growing seasons continue to attract the attention of technologists and agronomists. Potential advantages claimed for controlled-release fertilizers are increased efficiency of uptake by plants; minimization of losses by leaching, fixation, or decomposition; reduction in application costs through reduction in number of applications; elimination of luxury consumption; and avoidance of burning of vegetation or damage to seedlings. This is an impressive list of potential advantages.

The term "controlled-release fertilizer," as used in the following discussion, refers to fertilizers that for any reason release their nutrient content over an extended period. Even a simple choice among materials inherently slow to dissolve is viewed as a measure of control. Also, the release rate of water-insoluble materials often can be controlled to some extent by particle size and placement in the soil.

Controlled-Release Phosphate Fertilizers

Numerous controlled-release phosphorus compounds have been tested, and some are in use. Prominent among them are ground phosphate rock, calcined aluminum phosphate ore, basic slag, defluorinated phosphate rock (tricalcium phosphate), fused calcium magnesium phosphate, Rhenania phosphate, bone meal, dicalcium phosphate, magnesium ammonium phosphate, calcium metaphosphate, and potassium metaphosphate. (The so-called metaphosphates are more properly designated as polyphosphates.)

The use of ground phosphate rock, including calcined aluminum phosphate ores, has been discussed in detail in chapter XII. Basic slag, fused calcium magnesium phosphate, Rhenania phosphate, bone meal, dicalcium phosphate, defluorinated rock phosphate, calcium metaphosphate, and potassium phosphates were discussed in chapter XVI. Magnesium ammonium phosphates and similar compounds were discussed in chapter XIV.

Most of the insoluble or slightly soluble phosphate materials are used either because they are less expensive than soluble phosphates or because they supply other elements. Very seldom can any agronomic superiority be attributed to their slow release of phosphorus in the soil. In fact, the slightly soluble materials often give inferior results, particularly in the first year of application. However, some of them are valued for specialty uses because they may be safely placed in contact with seeds or roots in some situations. Some of the slightly soluble phosphates may prove to be particularly useful in tropical agriculture where conditions are quite different from those in temperate zones. However, relatively little data are available regarding the use of these materials in tropical agriculture.

Soluble phosphates react rapidly with the soil to form relatively insoluble products (1). Therefore, even fully soluble phosphates become slow-release fertilizers in the soil. The main effort has been to find ways to increase the release rate. When soluble phosphates are applied in granular form, the reaction with the soil is delayed, and pockets of relatively soluble phosphate may persist at the granule sites for several weeks. Thus, good results usually are obtained by placement of soluble granular phosphate fertilizers near the seed.

Controlled-Release Nitrogen Fertilizers

The need for a slow-release nitrogen fertilizer is much more acute than for phosphate (or potash), particularly under certain soil and climatic conditions. In most cases phosphate not utilized in the year of application remains in the soil and benefits future crops; therefore, the long-range utilization often is high. A similar situation applies to potash. In contrast there is seldom much carryover of fertilizer nitrogen from one crop to the next. Nitrogen applied as fertilizer is lost from the soil in several ways.

1. Leaching or Surface Drainage--Heavy rains or poorly controlled irrigation may leach the nitrogen beyond the reach of plant roots or carry it away in surface drainage. In either case the nitrogen is lost to the cropland and may contaminate streams, lakes, or underground water supplies.

2. Volatilization as Ammonia--Surface-applied urea rapidly hydrolyzes to ammonia and carbon dioxide. Part of the ammonia may be volatilized into the atmosphere. Also, ammonia may be volatilized from surface-applied ammonium salts, particularly from high-pH soils. In flooded rice fields, part of the ammonia dissolved in the surface water may be volatilized.

3. Decomposition--Under anaerobic conditions (flooded or waterlogged soils), nitrates are reduced to nitrites, which are unstable and decompose forming elemental nitrogen or nitrogen oxide that escapes to the atmosphere (denitrification). Ammonia nitrogen is rapidly oxidized to nitrate under aerobic soil conditions and may subsequently be lost by denitrification when it leaches into an anaerobic subsoil layer or when the soil becomes waterlogged or flooded.

Thus, inefficient use of applied nitrogen is closely related to nitrogen losses. Utilization of nitrogen fertilizer by crops seldom exceeds 50% and may be as low as 20% under some conditions.

With the present and prospective high price of nitrogen fertilizer, improved utilization is particularly important. If the recovery of nitrogen could be increased by one-third, for example, the effect would be equivalent to increasing the nitrogen supply by that amount. Nitrogen losses are heavy with flooded rice, especially when grown under conditions of intermittent flooding or poor water control.

Slightly Soluble Materials

One group of controlled-release nitrogen fertilizers comprises chemical compounds that are inherently only slightly soluble in water or soil solution. It may be noted that the rate of release of nutrient in the soil from most of these slightly soluble compounds is not necessarily a function only of their water solubility. Instead, the release rate is related to microbiological attack or hydrolysis which converts the nitrogen to forms that can be utilized by plants. However, the rate of attack is related to the rate of solution which depends, in turn, on solubility, particle size, and other factors.

Urea-aldehyde compounds are the principal representatives of this group that are produced commercially. Isobutylidene diurea (IBDU) is produced in Japan through the reaction of urea with isobutyraldehyde in a 2:1 mole ratio. When pure, it contains 32.18% N. Hamamoto reported methods for its preparation and discussed its usefulness as a fertilizer (2). Crotonylidene diurea (CDU), also called cyclodiurea, is produced in Japan and Germany through the reaction of urea with crotonaldehyde or acetaldehyde. The pure compound contains about 32% N.

Ando reported a Japanese consumption of 1,800 tons of N as IBDU and 1,400 tons as CDU in 1968--a total of 3,200 tons of N or 10,000 tons of the two slow-release materials (3). This was more than twice the 1966 use. Tsuno reported construction of a 40,000-tpy plant (13,000 tons of N) in Japan in 1972 (4). He has described the production process and use of the product to prepare compound fertilizers in which about half of the nitrogen was in slow-release form.

Hamamoto discussed agronomic studies made in Japan with IBDU and other slow-acting nitrogen materials (2). The release rate from these slightly soluble materials is a function of the particle size. Under Japanese conditions, use of these materials was often advantageous in improving yields and in saving labor by decreasing the number of applications. Hamamoto stated that the cost of IBDU to farmers was over twice that of conventional nitrogen fertilizers per unit of nitrogen. Compound fertilizers of 1:1:1 ratio, with half of the nitrogen supplied as IBDU, cost about 20% more than conventional fertilizers. For this reason, they were used mainly on vegetables and cash crops and not so much on grains.

Urea-formaldehyde reaction products, usually called "ureaform," are produced by about six manufacturers in the United States and in several other countries. Unlike IBDU and CDU, ureaform is not a definite chemical compound. It contains methylene ureas of different chain lengths; the solubility increases with decrease in chain length. It usually contains about 38% N.

Perhaps the most useful component of ureaform as a slow-release nitrogen material is trimethylene tetraurea; shorter chain lengths are too rapidly decomposed, and longer chains are highly resistant to decomposition. Unfortunately, it is very difficult to produce commercially a pure trimethylene tetraurea; ureaform contains both shorter and longer chains.

A typical ureaform may contain 30% of its nitrogen in forms that are soluble in cold water (25°C). The quality of the remaining 70% is judged by the percentage that is soluble in hot (boiling) water as determined by prescribed analytical procedures. At least 40% of the nitrogen insoluble in cold water should be soluble in hot water for acceptable agronomic response; typical values are 50%-70%.

Ureaform is produced by reaction of urea with formaldehyde in aqueous solution in the presence of an acid which catalyzes the reaction. The degree of polymerization depends on the mole ratio of urea to formaldehyde and on the pH, time, and temperature of reaction. The reaction is stopped by neutralizing the acid. Production processes have been described by Clark and by Kolterman and Rennie (5, 6).

In Japan ureaform is also produced as a component of compound fertilizers by addition of formaldehyde solution to the urea solution fed to the granulator (3). Kuwabara described the use of a methylene urea reactor to react urea and formaldehyde solution to produce a slurry that fed directly to a granulation plant with other materials to make compound fertilizers (7). Some slow-release nitrogen was formed, and the physical properties of the products were improved.

In the United States, ammoniating solutions containing urea, formaldehyde, and ammonia are used to prepare compound fertilizer containing water-insoluble nitrogen. The composition of one such solution is: urea-35.3%, formaldehyde-8.0%, CO_2-8.4%, NH_3-25.0%, and H_2O-23.3%. Other solutions with high formaldehyde content (up to 60%) are available for use with additional urea (8).

Addition of sulfuric or phosphoric acid (or superphosphate) neutralizes the ammonia and catalyzes the formation of methylene urea. Products containing about 20%-30% of their nitrogen in a water-insoluble form are produced. Good control of conditions in the granulator and dryer is needed to produce a satisfactory quality of water-insoluble nitrogen. In some cases, a prereactor is used prior to the granulator (7).

The consumption of ureaform in the United States is approximately 50,000 tpy, not including that formed in compound fertilizers from solutions. Most of the production goes into compound fertilizer for specialty uses, such as for lawns, flower gardens, and golf courses. The wholesale price of ureaform per unit of nitrogen is about three times that of urea, ammonium nitrate, or ammonium sulfate.

In tests made by TVA of many other organic nitrogen-containing compounds as fertilizers, some proved readily available, some slowly available, some inert, and some toxic. Among those that showed promise as slow-release fertilizers were oxamide, glycouril, cyanuric acid, ammeline, and ammelide. For lack of an economical process, none of these materials have been manufactured commercially for fertilizer use.

Magnesium ammonium phosphate ($MgNH_4PO_4$) is a slowly soluble source of nitrogen although it contains more phosphate than nitrogen. The commercial product called "Mag Amp" contains a variable amount of water of crystallization and some impurities; a typical grade is 8-40-0. A similar product containing potash is marketed under the trade name "En Mag" in the United Kingdom. The grade is 5-24-10. The rate of solution of these slightly soluble materials is controlled by the size and hardness of the granules.

Guanyl Urea Sulfate (GUS) and Guanyl Urea Phosphate (GUP)

These compounds are unique among slow-release fertilizers in that they are readily and completely soluble in water but are adsorbed on the soil colloids. Once the compounds are adsorbed, mineralization is reported to be very slow under aerobic conditions but satisfactory under anaerobic conditions (9). Hence, the most promising use is on flooded rice.

Limited quantities of these materials are produced in Japan. Apparently, GUS is being marketed, but it is not known whether GUP is produced commercially or only for experimental use.

Coated Soluble Materials

A wide range of materials and techniques has been explored with the object of making controlled-release fertilizers by coating soluble fertilizer materials with plastic films, resins, waxes, asphaltic materials, or other barriers. The first commercial production of coated controlled-release fertilizer utilizes a process developed by Archer Daniels Midland Company (ADM). The main component of the coating is a copolymer of dicyclopentadiene with a glycerol ester (10). Applied in several layers that vary in composition, the coating releases fertilizer solution by osmotic exchange with moisture from the soil. The coated granular fertilizer was manufactured by ADM under the trade name Osmocote starting in 1964. It now is produced and marketed by Sierra Chemical Company under exclusive license from ADM. Three grades of Osmocote are available: 14-14-14, 18-9-9, and 16-4-8. The weight of the coating ranges from 10% to 15% of the gross weight.

Osmocote products are recommended for turf, floriculture, nursery stock, and high-value row crops. The retail price was reported to be about $0.73-$0.95/kg in 1974.

Sulfur-coated urea (SCU) is a controlled-release material that has been under development by TVA for 15 years (11). Sulfur was selected as the coating material on the basis of economy and efficiency after many coating materials were tried. Urea was selected as the material to be coated because of its high nitrogen content, low cost, and commercial availability.

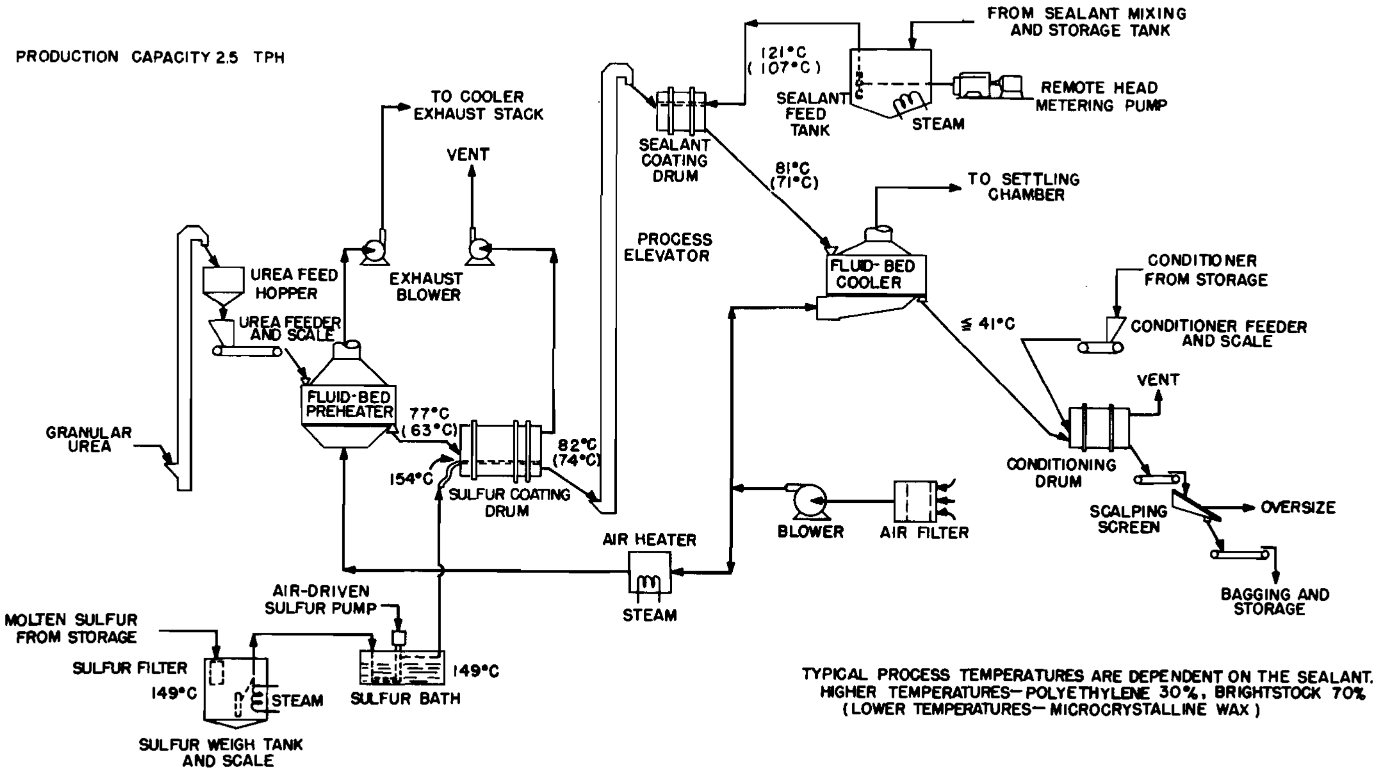
Initial studies indicated that sulfur alone was not adequately resistant to moisture penetration. However, it was discovered that addition of an oily wax sealant over the sulfur coating provided a successful coating. Subsequently sulfur-only coatings were developed that may be satisfactory under some conditions.

In early laboratory work, 1- to 7-kg batches of urea were coated in small drums. The development then was shifted to a small continuous pilot plant with a production rate of about 150 kg/hour. Development of the process was completed in a large pilot plant with a design capacity of 1 tph but which now has a capacity of over 2 tph. Shirley has summarized results from the large pilot-plant operation (12). In October 1978 TVA began producing sulfur-coated urea in its demonstration-scale plant at a rate of 10 tph. A sulfur-coated prilled urea (trade name "Gold N") was produced and marketed by Imperial Chemical Industries (ICI), and a similar material is produced in Canada by Canadian Industries, Ltd. (CIL).

A schematic flow diagram of the TVA pilot plant is shown in figure 1. Granular urea is preheated in the first rotating drum to 77°C with electric radiant heaters to prevent the sulfur from freezing too rapidly on the granules. Later, a fluidized bed preheater was used as shown in figure 1. The molten sulfur is atomized and sprayed onto the rolling bed of granules in the second drum. Both air atomization and hydraulic atomization were studied. Wax is applied in the third drum. The coated granules are then cooled in a fluidized bed cooler, and an absorbent powder is applied in a fourth drum to eliminate the tacky condition of the wax and to prevent the granules from floating when applied in water (as in a rice paddy).

Figure 2 shows arrangements of nozzles and other internal parts in the sulfur-coating drum when using pneumatic or hydraulic nozzles. The hydraulic nozzles have the advantage that they produce less sulfur mist which must be collected and recycled or disposed of. The reduction in mist makes possible other alterations which result in increased capacity and improved operation.

Most of the work was done with commercial granular urea (1.7-3.3 mm) produced by the spray-drum granulation process or with pan-granulated urea. Some tests were made with prilled urea, but its smaller particle size results in greater surface area per unit weight of urea; this greater surface requires a coating that is higher in percentage by weight of the product for a given coating thickness. Also most urea prills contain a hole or dimple which makes it difficult to



TYPICAL PROCESS TEMPERATURES ARE DEPENDENT ON THE SEALANT.
HIGHER TEMPERATURES—POLYETHYLENE 30%, BRIGHTSTOCK 70%
(LOWER TEMPERATURES—MICROCRYSTALLINE WAX)

Figure 1. Flow Diagram for Sulfur-Coated Urea Pilot Plant.

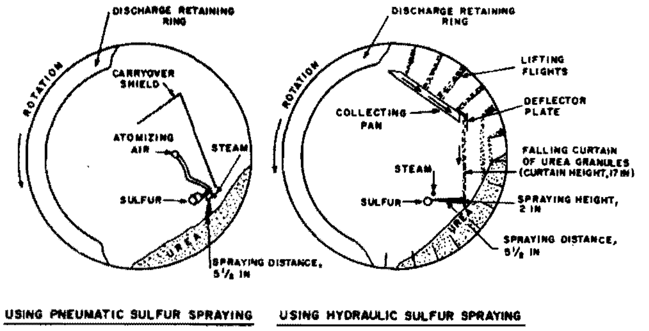


Figure 2. Sulfur Coating Drum Operation.

apply a satisfactory coating. For these reasons, large, well-rounded granules are preferred for coating.

The rate of dissolution of coated urea can be varied by varying the thickness of the sulfur coating and, to some extent, by varying the amount of sealant. As an indication of the dissolution rate, a laboratory test is used in which the percentage of the urea that dissolves in 7 days in water at 38°C is measured. Current agronomic information indicates that, in general, the best results are obtained with materials that have a 7-day dissolution of 17%-35%. Such material is produced in the TVA demonstration-scale plant with a total coating weight of 20.6% (16.0% sulfur, 2.1% sealant, and 2.5% conditioner), starting with granular urea sized at 1.2-3.3 mm (the coating weight could be reduced by using larger granules). The calculated mean thickness of the sulfur coating is about 55 µm for a 3-mm sphere which agrees approximately with microscopic observations. A similar dissolution rate can be obtained when using a coating of sulfur only at a coating weight of about 21% (36% N in product).

Dissolution rates in soil at three temperatures are shown in figure 3 for a TVA pilot-plant product coated with 20% sulfur without sealant. For comparison, dissolution rate in water at 25°C is shown. This product had a dissolution rate of 26% by the standard laboratory test procedure (7 days in water at 38°C). While these tests indicate that the dissolution rate increases with temperature, tests reported by Davies showed little effect of temperature in the range of 10°-25°C (9). However, many factors may affect the rate of dissolution in soil. Allen, et al., have published data on the rate of dissolution in the soil as affected by coating weight, temperature, and placement (13).

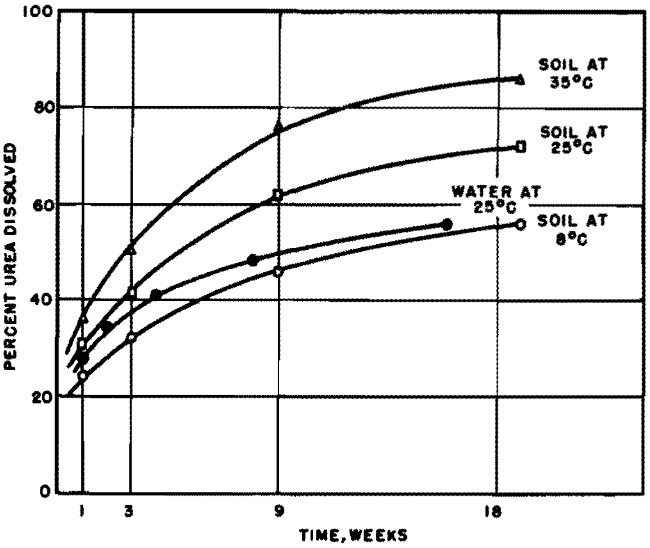


Figure 3. Dissolution of Sulfur-Coated Urea in Soil or Water (Sulfur Coating, 20%, No Sealant).

Figure 4 shows the results of TVA studies (unpublished) on the rate of dissolution of SCU in soils. The SCU used in these studies had a coating weight of 16.5%, S; 2.0%, sealant; and 2.4%, conditioner.

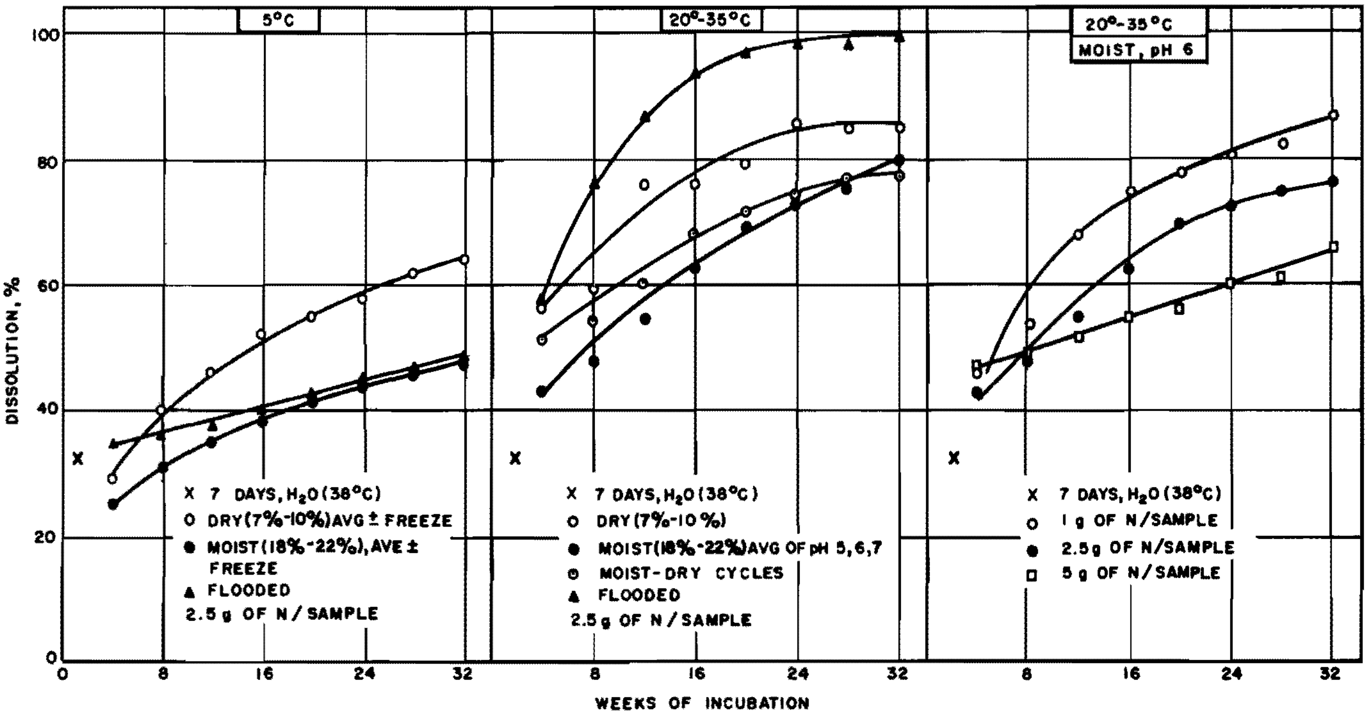


Figure 4. Dissolution of SCU as Affected by Temperature, Soil Moisture, Sample Size, and Time of Incubation.

The sealant was a 30:70 mixture of polyethylene wax and brightstock oil. The data show that dissolution was more rapid at 20°-35°C than at 5°C. Freezing samples of the soil containing SCU at -25°C for 48 hours had no effect on subsequent dissolution rates at the temperature indicated in figure 4. The dissolution rate was more rapid in dry soil (7%-10% water) than in moist soil (18%-22% water). However, the dissolution rate in flooded soil was higher than that of either dry or moist soil in experiments at 20°-35°C but not at 5°C.

The rate of dissolution decreased as the ratio of SCU to soil increased. The ratios were varied by adding 1.0, 2.5, or 5.0 g of nitrogen as SCU to a fixed amount of soil. The resulting concentrations expressed as soil volume per granule were 2.9, 1.2, and 0.6 cm^3. (The 6-10 mesh granules averaged 5.6 mg of N per granule.) The inference is that a concentrated placement (spot or band) would result in a slower dissolution rate than uniform mixing with the soil, especially at high application rates. There was no effect of soil pH in the range of 5-7.

In addition to the controlled-release characteristics, coated urea has excellent storage and handling characteristics and might even be handled in bulk in humid climates. Also, it may be blended with triple or single superphosphates, which are incompatible with uncoated urea. Also the sulfur coating is a slowly available source of sulfur which would be an advantage in sulfur-deficient areas.

Agronomic tests have been completed or are in progress in 54 countries and in all 50 states of the United States. Results of tests by TVA, ICI, and others have been reported (9, 11, 14).

Coated urea was advantageous for use on sugarcane, pineapple, and rice grown with delayed or intermittent flooding and, in general, for long-season crops or for conditions conducive to heavy leaching or to decomposition losses.

TVA estimates indicate that with granular urea at $170/ton and sulfur at $48/ton, a coated product (37% N) could be produced on a large scale at a cost of about $179/ton (15). Thus, the cost per ton of SCU would be about the same as straight urea although the cost per ton of N would be about 31% higher. Agronomic tests indicate that in many cases the increase in cost could readily be justified. The improved physical properties of the product would be an additional advantage.

In most trials with rice, SCU was superior to either preplant or topdressed urea under delayed and intermittent flooding. With continuously flooded rice, however, SCU showed no advantage. Benefit:cost ratios (dollar return per dollar invested in coating), calculated on individual experiments, favored SCU over urea in 75% of the tests when both were applied to the soil before planting. Many comparisons showed a benefit:cost ratio of 10:1 or better. When the urea was topdressed as the rice was growing, returns from coating were not as favorable (14).

The sulfur-coating technique may be applied to fertilizers other than urea. Experimental work has included coating of diammonium phosphate, potassium chloride, potassium sulfate, and various compound fertilizers, including a pan-granulated urea-potassium chloride product of 32-0-16 grade.

Nitrification Inhibitors

Nitrogen fertilizers in the ammonium form are immobilized by sorption on clay particles and hence are resistant to leaching. However, the ammonium form is converted to the nitrate form under aerobic conditions by microbiological processes known as nitrification. The rate of conversion depends on the temperature; below 10°C it is very slow, but at 20°C and higher it is rapid. The nitrate form is more readily available to most plants although some plants (e.g., rice) can readily use the ammonium form. Thus, some of the purposes of controlled release (resistance to leaching, prevention of denitrification losses, and delayed availability) may be attained by delaying nitrification of ammonium nitrogen.

Numerous organic chemicals have been identified as nitrification inhibitors. The inhibition is due to the toxicity of these chemicals to organisms that convert ammonium nitrogen to nitrite, which is the first step of the nitrification process.

One of the nitrification inhibitors that has received attention in the United States is 2-chloro-6-(trichloromethyl) pyridine. The Dow Chemical Company is promoting it under the trade name, N-Serve. The minimum concentration of N-Serve in the soil for delaying nitrification at least 6 weeks is said to range from 0.5 to 10 ppm.

Dow points out that a nitrification inhibitor is helpful only when conditions favor high nitrogen loss from the soil. Such conditions are heavy rainfall or heavy irrigation, coarse-textured soil, and soil in the pH range where nitrification readily occurs. Nitrate thus formed will leach down into anaerobic soil layers.

Potassium azide (2%-6% KN_3) dissolved in anhydrous ammonia was effective in lowering the rate of nitrification in tests conducted by the U.S. Department of Agriculture in cooperation with agricultural experiment stations in the states of Louisiana and Washington. PPG Industries, Inc., is exploring this and other agricultural uses (e.g., as a herbicide in rice culture) for the azide.

Another nitrification inhibitor that has received much attention in Japan is 2-amino-4-chloro-6-methyl pyrimidine. It is manufactured by Mitsui Toatsu Chemicals, Inc., (formerly Toyo Koatsu Industries, Inc.) under the trade name AM. Other nitrification inhibitors that have been used in Japan in compound fertilizers are sulfathiazole, dicyandiamide, thiourea, N-2, 5-dichorphenyl succinamide, 4-amino-1, 2, 4-triazole hydrochloride, and guanylthiourea (7).

In flooded or waterlogged soils, as for example in continuously flooded rice paddy, anaerobic (reducing) conditions exist in the soil below the surface, and hence nitrification of ammoniacal nitrogen does not occur in this layer. Therefore, when ammonia, ammonium salts, or urea (which hydrolyzes in the soil to ammonia and carbon dioxide) is placed in the reducing zone of the soil, it remains in the ammonium form and is more or less immobilized by sorption on the clay. Some of the advantages of controlled release may be attained by placement of ammoniacal nitrogen in the reducing zone of the rice paddy soil. However, this placement is difficult since applicators quickly become clogged with mud and wet fertilizer. To facilitate subsurface placement, large granules or briquettes of urea have been produced experimentally which can be pressed into the soil by hand (or foot). Experiments with this placement have shown substantially increased efficiency of nitrogen utilization by rice as compared with the usual broadcast placement. The advantages of this placement can be realized only when the rice paddy is continuously flooded. With intermittent flooding, nitrification will occur during dry periods; during subsequent flooding, the nitrate will be reduced to nitrite which is unstable and decomposes to elemental nitrogen or N_2O and is thus lost by volatilization.

Controlled-Release Potash Fertilizers

Some interest has been shown in controlled-release potassium fertilizers. TVA conducted tests with potassium polyphosphates and potassium calcium pyrophosphates. Some of the materials were only slightly soluble in water by AOAC procedure. Agronomic evaluation of the materials was reported by Engelstad (16). Their only advantage was reduced injury to germinating seeds. Most of the materials were as readily available as soluble potash salts. Some of the least soluble materials showed slow-release characteristics when applied as large particles (about 7 mm), but there was no conclusive evidence of increased efficiency.

More recently, sulfur-coated potassium chloride has been prepared by TVA for agronomic tests. Some of these tests were promising in that yields were increased in comparison with uncoated potassium chloride. More information is needed for agronomic and economic evaluation. Controlled-release NK products may also offer some promise and are under study at TVA.

Conclusions About Controlled-Release Fertilizers

Controlled-release nitrogen fertilizers very probably will prove useful for some field crops in some situations. Much more study will be required, however, to determine the place of controlled-release nitrogen fertilizers in the farm economy and under tropical and subtropical conditions. Recent and probable future increases in the price of nitrogen fertilizers should enhance the attractiveness of controlled-release fertilizers for some uses.

Controlled-release fertilizers are likely to prove advantageous where labor is scarce and expensive. In developing countries where labor is plentiful and inexpensive, multiple applications of soluble fertilizer often can be used to attain improved yields and higher efficiency of utilization with less cost. However, field results have shown that use of sulfur-coated urea on intermittently flooded rice increases yields in comparison with the use of uncoated urea, even when the latter is applied in split applications.

Prospects for improvement of phosphate and potassium fertilizers through controlled-release seem relatively less hopeful than for nitrogen. However, more study is needed, particularly in tropical agriculture. Slightly soluble phosphates may be favored when they are cheaper or when they supply other needed nutrients.

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XXII Physical and Chemical Properties of Fertilizers and Methods for their Determination

Introduction

The physical form in which a fertilizer is produced is of considerable importance, both agronomically and in regard to satisfactory handling, transport, storage, and finally application to the field. Most of the problems encountered with fertilizers probably are those resulting from deficiencies in physical properties; frequent problems include caking, dustiness, poor flowability, segregation, and excessive hygroscopicity. Customer acceptance or preference for a particular fertilizer over another of equal plant-food content almost always is based on physical properties of the product. Good physical condition, which is relatively easy for the customer to evaluate by simple observation, ensures him of easier, faster, more uniform, and less expensive application to the field. Also, in the various handling, transport, and storage steps that usually are involved between production and final use of fertilizers, it is essential that physical properties be such that the material remains free flowing (noncaking), that it be relatively nondusty, and that it withstand a reasonable amount of exposure to normal atmospheric humidity. Many production techniques, including various physical "conditioning" treatments, have been developed especially to provide favorable physical properties.

Physical properties of fertilizers, unlike the chemical compositions, normally are not governed in commerce by laws. Physical condition usually is a matter only of private agreement between purchaser and supplier. As a result, there are few "official" methods for measurement and evaluation of physical properties. Various producers tend to adopt or develop methods that appear to best suit their particular needs. However, some government-sponsored research organizations such as the U.S. Department of Agriculture and the Tennessee Valley Authority in the United States have developed and published procedures intended for general application to a variety of fertilizers; references to these procedures are included in this chapter. Also, the International Standards Organization, Technical Committee 134/SC3, is actively engaged in efforts to establish international standard methods for measurement of various physical properties of fertilizers (1).

The present chapter includes brief discussions of the effects and importance of various pertinent physical properties of fertilizers and descriptions of some of the methods that have been used and reported for measuring these properties. Some of the chemical properties that affect the reaction of fertilizers in the soil are also discussed in this chapter. Numerous literature references are given from which details of test procedures usually can be obtained.

Particle Size

Measurement of particle size is an important physical test that is routinely applied to fertilizer materials almost as frequently as is chemical analysis; almost all producers are equipped to check particle size regularly. The importance of particle-size control varies with the type of product, the intended method of handling, and the final use. Some of the reasons for size control follow.

Effects on Agronomic Response

Fertilizer materials of very low water solubility generally must be ground to small particle size to ensure sufficiently rapid dissolution in the soil and utilization by plants. For example, the effectiveness of raw phosphate rocks generally increases with fine grinding down to a particle diameter of about 0.15 mm; below that, little further benefit has been established (2). Other materials of low solubility that require relatively fine grinding include basic slags, limestone, dolomite, dicalcium phosphate, and fused phosphates such as calcium-magnesium phosphates, defluorinated phosphate rock, and calcium metaphosphates. Micronutrient or secondary nutrient sources of low solubility, such as sulfur, metallic oxides, and glasses ("frits"), likewise require fine grinding.

The fine grinding required for these materials often results in undesirable dustiness and other handling difficulties. Therefore, some research and development has been directed toward regranulating the pulverized materials, especially rock phosphate, with soluble binders to give granules that will handle well and then revert to pulverulent form in moist soil (2, 3, 4). Phosphate rock granules of relatively small size (0.1-0.3 mm), sometimes referred to as "minigranules," have in some tests been more effective than larger granules in this application (5, 6). Methods of dust control other than granulation include spraying the pulverized materials lightly with oil, water, or amine formulations. In the case of granular nitric phosphates, which normally contain phosphate in water-insoluble form as dicalcium phosphate or apatite, the crystal size of these materials is usually quite small, and there are sufficient water-soluble salts in the granule to ensure disintegration of the granule in moist soil with resultant increase in soil-phosphate contact. In such products, however, it has been considered desirable to have a reasonable proportion of the phosphorus in water-soluble form to ensure early response of crops (7, 8, 9).

Particle-size control of water-soluble fertilizers usually is for reasons other than agronomic ones, as will be discussed later. However, there apparently can be agronomic benefits also. For example, it has been found that in the application of water-soluble phosphates such as superphosphates and ammonium phosphates, especially to acid soils of high phosphate-fixation capacity, an increase in the fertilizer particle size in the range up to about 5 mm in diameter may increase early growth response of crops (7, 10).

Another potentially useful application of particle-size control for improvement of agronomic properties is in connection with some sparsely soluble slow-release nitrogen fertilizers such as urea-formaldehyde, isobutyldiurea, and oxamide. The rate of dissolution, and hence the rate of nitrogen availability from these materials, has been shown to be dependent on particle size; the larger the particles, the slower the release.

Effects on Storage and Handling Properties

Particle-size control of fertilizers is important to ensure satisfactory storage and handling properties. Before about 1950 almost all fertilizer materials were produced as relatively fine powders or small crystals. As a result, fertilizers usually were dusty in handling and very susceptible to hard caking during storage in piles or bags. Considerable labor usually was required to break up the lumps and make the products suitable for field application. The rapid growth of granulation in the early fifties, however, resulted in great improvement in storage and handling properties. This growth of granulation was paralleled by improvements in application equipment that took advantage of the better flow properties and absence of caking in granular products. Farmer demand for the granular products and for the improved application equipment soon was overwhelming. In the United States, the generally accepted nominal particle-size range for granular materials became 1.00-3.35 mm which represents material that will pass a U.S. Standard No. 6 screen but be retained by a No. 18 screen. There are, however, no state or federal regulations in the United States that specify allowable size or size tolerances for granular products; control is left to individual producers. The U.S. Agency for International Development (USAID), in purchasing granular fertilizers for its aid programs, generally specifies 90% minimum in the 1.00- to 3.35-mm (U.S. 6- to 18-mesh) range, 0% larger than 4.75 mm (U.S. 4-mesh), and no more than 2% finer than 0.6 mm (U.S. 30-mesh) (11). In European countries and Japan, granular fertilizers generally are produced in somewhat larger particle size; sizes reported are generally in the range of 2.0- to 4.0-mm diameter (U.S. 5- to 10-mesh) (12, 13, 14, 15, 16).

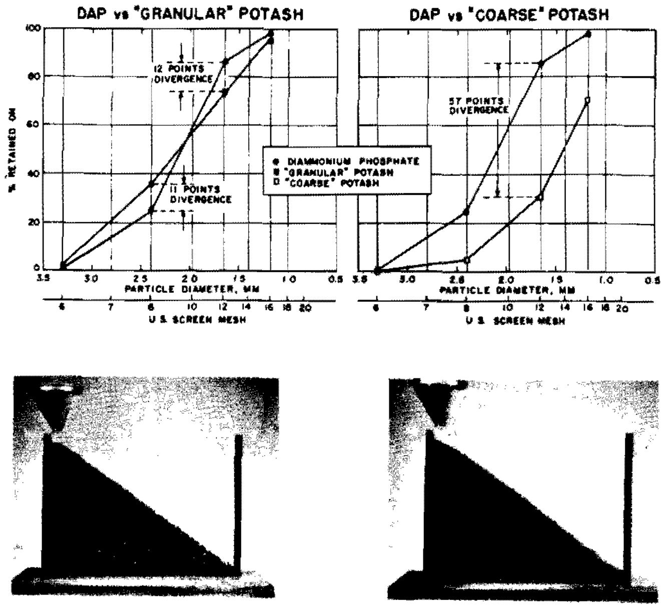
Fertilizers preferably should be free from particles so small that they generate air-borne dust on handling, both to ensure farmer acceptance and to prevent unpleasant or unhealthy working conditions in areas such as bulk-blending plants or bulk-handling operations. A frequent cause of dustiness in granular fertilizers is poor adherence of powdery conditioners (coating agents). The test methods for determining dustiness due to that cause will be described in a subsequent section of this chapter. The method can be adapted to measure dustiness resulting from any cause such as attrition during handling.

Granules of especially large size (> about 4 mm) have been found to be desirable for aerial application to forests. The large size minimizes wind drift and reduces lodging of granules in tree branches. In several countries there is either commercial or experimental production of "forestry-grade" urea or ammonium nitrate of large size for this purpose.

Effects on Blending Properties

Since the advent (about 1958) of bulk blending as an important system of mixing and distributing granular fertilizers, control of particle size has assumed additional importance as a method for reducing the segregation tendency of blends. The practice of bulk blending is described in UNIDO publication, Monograph No. 8 (Fertilizer Industry Series, ID/SER.F18) titled "A Fertilizer Bulk Blending and Bagging Plant," and in less detail in chapter XIX. In some early blending operations, materials were blended without regard to matching of particle sizes, with the result that the blends were very susceptible to segregation (unmixing) during handling. Subsequent studies by TVA and others identified particle-size matching of blend ingredients as by far the most important factor in producing a blend that is resistant to segregation (17, 18, 19, 20, 21). The effects of mismatches in other physical properties, namely density and particle shape, were insignificant in comparison with the effect of mismatch in the particle size.

The general size range of 1.00 to 3.35 mm (minus 6- plus 18-mesh, U.S. Standard) which defines granular fertilizer in the United States is not sufficiently restrictive to ensure good size matching for bulk blending. It has been found that materials for blending should agree not only in regard to their upper and lower size limits but should also be reasonably similar in particle-size distribution between these limits (17, 19). Agreement of size distribution curves within plus or minus 10 percentage points has been suggested as an effective criterion (18). The effects of adherence and nonadherence to this criterion are shown in figure 1. In the tests illustrated, granular diammonium phosphate of typical particle-size distribution was used in two bulk blends, one with a potash ("granular" grade) of very similar particle-size distribution (12 percentage points maximum divergence of size distribution curves) and another with much finer potash ("coarse" grade; 57 percentage points divergence). Each blend was poured to form a sloped pile in a small plastic view box (see later section on segregation tests). From the figure, it is obvious that during the pouring operation there was serious segregation in the blend of unequally sized materials but little obvious segregation in the blend of matched sizes.



DAP+"GRANULAR" KCL

DAP+"COARSE" KCL

Figure I. Particle-Size Matching Decreases the Segregation Tendency of Bulk-Blend Fertilizers (18).

In spite of the importance of particle-size matching to bulk blenders, there are no laws or published standards governing the particle size of materials furnished blenders in the United States. As a result, there are some wide divergences among different types of materials and among supplies of the same material from different manufacturers; however, major producers of materials for blending have been aware of the problem and have generally made efforts to provide reasonably matched materials. A survey of the particle size of materials being produced in the United States for blending was made in 1973; average particle-size data from this survey are given in table 1 (22). These data showed rather close agreement between the average particle-size distributions for diammonium phosphate and granular potassium chloride, two major ingredients in most bulk blends. As a result, the analyses shown for these materials in table 1 have come to be regarded by at least some producers as a "target" size for all materials intended for bulk blending in the United States. The data in the table show that the sizes of triple superphosphate and of one of the granular ureas also did not vary greatly from that criterion, but divergences were excessive in the cases of "coarse" potassium chloride, prilled ammonium nitrate, and prilled urea. Since the 1973 survey, there has been increased recognition among blenders that the coarse grade of potassium chloride is too small for use in blends. Also, there has been considerable replacement of prilled urea with larger, granular urea and some replacement of prilled ammonium nitrate with granular forms.

TABLE 1. AVERAGE PARTICLE-SIZE DISTRIBUTIONS OF GRANULAR FERTILIZERS FROM SOME MAJOR U.S. PRODUCERS IN 1973

Product	Typical Grade ($N-P_2O_5-K_2O$)	Sources Represented[a]	Cumulative % Retained on Indicated U.S. Standard Sieve 6	8	12	16	20
Diammonium phosphate	18-46-0	9	<1	36	86	99	100
Potassium chloride							
"Granular"	0-0-60	13	5	37	78	95	98
"Coarse"	0-0-60	14	-	6	31	73	94
Triple superphosphate	0-46-0	6	1	20	81	97	100
Ammonium nitrate (prills)	34-0-0	8	-	10	74	97	100
Urea[b]							
Prills[c]	46-0-0	9	<1	4	48	92	100
Granular A	46-0-0	1	1	88	100	100	100
Granular B	46-0-0	1	0	30	85	98	100

a. Unless otherwise noted, data from each source represent the average of 1 month's plant production analyses from survey by The Fertilizer Institute (22).

b. Data for urea obtained on spot samples--not part of the survey by The Fertilizer Institute.

c. Fertilizer-grade only--does not include feed-grade microprills, which are smaller.

Screen-Analysis Procedures

Particle-size distribution is normally measured by conducting a "screen analysis" (sieve analysis) on a representative sample. Obtaining a representative sample for screen analysis, however, is particularly difficult, because of the tendency of particles of different sizes to segregate during any movement of the fertilizer. Spot samples ("grab" samples) from fertilizer piles will not be representative of average size in the pile because piles usually are severely segregated during pile building (see section on segregation). Multipoint sampling and compositing by approved procedures are recommended. Composites should be mixed well (with minimum attrition) and riffled to suitable size (100-500 g); an entire riffle split from the last riffling should be used as the sample for screen analysis. A "gated" type riffle has been shown to be the preferred type to avoid size segregation during riffling (23).

Equipment required to carry out a screen analysis on a fertilizer sample consists of the following:

1. A set of standardized wire-mesh test sieves, each with different mesh aperture, covering the range of particle sizes expected in the sample. Typical test sieves, as pictured in figure 2, are 8 in (203 mm) in diameter by 2 in (50 mm) deep. Stainless-steel construction is much preferred to withstand corrosion by fertilizers. The sieves are so constructed that they can be stacked or "nested" with sieve apertures progressing in size from bottom to top in the stack; a solid pan is normally fitted under the lowest (finest) sieve and a solid cover over the uppermost (largest) sieve.
2. A means for shaking the sieve stack. It is much preferred to use a mechanical shaker of which numerous models are marketed. Hand-driven shakers are marketed also. In the absence of a shaker, the nested stack may be shaken by hand and tapped briskly on a table top to effect sieving. Shaking the sample by hand is time consuming and less reproducible, especially on the finer products.
3. A balance for weighing the sample and the size fractions developed in the sieve test. Capacity should accommodate sample weights up to about 500.0 g, and accuracy should be at least within 0.1 g for usual work.

Sample size recommended for testing on 8-in diameter sieves varies according to the size range of the material. For material in the range of granular fertilizers, sample size of 200-500 g is satisfactory. For finer materials, such as phosphate rock, smaller samples (100 g) are believed to give more reproducible results (24). The sample is placed on the uppermost screen of the stack, and shaking is begun. A shaking time of 5 minutes usually is satisfactory on a mechanical shaker; longer time can be tested if there is doubt. During shaking, each particle in the sample

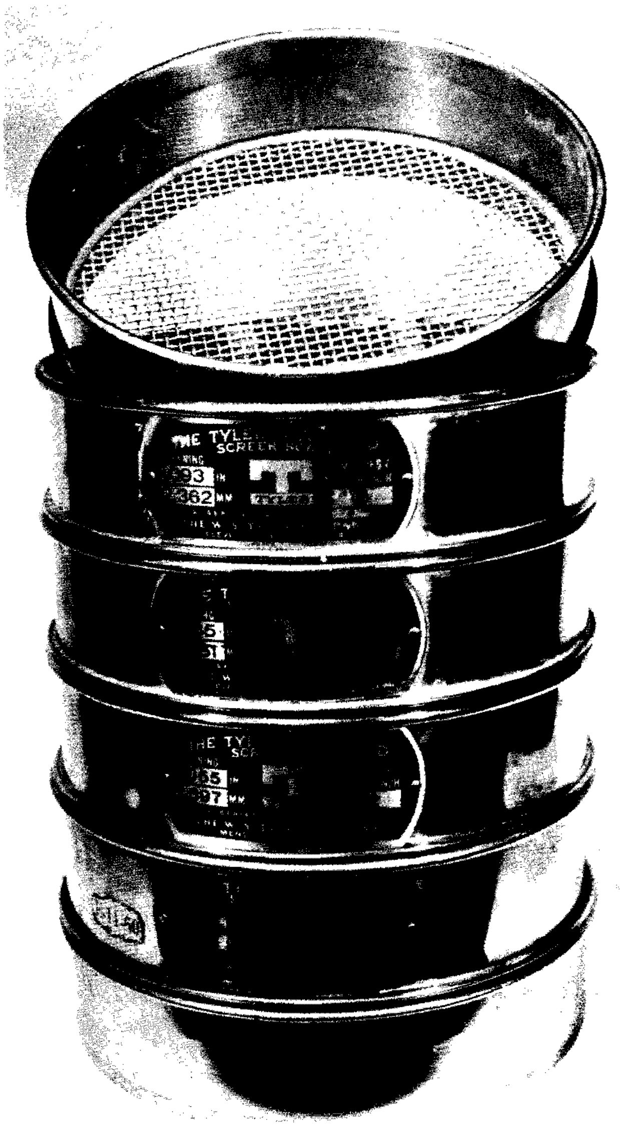


Figure 2. Set of Test Sieves as Used for Determination of Particle-Size Distribution in Fertilizer.

gravitates downward through screen apertures until it reaches a screen too fine to allow its passage. At the end of the shaking period, material on each screen is weighed individually, and the particle-size distribution of the sample is thus determined. The usual method of reporting results is as "cumulative percent" retained on each screen. Cumulative percent refers to all material in the sample that was too large to pass the screen in question; it includes, therefore, not only the material retained on the screen in question but also all material retained on coarser screens above it in the stack. The screen analysis curves that were given in figure 1 were plotted on a cumulative-percent-retained basis.

Selection of an appropriate series of sieve sizes (apertures) for a given material and for a given use is important. Several standards for the manufacture of test sieves and the reporting of sieve analyses are in use throughout the world. These vary somewhat in regard to the aperture sizes available, the sizes of wire used, and some minor details. A comparison of the U.S. Standard, Tyler, Canadian, British, French, German, Italian, and U.S.S.R. standards is given in table 2. The International Standards Organization, in an attempt to unify standards, has recommended three basic sieve series designated as R-10, R-20, and R-40, with a suggestion that preference be given first to the R-10 series, in which screen apertures progress in the ratio of the 10th root of 10 (25).[1] Screens in the French, German, Italian, and U.S.S.R. systems in table 2 correspond to this series. The R-20 and R-40 series are based on progressions according to the 20th and 40th roots of 10, respectively; thus, these two series include twice and four times the number of sieves included in the R-10 series. Sieves in the U.S. Standard series (table 2) correspond to every third sieve in the R-40 series. Screen numbers referred to in the remainder of this chapter are in the U.S. Standard series.

In selecting screen sizes for a test, a sufficient number of screens in the appropriate size range should be included so that no one screen is overloaded with an excessive proportion (more than half) of the total sample. For testing granular fertilizers, a series of sieves suggested is U.S. Standard 4-, 6-, 8-, 10-, 14-, 18-, and 30-mesh, or the approximate equivalent in other sieve series. When the material is intended for bulk blending, inclusion of the 8-mesh screen (2.38 mm) is particularly important to establish the degree of size matching with other materials.

For screen analysis of extremely fine, insoluble materials, such as ground phosphate rock, it is common to perform a "wet screen analysis." In this procedure, the shaking operation is replaced by washing the sample through the screens with a jet of water (24, 26). After thorough washing, material on the screens is dried and weighed.

Further general information on performing screen analyses is available in several publications (24, 26, 27).

Segregation Properties

Bulk handling of a fertilizer may induce nonuniformity of composition throughout the bulk; this phenomenon is referred to as "segregation." Segregation is undesirable because the resultant nonuniformity can affect agronomic response and make it impossible to obtain proper samples and meet analytical guarantees (17, 18). A desirable physical property of a fertilizer, therefore, is the ability to resist segregation during handling.

Segregation occurs when individual granules or particles in a fertilizer differ in physical properties to such an extent that they respond differently to the mechanical disturbances caused by handling processes. During these disturbances, particles of similar physical properties tend to congregate; therefore, homogeneity of the particle mix is destroyed. If all particles in a fertilizer were physically identical, no amount of handling would affect homogeneity. Numerous tests have shown that the physical characteristic of a fertilizer particle that most affects its tendency to segregate is the particle size; particles of unequal size tend to segregate during handling (17, 19, 20, 21, 28). Neither the density nor the shape of particles, within ranges normally found in fertilizers, affects segregation tendency to an important degree (17, 19).

If all particles in a fertilizer were of identical chemical composition but of differing sizes, handling would induce physical segregation but would not affect chemical uniformity. To a considerable extent, this is the condition that prevails in well-granulated compound fertilizers; thus, segregation in this type of fertilizer normally is not a serious problem. Occasionally, however, granulation is so imperfect that the smaller particles differ in composition from larger ones, or some feed materials may remain unincorporated in the gran-

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[1] International Standards Organization, Post Office Box 56, CH-1211, Geneva 20, Switzerland.

TABLE 2. STANDARD TEST SIEVE SERIES OF SEVERAL COUNTRIES

United States and Canada[a]										
U.S. Standard Series[b]		Tyler Series[c]		France[d]		England[e]		Germany[f,i]	Italy[g,i]	U.S.S.R.[h,i]
Opening, mm	Sieve No.	Opening, mm	Sieve No.	Opening, mm	Module No.	Opening, mm	Sieve No.	Opening, mm	Opening, mm	Opening, mm
7.925	5/16 in	7.925	2.5	-	-	-	-	8.0	-	-
6.731	0.265 in	6.680	3	-	-	-	-	6.3	-	-
5.664	3.5	5.613	3.5	-	-	-	-	-	-	-
4.750	4	4.699	4	5.00	38	-	-	5.0	-	-
3.987	5	3.962	5	4.00	37	-	-	4.0	4.0	-
3.353	6	3.327	6	-	-	3.353	5	-	3.35	-
-	-	-	-	3.15	36	-	-	3.15	3.15	-
2.819	7	2.744	7	-	-	2.812	6	-	2.8	-
-	-	-	-	2.50	35	-	-	2.5	2.5	2.5
2.380	8	2.362	8	-	-	2.411	7	-	2.33	-
1.999	10	1.981	9	2.00	34	2.057	8	2.0	2.0	2.0
1.679	12	1.651	10	-	-	1.676	10	-	1.7	-
-	-	-	-	1.60	33	-	-	1.6	1.6	1.6
1.410	14	1.397	12	-	-	1.405	12	-	1.4	-
-	-	-	-	1.25	32	-	-	1.25	1.25	1.25
1.191	16	1.168	14	-	-	1.204	14	-	1.18	-
1.001	18	0.991	16	1.00	31	1.003	16	1.0	1.0	1.0
0.841	20	0.833	20	-	-	0.853	18	-	0.85	0.9
-	-	-	-	0.80	30	-	-	0.800	0.80	0.8
-	-	-	-	-	-	-	-	-	0.75	-
0.706	25	0.701	24	-	-	0.699	22	-	0.71	0.7
-	-	-	-	0.63	29	-	-	0.630	0.63	0.63
0.594	30	0.589	28	-	-	0.599	25	-	0.6	0.56
0.500	35	0.495	32	0.50	28	0.500	30	0.500	0.5	0.5
0.419	40	0.417	35	-	-	0.422	36	-	0.425	0.45
-	-	-	-	0.40	27	-	-	0.400	0.4	0.4
0.353	45	0.351	42	-	-	0.353	44	-	0.355	0.355
-	-	-	-	0.315	26	-	-	0.315	0.315	0.315
0.297	50	0.295	48	-	-	0.295	52	-	0.3	0.28
0.249	60	0.246	60	0.250	25	0.251	60	0.250	0.25	0.25
0.211	70	0.208	65	-	-	0.211	72	-	0.212	0.224
-	-	-	-	0.200	24	-	-	0.200	0.2	0.2
0.178	80	0.175	80	-	-	0.178	85	-	0.18	0.18
-	-	-	-	0.160	23	-	-	0.160	0.16	0.16
0.150	100	0.147	100	-	-	0.152	100	-	0.15	0.14
0.124	120	0.124	115	0.125	22	0.124	120	0.125	0.125	0.125
0.104	140	0.104	150	-	-	0.104	150	-	0.106	0.112
-	-	-	-	0.100	21	-	-	0.100	0.1	0.1
0.089	170	0.089	170	-	-	0.089	170	0.090	0.09	0.09
-	-	-	-	0.080	20	-	-	0.080	0.08	0.08
0.074	200	0.074	200	-	-	0.076	200	0.071	0.075	0.071
0.064	230	0.061	250	0.063	19	0.064	240	0.063	0.063	0.063
-	-	-	-	-	-	-	-	0.056	-	0.056
0.053	270	0.053	270	0.050	18	0.053	300	0.050	0.05	0.050
0.043	325	0.043	325	-	-	0.044	350	0.045	-	0.045
0.038	400	0.038	400	0.040	17	-	-	0.040	0.04	0.040

a. Canadian standard series corresponds to U.S. standard series.
b. American Society for Testing Materials, Specification E-11-70.
c. W. S. Tyler, Inc., Mentor, Ohio.
d. French Standard Specification AFNOR NF-X11-501.
e. British Standards Institution, London BS-410-62.
f. German Standard Specification DIN 4188.
g. Italian Specification UNI-2332.
h. Specification COST 3684-63.
i. Sieves in German, Italian, and U.S.S.R. series are specified only by mm-opening size.

ulation process. In these instances, physical segregation that occurs during handling can also result in significant variation in analysis, even in granular compound fertilizers (29). Solutions to this problem are (1) better granulation, (2) screening to narrower size range of particles, or (3) use of special handling procedures that are less conducive to segregation (discussed later).

Segregation is a major problem in the handling of bulk-blended fertilizers. This type of fertilizer, by definition, contains particles of at least two ingredients of distinctly different compositions; thus, any mechanical segregation of the two ingredients will result in significant chemical variation. Segregation of ingredients can, however, as discussed in an earlier section, be minimized by matching particle-size distributions of the ingredients. A practical criterion, mentioned in that section, is that particle-size distribution curves of ingredients do not diverge more than plus or minus 10 percentage points (18). It is of interest also that blends of relatively small particles, such as blends of nongranular ingredients, are less prone to segregation and less sensitive to particle-size matching than are granular blends (20); however, nongranular blends have the typical disadvantages of nongranular fertilizers, which include greater dustiness, greater caking tendency, and poorer flow characteristics.

Three distinct types of segregation are recognized in connection with handling of fertilizers. These are discussed below, and methods are outlined for determining the susceptibility of a fertilizer to each type of segregation. All three types of segregation are promoted chiefly by particle-size differences in the fertilizer mixture.

Segregation Due to Vibration

Fertilizers are subject to vibration during their transportation by trucks, by rail, or by other means. Various studies have shown, however, that such vibration is not a significant cause of segregation in most fertilizers, including typical bulk blends. Segregation due to vibration becomes significant only when the size differences between blend ingredients are extreme to the extent that particles of one ingredient are sufficiently small to "sift" downward through the void spaces between particles of another, larger size ingredient. Tests, confirmed also in unreported work by TVA, have shown that even in a blend of 2.36- to 3.35-mm particles (minus 6- plus 8-U.S. mesh) with another material of 1.00- to 1.18-mm (minus 16- plus 18-U.S. mesh) size there was no segregation resulting from even severe vibration (30). Segregation was significant, however, when the size of the smaller material was reduced to 0.300 mm (minus 50-U.S. mesh) or smaller. This degree of size difference would not normally be encountered in blending of granular ingredients but would be encountered if a nongranular micronutrient, or other nongranular ingredient, were incorporated in a bulk blend of granular-size material; segregation due to vibration, as well as other causes, then should be expected. Other studies showed that vibration of typical granular bulk blends during 30-mile (48-km) transport in a spreader truck did not cause segregation of most blends tested (31).

One laboratory test method used to measure segregation due to vibration consists of placing a sample of the fertilizer blend in a vertical glass cylinder (100-ml graduate), vibrating the cylinder with a mechanical vibrator, and observing segregation (30). Upper and lower portions can be analyzed for quantitative determination of segregation. In unreported work by TVA, a similar procedure was followed using a small plastic hopper filled with blend.

Segregation Due to Flow (Coning)

The type of segregation most often encountered in handling fertilizers is segregation due to flow of material over itself. This often is referred to as segregation due to "coning" because in the buildup of conical storage piles there is a maximum opportunity for this type of segregation to occur when material dropped on the apex of the pile flows downward over the pile surface. Particle-size classification (segregation) occurs as the material flows; the smaller particles in the fertilizer, being retarded to a greater extent by frictional resistance of the pile surface, tend to remain behind and come to rest, whereas the larger particles continue to travel farther down the pile surface before coming to rest. The result is a size-classified (segregated) pile of material (see figure 1).

The tendency of a fertilizer mixture to segregate during coning can be determined conveniently in a qualitative manner by use of a transparent view box, as pictured in figure 3 (32). A suitable size is 14 x 10 x 1 in. A sample of the blend is poured through a funnel at one end of the box, as pictured, and the degree of segregation is observed visually. This method is particularly effective when blend ingredients differ considerably in color; artificial coloring of blend ingredients can be used for demonstration purposes.

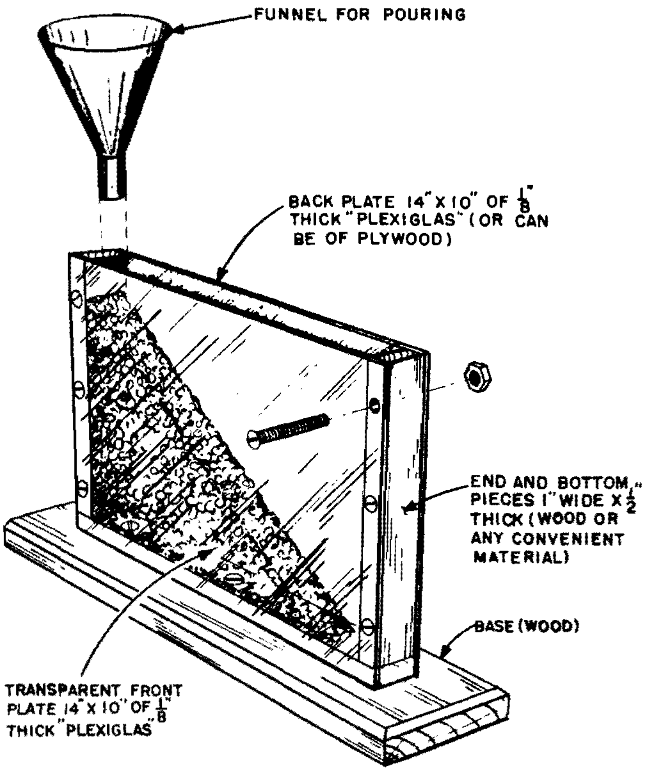


Figure 3. Transparent "View Box" for Visual Observation of Segregation of Fertilizer Blends During "Coning" (32).

An apparatus for quantitative determination of segregation tendency of a fertilizer during "coning" was described by Hoffmeister, et al. (17, 19). A sketch of this apparatus is shown in figure 4. It comprised a narrow box, 10 in high and 14 in long with a 1-in wide spacing between the front and back walls. The front wall was glass and was removable. The back wall was aluminum, slotted to receive eight aluminum vanes. In operation, a section of a conical

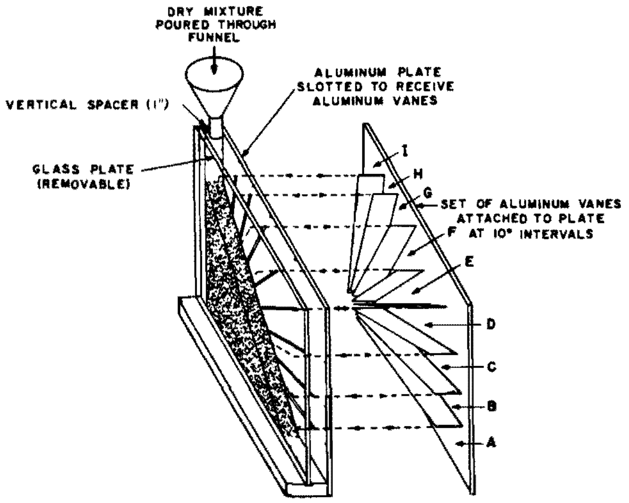


Figure 4. Apparatus Used for Quantitative Determination of Fertilizer Segregation Tendency During "Coning" (17, 19).

pile was formed by pouring the fertilizer blend into the box through a funnel at one end. The vanes were then inserted in the slots to cut the pile into 10-degree segments as shown. The apparatus was then turned on its side, the glass plate was removed, and the blend in each segment was collected individually for analysis. The decision to divide the pile into the pie-shaped segments for sampling was based on observations that lines of constant composition in segregated conical piles radiate from a point on the base immediately below the apex (see figure 1).

Typical data obtained with use of the described segregation apparatus are shown in figure 5. When a blend of minus 6- plus 8-mesh (2.4-3.3 mm) superphosphate (TSP) with an equal amount of minus 12- plus 16-mesh (1.2-1.7 mm) superphosphate (mix No. 1) was poured and segmented and the segments were subjected to sieve analysis, a high degree of segregation was found, as shown. On the other hand, when ingredients of equal particle size (minus 6- plus 8-mesh; 2.4-3.3 mm) were blended and poured (mix No. 7), there was essentially no segregation of ingredients in spite of shape differences of the two materials (irregular KCl and well-rounded TSP). In other tests, particle density variations covering the usual range of fertilizer materials (1.27-2.12 g/ml) were found to have little effect on segregation due to coning.

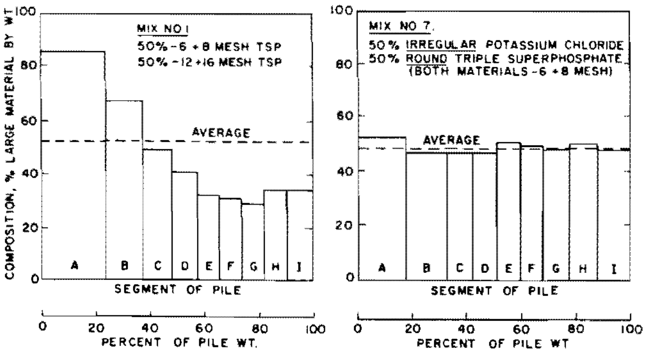


Figure 5. Quantitative Data on Segregation Due to Particle-Size Mismatch (Data Obtained with Apparatus Pictured in Figure 4).

Segregation Due to Ballistic Action

When fertilizer is propelled through the air, such as by the action of fan-type bulk spreaders, particles of different physical properties follow different paths because of varying effects of gravity and air drag. The result is segregation due to ballistic action. A quantitative study of this type of segregation involves actual casting of the fertilizer with a fan-type spreader and collection of ground samples at varying distances from the fan. Samples are analyzed to determine the degree to which composition of the delivered fertilizer varies with distance from the fan. Tests have been made with a stationary spreader and sample collection in a series of long troughs parallel to the normal direction of spreader travel (17, 19) or with a moving spreader passing over a series of collection boxes placed perpendicular to the direction of spreader travel (33, 34, 35). A significant conclusion of one series of tests was that, as in the case of segregation due to coning, particle-size differences are the greatest cause of ballistic segregation of granular fertilizer blends during spreading; the larger granules tended to travel farther from the spreader than did smaller ones (17, 19). Thus, matching of the particle size of blend ingredients is a sufficient measure to minimize segregation by both coning and ballistic actions, the two most troublesome causes of fertilizer segregation. The fact that fertilizer particle size has a much greater effect on ballistic segregation than does particle density is not surprising when consideration is given to the relative effects on granule weight and thus on inertia of moving granules. Increasing granule diameter from 1.19 mm (16-mesh screen) to 3.35 mm (6-mesh screen) increases granule weight more than twentyfold, whereas the usual range of fertilizer granule densities (1.27-2.12) can cause only less than a twofold variation. Air drag, although less on a small particle, is, according to Stokes' law, reduced only in direct proportion to particle diameter (36).

Antisegregation Measures for Blended Fertilizers

The most effective way to reduce segregation in dry-blended fertilizers is to use only ingredients that are matched in particle-size distribution (18, 37). As discussed above and in an earlier section (Particle Size--Effects on Blending Properties), a reasonable degree of particle-size matching will render the blend resistant to segregation by any of the three recognized segregation mechanisms--vibration, coning, and ballistic action. However, close size matching in blends frequently is not possible because of variations in available materials. In such instances segregation can be minimized only by limiting the amount of handling or by using special handling precautions (18, 37, 38). The incorporation of small amounts of micronutrients in blended fertilizers presents special segregation problems which were discussed in chapter XX and elsewhere (28).

Granule Hardness

Fertilizer granules should have sufficient mechanical stability to withstand normal handling without fracturing and without excessive sloughing to form dust. Three distinct types of mechanical strength are recognized as desirable and are discussed below; these are (1) granule crushing strength, (2) resistance to abrasion (sloughing), and (3) impact resistance. Granule hardness tests developed and used for fertilizers usually measure only one of these types of strength; however, in most cases good resistance to one type of mechanical action is a reasonable indication of good overall acceptability.

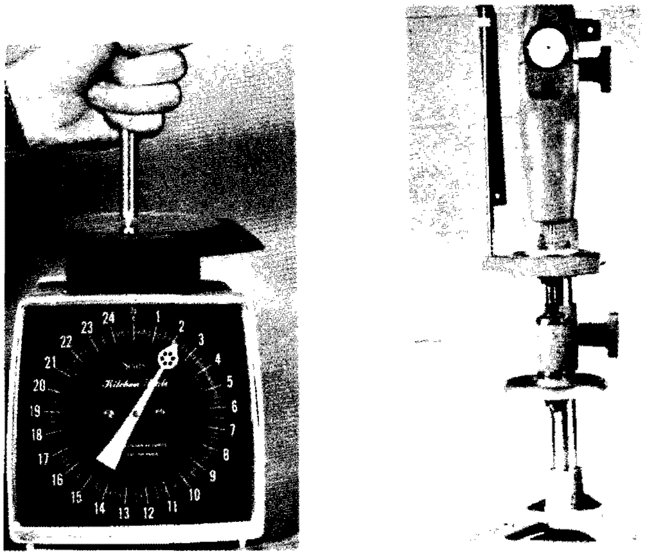
Crushing Strength

The simplest and most widely used tests of granule strength involve determination of the crushing strength of individual granules. The degree of refinement varies from simple application of finger pressure to the use of calibrated crushing test machines. Use of the simple finger test by one laboratory has been described as follows (39):

> "A granule which could be crushed between the thumb and forefinger was classified as 'soft.' If it could be crushed with the forefinger on a hard surface it was regarded as being of 'medium hardness.' If it remained intact when subjected to pressure by the forefinger against a hard surface, it was classified as 'hard.'"

In use of this method, as all methods involving single granules, it is necessary to crush at least 10, and preferably more, granules to obtain an average evaluation. Also, only granules of equal size should be compared because, as will be discussed, crushing strength increases significantly with increase in particle size.

A quantitative, yet simple, method of measuring the crushing strength of individual granules involves placing a granule on a flat glass or metal plate on the platform of a small spring scale of at least 15-lb (7-kg) capacity and applying downward pressure until the granule fractures. In use of this method by Hardesty and Ross (40), downward pressure was applied through a flat-ended metal rod driven by a rack and pinion mechanism. In a simpler TVA version (figure 6) pressure is applied through a hand-held flat-ended metal rod (41, 42). Various commercial compression testers, some motor driven, are available also and are convenient where numerous tests are to be made. A typical, commercial hand-powered tester also is pictured in figure 6.



Kitchen Scale

Compression Tester

Figure 6. Two Methods for Measuring Granule Crushing Strength (41, 42).

In making any of these tests, it is recommended that 15-20 granules of equal size be tested and that the scale readings at the time of fracture be averaged. The importance of comparing only granules of equal size is shown in figure 7. These data for granular triple superphosphates from four manufacturers show that crushing strength of each product increased twofold to threefold with increase in granule diameter from 1.5 mm (minus 12- plus 14-mesh) to 3.0 mm (minus 6- plus 7-mesh). Standard procedure at TVA is to screen granular samples to the narrow size range of minus 7- plus 8-mesh (2.4-2.8 mm) prior to hardness testing (42). Typical crushing strength data on this size granule of several common fertilizers are given in figure 8. Of the materials included, the weakest granules were those of prilled urea; crushing strength was only 2.0-2.8 lb (1.0-1.3 kg) (see chapter IX for information on the effect of formaldehyde on the hardness of prilled and granular urea). This is indicative of the known tendency of prilled urea to fracture easily and form dust during handling. Other data in the figure show the much greater hardness of granulated ureas that contained formaldehyde additive (up to 7.5 lb; 3.4 kg); this is one significant advantage of the granular form of this fertilizer. In this series of tests, the hardest granules were those of diammonium phosphate with crushing strengths up to 11.5 lb (5.2 kg). Experience based on these and other data has shown that granules with a crushing strength less than about 3 lb (1.4 kg) (minus 7- plus 8-mesh granules) are too weak for good handling. A strength of 5 lb (2.3 kg) or above is highly desirable.

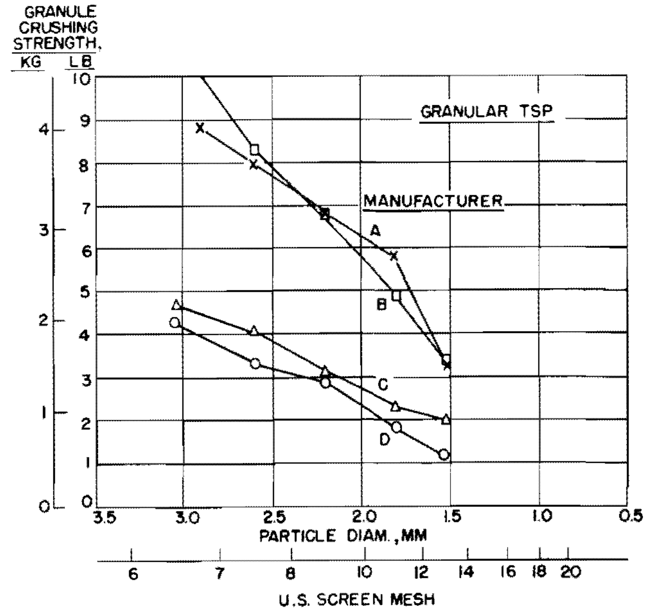


Figure 7. Effect of Particle Size of Triple Superphosphates on Granule Crushing Strength (41).

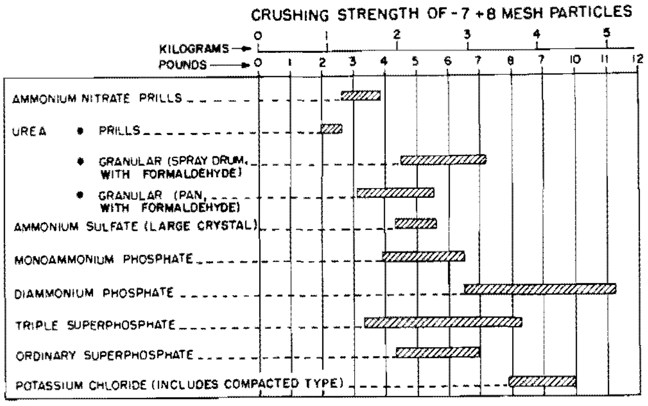


Figure 8. Observed Crushing Strength Range of Fertilizer Materials from Various Manufacturers (41).

Another reported method of measuring crushing strength of fertilizer granules involves determination of the compressibility of a small volume (200 ml) of the fertilizer in a steel cylinder 70 mm in diameter (39). A Plexiglas piston is brought to bear on the sample by means of a hydraulic press, and the pressure required to cause a 10-mm compression is determined as a measure of granule strength. The method is useful in determining the "bearing strength" of fertilizers and thus the maximum pressures that can be withstood in storage stacks or accelerated caking test apparatus.

Abrasion Resistance

As fertilizers are handled, abrasion between granules can cause degradation and dust formation. Several tests have been reported which measure stability of granular fertilizers in this regard.

One test, reported by TVA, employs the small rotary drum shown in figure 9 (41, 42). This is a 7 in-diameter, stainless-steel, totally enclosed rotary drum equipped with six lifting flights. The fertilizer first is screened well to remove any minus 18-mesh (<1.0 mm) material. Then a 100-ml weighed sample is placed in the drum together with 50 steel balls which are 5/16 in (7.9 mm) in diameter. The drum then is

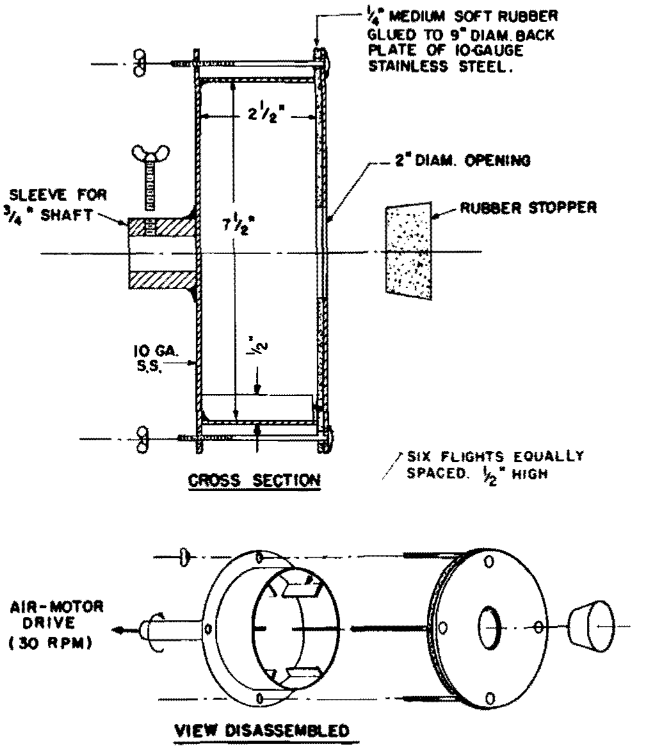


Figure 9. Rotary Drum Used in Abrasion-Shatter Test of Fertilizers (41, 42).

closed and rotated for 5 minutes at 30 rpm. The contents are removed; they are then screened over a 4-mesh (4.7 mm) screen to remove the balls and over an 18-mesh screen to determine the percent degradation to fines. Percent degradations reported for samples of several fertilizers were as follows:

	%
Ammonium nitrate prills	4.6
Urea	
Prills	19.7
Granular (spray drum)	0.2[a]
Granular (pan)	1.7[a]
Ammonium sulfate	1.1
Monoammonium phosphate	1.3
Diammonium phosphate	0.7
Triple superphosphate	0.7
Ordinary superphosphate	2.5
Potassium chloride (compacted)	3.3

a. Contained formaldehyde additive.

Urea prills, which have low single-particle crushing strength (figure 8), showed relatively high degradation in the abrasion test (19.7%). The granular ureas had much greater abrasion resistance; degradation was only 0.2%-1.7%. Ammonium nitrate prills showed considerable degradation also (about 5%) while the other materials generally showed only little or moderate degradation. Compacted potassium chloride, although one of the hardest materials in crushing strength tests (figure 8), showed 3.3% abrasion degradation, probably because of the irregular, chip-like particle shape.

Another type of abrasion test, reportedly used by at least one potash producer, involves shaking a sample with steel balls on a test sieve and measuring size degradation (43, 44). In one version of this procedure, a sample of 250 g of 6- to 12-mesh (1.6-3.3 mm) fertilizer was put into a 12-mesh, 8 in-diameter test sieve together with five hundred 3/16-in (4.8-mm) steel balls (44). The mixture was shaken with a screen vibrator for 60 minutes. A screen analysis then was made of the granules, and the "shatterability" was evaluated by the amount of fines produced. The degradation to minus 12-mesh (<1.6 mm) of 11 different fertilizer samples ranged from 4% to 32%.

Impact Resistance

Impact resistance is of interest chiefly in connection with the impact imparted by fan-type fertilizer spreaders. Several tests have been reported which specifically measure granule breakdown as a result of impact. One involves introducing a minus 6- plus 12-mesh (1.6- to 3.3-mm) sample into a high-velocity airstream impinging on a steel plate; percent degradation to minus 12-mesh (<1.6 mm) is measured by screen analysis (44, 45). In tests of 11 different fertilizers by this method, degradation ranged from 2% to 19% (44).

In TVA studies of sulfur coating of granular urea to impart slow solubility in the soil, the effect of spreader fan impact on mechanical stability of the coating was of interest. Studies showed that a test involving dropping of a sample of coated urea from a height of 30 ft into an empty steel drum simulated the impact effects of a medium-speed (600- to 700-rpm) spreader fan (41). However, some wide-swath spreaders operate at higher speeds and impart considerably more impact.

Bulk Density

Bulk density is defined as the weight per unit volume of a bulk fertilizer. Value for this property is required for bag sizing, to determine the capacity of storage bins and transport vehicles, and sometimes for the calibration of volumetric feeders. For routine determinations of bulk density in units of pounds per cubic foot, it is convenient to provide an open-top metal or plywood box having exactly 1 x 1 x 1 ft (30.5 x 30.5 x 30.5 cm) internal dimensions. "Loose-pour density" is determined by simply pouring fertilizer into the box from a height of about 6 in above the top of the box, leveling the top with a straightedge, and weighing on appropriate scales. It is desirable to move the fill point during filling to avoid coning and resultant segregation. The value obtained in this manner represents the minimum weight likely to be found in a unit volume of the material. "Packed density" (also called "tapped density") is determined in the same manner except that, after filling, the box is tapped, lifted, dropped several times from a height of about 6 in, refilled, and redropped until there is essentially no further compaction. The material then is leveled and weighed. The value obtained in this manner represents the maximum weight of material likely to be found in a unit volume of the material even after settling under the influence of vibration during transport or other handling. Tapped density of granular fertilizer usually is 6%-12% higher than loose-pour density. Detailed procedures for measurement of bulk density have been published (27, 46). Measurements on less than a cubic foot of fertilizer can be made by use of a half-cubic-foot box or even a 1- or 2-liter graduate. Bulk densities of granular fertilizers vary from about 45 to 75 lb/ft^3 (0.72-1.20 tons/m^3); typical densities of some common fertilizers are given in table 3.

Angle of Repose

The angle of repose (kinetic) of a fertilizer is the angle with the horizontal at which the fertilizer will stand when poured or dropped into a pile from a fixed overhead point. This property affects the capacity of storage areas and bins; it is of interest also in designing the sloped roofs of bulk storage buildings

TABLE 3. TYPICAL BULK DENSITIES, ANGLE OF REPOSE, AND APPARENT SPECIFIC GRAVITIES OF SOME FERTILIZERS[a]

Nongranular Products	Bulk Density (Loose) lb/ft^3	kg/m^3	Angle of Repose, Degrees	Apparent Specific Gravity of Granules[b]
Nongranular Products				
Phosphate rock (Florida)				
Unground pebble	85-95	1,360-1,520	35	-
Flotation concentrate	88-96	1,400-1,530	35	-
Pulverized (90%--100-mesh)	80-90	1,280-1,440	-[c]	-
Ordinary superphosphate	60-70	960-1,120	30-35	-
Triple superphosphate	55-65	880-1,040	30-35	-
Agricultural limestone[d]	80-95	1,280-1,520	45-50	-
Ammonium sulfate	64	1,020	36	-
Potassium chloride	71-75	1,140-1,200	31	-
Monoammonium phosphate	55-57	880-910	-[e]	-
Granular Products				
Ammonium nitrate				
High-density prill	56	900	31-38	1.65
Low-density prill	45	720	34	1.29
Granular	52	830	36	1.50
Urea				
Prill	46	740	28	1.32
Granular	45-48	720-770	34-37	1.22
Ammonium sulfate				
Large crystal	63-66	1,010-1,060	29	1.75
Granulated	49	785	38	1.58
Ordinary superphosphate	70	1,120	34	-
Triple superphosphate	65-75	1,040-1,200	30-35	2.12
Diammonium phosphate	60-65	960-1,040	30-35	1.63
Monoammonium phosphate	60-65	960-1,040	35	1.67-1.78
Ammonium polyphosphate	56	900	35	1.75
Potassium chloride				
"Coarse" size	68	1,090	35	1.96
"Granular" size	65	1,040	39	1.96
Potassium sulfate	74	1,180	35	1.76
Potassium-magnesium sulfate[f]	95-98	1,520-1,570	32	2.65
Sulfate-based NPK (13-13-13)	57	910	36	1.64
Nitrate-based NPK (17-17-17)	56	890	38	1.66
Urea-sulfate based NPK (17-17-17)	52	833	39	1.60
Nitric phosphate (20-20-0)	64	1,020	34	1.76

a. Where numerous measurements are available, ranges are given.
b. Determined by mercury pycnometer (see text).
c. Extremely low angle of repose; piling not feasible.
d. 100% < 2 mm, 50% < 0.15 mm.
e. Variable with moisture content.
f. Langbeinite ($K_2SO_4 \cdot 2MgSO_4$).

and in designing hoppers, chutes, and conveyors. Reliable measurement can be made with 10 kg or more of fertilizer by gently pouring the fertilizer into the form of a small conical pile while maintaining the pour point only a few centimeters above the apex of the forming pile. The angle between the pile surface and the horizontal can be measured directly or, by use of a suitable light source, can be projected as a shadow onto a vertical screen and measured (41). An alternate method, which requires less material, involves simply pouring a quarter section of a conical pile in the corner of a small box and measuring the slope of the surface (42). The angle of repose of most granular fertilizer materials is in the range of 30-40 degrees. Typical angles for some common fertilizers are included in table 3.

Apparent Specific Gravity

Apparent specific gravity of a fertilizer granule may be defined as the ratio of the weight of a single granule to that of an equal volume of water (at 4°C). The granule volume is that enclosed by the surface of the granule and includes any internal pores. It is numerically equal to density in g/ml. If the chemical constitution is known, the "true specific gravity" (exclusive of pores) can be calculated from published data and compared with apparent specific gravity to give a measure of porosity. Apparent specific gravity is not a property that is measured frequently, but it has been of special interest in connection with studies of particle segregation characteristics and in the development of granulation processes. For a given product, variations in apparent specific gravity of the granules can result in variations in hardness, moisture-holding capacity, and storage properties.

For measurements at TVA, the mercury pycnometer pictured in figure 10 was developed (41, 42). This apparatus consists primarily of a tightly sealed glass sample chamber of about 10-ml volume connected, through stopcocks, to (1) a source of vacuum for use in evacuating air from the chamber and (2) a reservoir of mercury for use in flooding of the chamber with mercury. A graduated (5-ml) microburette is provided in the mercury supply system to measure the difference in volume of mercury required to flood the sample chamber with and without sample in the chamber. In operation, a burette reading is obtained first with the

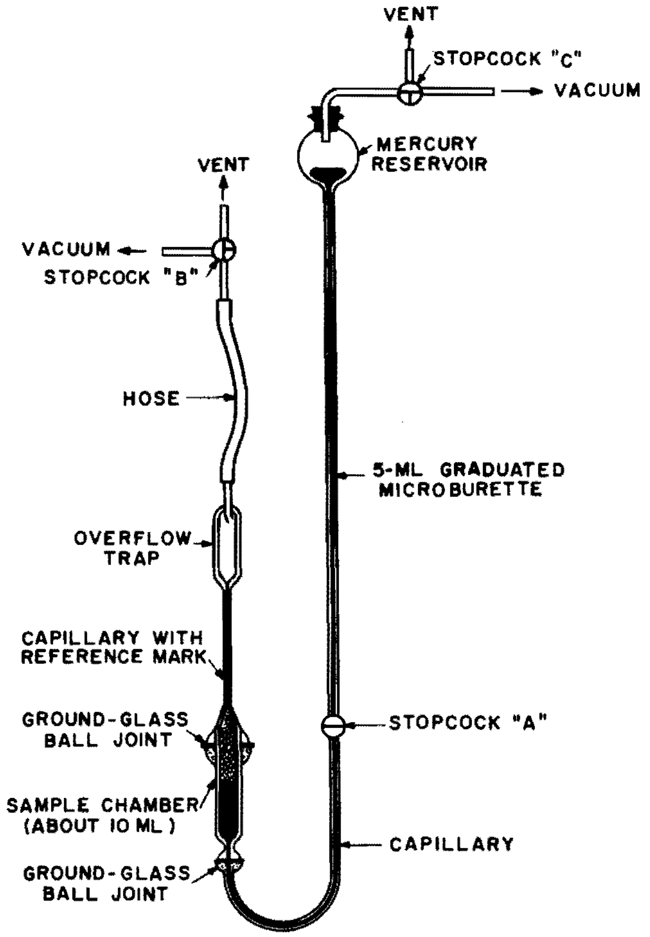


Figure 10. Mercury Pycnometer Used to Measure Apparent Specific Gravity of Fertilizer Granules (41, 42).

sample chamber filled (to reference mark) with only mercury. The mercury then is withdrawn from the sample chamber, the chamber is opened (ground glass joint), and an accurately weighed sample (4-7 g) is introduced. The chamber then is resealed, and a partial vacuum (500 mm Hg) is applied to exhaust most of the air. Mercury then is allowed to flow back into the evacuated sample chamber, again to the reference mark. A final reading of the mercury burette is taken; the difference from the initial reading (no sample) represents the volume of the granules in the sample. From the known weight of the sample, the weight per unit of volume (apparent specific gravity) is calculated.

Accuracy of the method is based on an assumption of no significant penetration of mercury into pores of the granules. In practice, this assumption usually has been valid. Calculations based on published information indicated that, with evacuation of the sample under 500-mm vacuum, the mercury should penetrate any pores larger than 22 micrometers in diameter; however, not all such pores are accessible to penetration from the granule surface (47). If penetration is found to be significant, lower vacuum can be used. With no vacuum, there should be no penetration, but entrapment of air in the interstices between granules becomes a problem.

Values for apparent specific gravity of several fertilizer materials are included in table 3. Maximum variation among these materials was from 1.22 (urea) to 2.65 (potassium magnesium sulfate) which has been shown to be insufficient variation to cause significant segregation problems in bulk handling or spreading of blends (see section on segregation) (17, 19).

Critical Relative Humidity

Critical humidity of a fertilizer material can be defined simply as that humidity of the atmosphere above which the material will spontaneously absorb moisture and below which it will not. All soluble salts, including fertilizer salts, have characteristic critical humidities. Chemically speaking, the critical humidity of a salt is that humidity of air at which the partial vapor pressure of water in the air exactly equals the equilibrium water vapor pressure above a saturated solution of the salt at any given temperature (30°C, for example). For a fertilizer material, a relatively high critical humidity is an advantage since such a material can be exposed and handled under more humid atmospheric conditions without becoming wet and nonflowable or without absorption of moisture that might later promote caking. The critical humidity of a fertilizer material determines, to a large extent, the type of bag (degree of moistureproofing) required and governs the amount of bulk handling and open storage to which a material can be subjected. However, the importance of critical humidity in other regards should not be overestimated. For example, critical humidity sometimes is mistakenly taken as a universal measure of caking tendency of a fertilizer. Actually, if a fertilizer is stored in a moistureproof bag or in a protected (plastic covered) bulk storage pile, atmospheric humidity is effectively excluded and critical humidity is of relatively little importance. In those situations, caking, when it occurs, is related to other factors, such as constituent moisture content of the fertilizer, chemical reactions, temperature and pressure of storage, presence of fines, and efficiency of conditioning treatment. Even in regard to bulk exposure of fertilizer, critical humidity is not the only property that governs behavior under humid conditions. Critical humidity determines whether or not moisture will be absorbed under given conditions but says nothing as to how well or how poorly the fertilizer will tolerate the absorbed moisture. Other tests (absorption-penetration and flowability) are required for full evaluation.

Critical humidity usually is expressed as "critical relative humidity" (CRH) which, simply stated, is the water content of air expressed as a percentage of that required to saturate the air at the specified temperature.

Direct Method

The simplest, most relevant method by which to measure critical relative humidity (CRH) of a fertilizer material is to expose a sample to various controlled humidities and temperatures and to determine at what humidity the sample gains significant weight (moisture absorption). This determination is most conveniently made in a standard laboratory environmental chamber equipped with forced air circulation and mechanical refrigeration for humidity control. Such units are available commercially from several manufacturers. A unit with horizontal air flow, to provide good air-sample contact, is recommended. A photograph of samples in such a unit is shown as figure 11.

In use of this procedure by TVA, samples of 2- to 3-g size, weighed on an analytical balance, are exposed in the cabinet in shallow (6-mm) open-top aluminum cups 5 cm in diameter (41, 42). The cups are removed and reweighed at 1-hour intervals to determine moisture absorption. Usually, it is apparent within 3 hours whether or not there is sustained absorption, which would be indicative that CRH of the sample is below the prevailing humidity in the cabinet. Depending on this 3-hour result, relative humidity in the cabinet then is either lowered or raised by 5 percentage points, and the test is repeated until the CRH is located. If desired, the CRH can be determined within about 2 percentage points. The procedure is

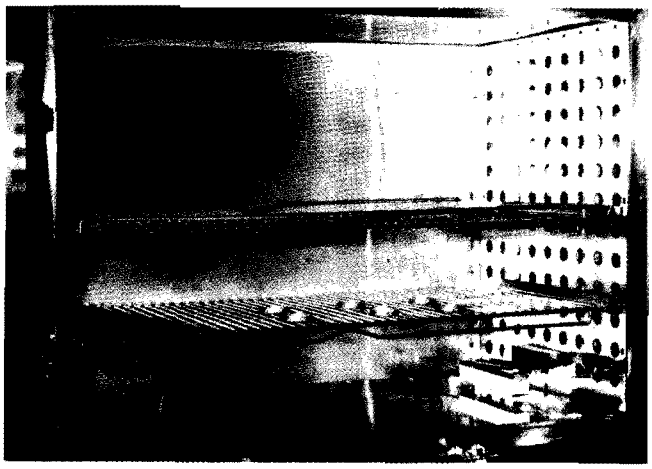


Figure 11. Fertilizer Samples in Shallow Cups in Controlled-Humidity Cabinet for Determination of Critical Relative Humidity.

somewhat time consuming, but samples of several materials can be run simultaneously. Data obtained in typical CRH determinations at 86°F (30°C) are shown in figure 12. The results with the prilled urea represent typical behavior of a relatively pure material, in that the critical point is very definite. There was no moisture absorption in 3 hours at 70% humidity, but there was continuous absorption at 75%. The data shown for diammonium phosphate made from wet-process acid, on the other hand, illustrate typical behavior of phosphates made from wet-process acid and of other fertilizers that contain small amounts of soluble impurities. The impurities exert an initial lowering effect on critical humidity, but as moisture content of the sample increases, the effect of the impurities diminishes. This effect of moisture content on the apparent CRH of impure fertilizers is well known (48, 49, 50). In this case, for diammonium phosphate, it is obvious that the CRH of the main constituent was between 70% and 75%, but, for practical purposes, it would have to be recognized that exposed product would pick up some moisture at relative humidities between 60% and 70%. At 70% relative humidity a maximum of 2% would be absorbed. This is insufficient to cause intergranule transfer of moisture (see a later section), thus only the surface granules would be affected in a bulk pile. One of the chief advantages of the direct determination method is this ability to distinguish between true critical humidity and secondary absorptions due to impurities. Some "static" methods lack this advantage.

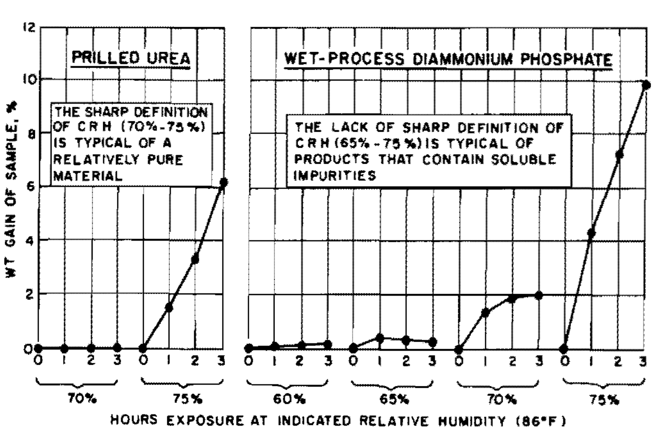
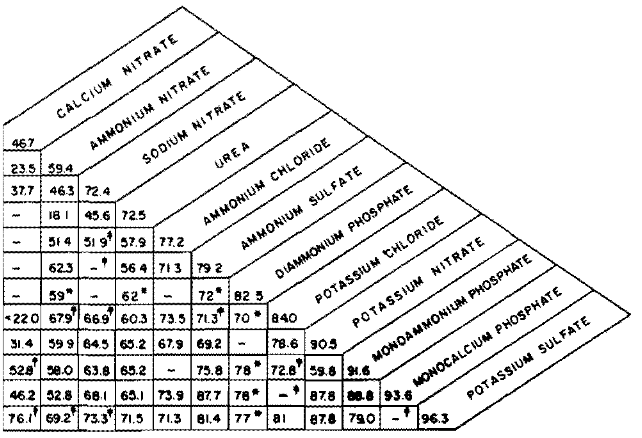


Figure 12. Data Obtained by "Direct Method" for Determination of Critical Relative Humidity (41, 42).

Mixtures of fertilizer salts usually have lower critical humidities than either of the constituents. Critical humidity of mixtures can be determined by intimately mixing the pulverized salts and exposing the mixture. The chart given in figure 13 shows CRH data for pure salts and two-component mixtures. Most of these data are from a literature source and were obtained by more precise methods than the direct method described above (51). The data in the figure are based on the vapor pressures of solutions saturated with respect to both salts.



CALCIUM NITRATE	AMMONIUM NITRATE	SODIUM NITRATE	UREA	AMMONIUM CHLORIDE	AMMONIUM SULFATE	DIAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE	POTASSIUM NITRATE	MONOAMMONIUM PHOSPHATE	MONOCALCIUM PHOSPHATE	POTASSIUM SULFATE
46.7											
23.5	59.4										
37.7	46.3	72.4									
–	18.1	45.6	72.5								
–	51.4	51.9†	57.9	77.2							
–	62.3	–†	56.4	71.3	79.2						
–	59*	–	62*	–	72*	82.5					
<22.0	67.9†	66.9†	60.3	73.5	71.3†	70*	84.0				
31.4	59.9	64.5	65.2	67.9	69.2	–	78.6	90.5			
52.8†	58.0	63.8	65.2	–	75.8	78*	72.8†	59.8	91.6		
46.2	52.8	68.1	65.1	73.9	87.7	78*	–†	87.8	88.8	93.6	
76.1†	69.2†	73.3†	71.5	71.3	81.4	77*	81	87.8	79.0	–†	96.3

* APPROXIMATE VALUES OBTAINED BY TVA. OTHER DATA ARE FROM LITERATURE (51).

† UNSTABLE SALT PAIR; VALUE GIVEN IS FOR THE STABLE PAIR.

Figure 13. Critical Humidities of Pure Salts and Mixtures at 30°C (86°F) (Values are Percent Relative Humidity).

In several cases, the two salts in a mixture will react chemically with each other as soon as enough water is absorbed to permit the reaction to proceed. For example:

$$NH_4NO_3 + KCl = NH_4Cl + KNO_3$$

The two salts on the right side of the equation are called the stable salt pair, and those on the left are the unstable salt pair. In figure 13, the CRH values are for stable salt pairs. However, if the two salts are not present in stoichiometric proportion, the CRH of the mixture will depend on which salt is in excess. For example, the CRH of a mixture of NH_4NO_3 and KCl is shown in figure 13 as 67.9%. This value is applicable if the two materials are present in stoichiometric proportion or KCl is in excess and the above reaction has gone to completion. If NH_4NO_3 is in excess the CRH of the mixture will be 59.4 (that of NH_4NO_3) or perhaps less since the mixture will actually contain three salts. The effect of salt mixing is most dramatic in the case of ammonium nitrate with CRH of 59.4% at 86°F (30°C) and urea with CRH of 72.5%. The mixture, as shown, has the extremely low CRH of 18% and, hence, is one to be avoided--except in liquid fertilizers.

In the absence of a prefabricated environmental chamber in which to determine CRH, sample exposures can be made in a simple, insulated, moisture-tight cabinet (such as a biological incubator) equipped with an electric circulating fan, an electric heater, a wire-mesh sample shelf, and a large glass dish to hold a humidity-controlling salt solution. Procedure is generally the same as with the more sophisticated cabinet, except that time must be allowed for air-solution equilibrium to be reached, and door openings must be minimized to retain humidity. Vigorous fan action is essential. In preparing humidity-control solutions, a suitable salt or salt pair is first selected from published vapor pressure data (51, 52, 53). An excess of the salt or salts then is heated in distilled water to a temperature slightly above the box operating temperature, and the mixture (including some undissolved salt) is transferred to the solution tray, which is placed on the floor of the humidity chamber in the path of air from the fan. The chamber then is closed and, with the fan operating, time is allowed for equilibrium to be reached at the desired operating temperature. The method, although workable, is time consuming in the preparation and changing of humidity-control solutions. Solutions may be saved and reused.

Attempt to determine critical relative humidity by exposing samples over salt solutions in desiccator-type vessels is not recommended. With the lack of forced air movement in such a vessel, movement of moisture from the solution into the air and thence into the sample is dependent entirely on diffusion, an extremely slow process. In one reported series of such tests, a 1-week exposure time was necessary. In tests of the method at TVA, reproducible results could not be obtained. Improved results apparently can be obtained by installation of a fan through the top of the desiccator vessel to induce air movement (50, 54). Experience at TVA supports a conclusion that, for good reproducibility, critical humidity determinations and all other measurements of moisture absorption by fertilizer samples should be made with a fairly vigorous movement of air across the samples.

Several other procedures have been reported for determination of critical relative humidity of fertilizers or pure fertilizer salts. In general, these are static, indirect methods that do not simulate practical exposure conditions to the extent of the direct method already discussed. However, with recognition of their limitations, the following methods can be useful.

Isoteniscope Method

A rather complex laboratory apparatus was used by USDA investigators to measure the water vapor pressure above saturated solutions of pure fertilizer salts and salt pairs (51, 53). Vapor pressure was converted to critical relative humidity by virtue of the definition that identifies CRH of a salt as that humidity at which vapor pressure of water in the air equals water vapor pressure over a saturated solution of the salt. The method is applicable with high precision to pure salts but probably not to impure materials such as most fertilizers.

Electric Hygrometer Method

This method is based on the knowledge that a body of air in contact with fertilizer containing some moisture will equilibrate to a humidity equal to the critical humidity of the fertilizer (55). In the procedure, a 500-ml glass jar, fitted with an internal humidity sensor of the Dunmore type (56), was filled about one-third full with fertilizer, and the jar was tightly sealed. After a period of equilibration (about 30 minutes), humidity was read with the Dunmore instrument. The method is of limited value because it gives only an equilibrium value at one specific moisture content of the fertilizer; thus, the behavior of the fertilizer during actual exposure to humidity and absorption of moisture is not observed. Also, the method, being a static one, is largely dependent on diffusion which is slow and subject to variations.

Vacuum Line Technique

In this method, a 25-ml flask containing 1-5 g of fertilizer sample first is evacuated to 0.001 mm mercury (48, 57). Pure water vapor from another vessel then is allowed to fill the flask, which then is sealed, except for connection to a manometer. Time (1 hour or more) then is allowed for moisture absorption by the fertilizer to reduce water vapor pressure in the flask to the equilibrium value, which then is read from the manometer. The CRH is calculated from the manometer reading. The method, like the hygrometer method, is a static one which gives a vapor pressure reading at only one moisture content of the sample; however, by repeated exposures of the sample to pure water vapor, readings can be taken over a range of moisture contents.

Gas Chromatograph

In this method, air and fertilizer are allowed to equilibrate in a sealed flask, after which a small sample of the air is withdrawn for moisture analysis (58). Water content of the air is determined by use of a gas chromatograph and is converted to CRH. The method, although simple, has the limitations of other static methods.

Effects of Temperature

The critical relative humidity of most salts decreases with increase in temperature. Variations for some important nitrogen fertilizer salts are shown in figure 14; this figure is based on vapor pressure data from several sources (51, 59, 60). The salts with the largest coefficients of variation are ammonium nitrate and calcium nitrate; with either of these salts, increase in temperature from 0°C to 40°C (32°F to 104°F) decreases critical relative humidity by 22 percentage points. The salt shown with the smallest coefficient is ammonium sulfate; the same temperature increase results in a decrease in critical relative humidity of only about four percentage points. Variations for other salts can be calculated from published vapor pressure data or determined experimentally.

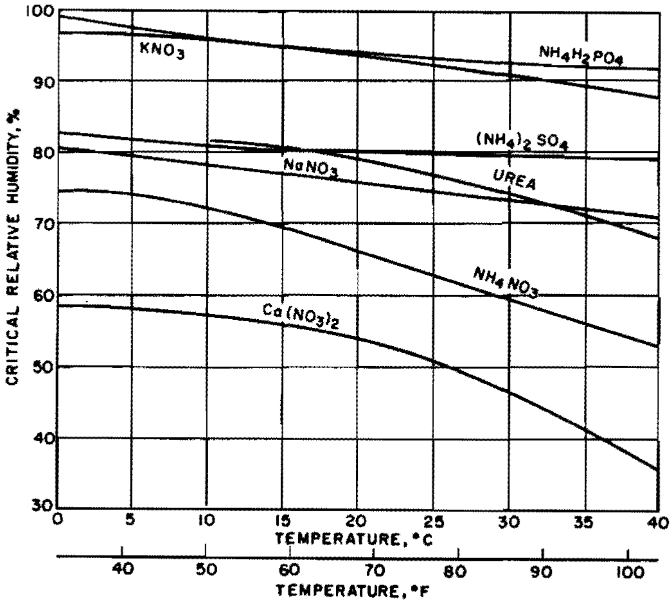


Figure 14. Effect of Temperature on the Critical Relative Humidities of Some Nitrogenous Fertilizer Salts.

Rate and Effects of Moisture Absorption

Determination of critical humidity, as outlined in the preceding section, defines the humidity above which a fertilizer will absorb moisture from the atmosphere. However, the critical humidity value alone gives no information as to how rapidly moisture will be absorbed or what effect the moisture absorption will have on the physical condition of the fertilizer. Fertilizers vary considerably in their ability to tolerate absorbed moisture; thus, methods to evaluate degree of moisture tolerance are of interest. The surfaces of bulk-storage piles frequently are exposed to humid atmospheres; thus, it is of interest to know how rapidly moisture will be absorbed and how rapidly and to what depth wetting and physical deterioration will progress. Two tests described below provide methods for evaluating these effects of pile exposure. The tests are the laboratory absorption-penetration test and the small-pile bulk-storage test. Other exposure of fertilizer to humid atmosphere frequently occurs during handling and spreading. In those operations, the effect of moisture on flowability is the major concern. Two tests to evaluate flowability under humid conditions are described also; these are a drillability test and a laboratory flowability test.

Laboratory Absorption-Penetration Test

The test described here was developed at TVA (41, 42). The principle of the test is simply to expose a bulk fertilizer surface of known area to moving air at a controlled temperature and humidity and to measure the rate of moisture absorption per unit of fertilizer surface and the rate of moisture penetration into the bulk of the fertilizer. Open-top cylindrical glass jars 6.8 cm in diameter are used. They are filled level with the fertilizer; the exposed surface is 36 cm^2. Jars of 5-cm or 20-cm depth have been used; results are the same except that the deeper jars permit deeper penetration and thus longer test periods. The filled jars are weighed accurately and then are exposed in a controlled humidity cabinet usually at 86°F (30°C), 80% relative humidity. Figure 15 is a photograph of samples after exposure in the humidity cabinet. Vigorous airflow across the tops of the jars is important. After 4, 24, 48, and 72 hours, the jars are removed and weighed, and the moisture absorption per unit of surface is calculated. Also, by looking through the glass wall of the jar, it usually can be determined to what depth moisture has penetrated. The usual mode of penetration is as a horizontal interface, with material below the interface being unaffected. However, with some nonabsorbent materials such as ammonium nitrate or urea, moisture frequently runs deep into the cup in streaks.

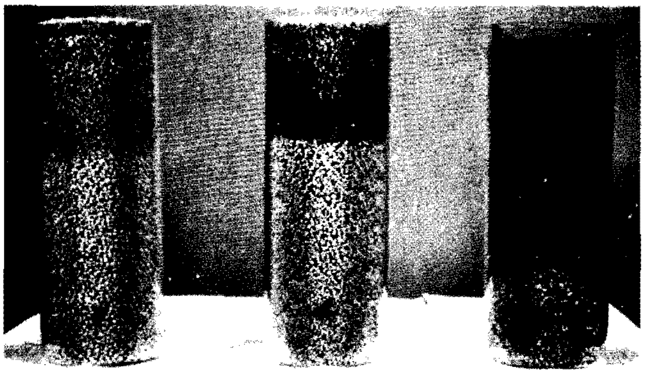


Figure 15. Fertilizer Samples After Exposure to Humid Atmosphere in Laboratory Absorption-Penetration Test (41, 42).

Typical data obtained in an absorption-penetration test series at 30°C (86°F) and 80% relative humidity are given in table 4. The materials are listed in order of increasing critical relative humidity (45%-73%); yet, it is interesting to note that neither rate of moisture absorption nor depth of moisture penetration correlate with critical humidity. Neither did depth of moisture penetration correlate with rate of moisture absorption; this is a result of differences in "moisture-holding capacity." Moisture-holding capacities of the various fertilizers were calculated (table 4) as milligrams of moisture per cubic centimeter of fertilizer by dividing the moisture absorption per square centimeter by the depth of penetration in centimeters. These values also were converted to percent moisture-holding capacity by weight (table 4) by use of the weight-per-unit volume (bulk densities) of the fertilizers in the cups. The holding capacities thus calculated represent the maximum amount of moisture that a granule will absorb before it becomes so wet that moisture will be transferred to adjacent granules by capillary action. High moisture-holding capacity is a desirable characteristic that can offset the effects of high rate of moisture absorption. For example, among the materials listed in table 4, the 19-19-19 urea melt-based NPK product had very low critical relative humidity (45%) and high rate of moisture absorption, (538 mg/cm^2 in 72 hours); yet, because of the unusually high moisture-holding capacity of the granules (18.5% moisture), penetration was only 3.4 cm in 72 hours. Prilled urea, on the other hand, in spite of high critical relative humidity (73%) and only moderate moisture-absorption rate (324 mg/cm^2 in 72 hours) was penetrated 13 cm in the same period because of very low moisture-holding capacity (3.2%) of the prills. Prilled ammonium nitrate (table 4) exhibited both high rate of moisture absorption (918 mg/cm^2 in 72 hours) and low moisture-holding capacity (2.1%); as a result, this product was penetrated at a rate equivalent to 46 cm (extrapolated value) in 72 hours. Moisture-holding capacity apparently is related to both the chemical makeup and the physical porosity of the granules. Pure crystalline salts generally are nonporous and have low moisture-holding capacities. Some impurities, for example iron and aluminum phosphates in fertilizers made from wet-process acids, are beneficial in increasing moisture-holding capacity.

Results of this absorption-penetration test are indicative of expected bulk fertilizer behavior under

TABLE 4. RESULTS OF TVA MOISTURE ABSORPTION-PENETRATION TEST OF GRANULAR FERTILIZERS

		72-hr Exposure at 30°C, 80% RH			
Grade and Type	Critical Humidity, %	Moisture Absorbed, mg/cm^2	Moisture Penetration, cm	Moisture-Holding Capacity	
				mg/cm^3	% by Weight
19-19-19 urea melt-based NPK	45	538	3.4	158	18.5
19-19-19 urea prill-based NPK	45	463	7.0	66	7.7
20-10-10 nitrate-based NPK	55	372	6.9	54	6.7
17-17-17 nitrate-based NPK	55	433	6.3	69	8.3
34-0-0 ammonium nitrate prills	59	918[a]	46.0[a]	20	2.1
13-13-13 sulfate-based NPK	70	238	2.7	88	11.0
11-55-0 ammonium polyphosphate (TVA)	70	88	1.4	63	7.9
18-46-0 diammonium phosphate	70	151	1.2	125	14.1
46-0-0 urea prills	73	324	13.0	25	3.2

a. Test terminated after 24 hours. Values shown for 72 hours obtained by extrapolation.

steady, high-humidity conditions, but it should be realized that under cycling conditions, such as occur in actual bulk storage, the results may be altered by crusting (self-sealing) of pile surfaces of some materials during dry cycles. Also, it should be realized that under such cycling conditions products with high critical humidity will be nonabsorbing a greater portion of the time than will products with low critical humidity. The test conditions can be modified to provide such cycling.

Small-Pile Tests

Bulk storage of fertilizer in open piles may incur either or both of two major problems; these are (1) caking or other physical deterioration deep within the pile and (2) wetting of exposed pile surfaces and penetration of moisture. Contrary to some misconceptions, these two problems usually are not related. Caking or deterioration deep within a pile usually occurs entirely as a result of factors not dependent on exposure of the pile surface. These factors include insufficient drying during manufacture, granule weakness, excessive fines, chemical reactions, excessive storage temperatures, excessive pile height (pressure), and, in the case of superphosphate products, insufficient curing.

Small-pile storage tests are not reliable as a method of predicting the caking or other deterioration that might occur deep in a large pile. The chief reason for this is that storage pressure, an important factor, is much less in a small pile than in a large one; also, heat loss from a small pile is greater. Use of a tall silo of small diameter has been suggested as a method of achieving the pressure condition of a deep pile; however, it has been found that this does not duplicate pile-storage conditions because wall effects relieve most of the pressure on the material. It has been the experience of TVA investigators that the best indications of probable behavior of fertilizers deep in bulk-storage piles are obtained by conducting bag-storage tests; this will be discussed later.

Small-pile storage tests are, on the other hand, useful for study of the behavior of pile surfaces during exposure. One disadvantage of the method is that a relatively large test area is required compared with that required for laboratory absorption-penetration tests. Also, unless a humidity-controlled area is provided, the results may be variable, depending on prevailing atmospheric conditions in the locality at the time of the test. For this reason, it is advisable to run parallel tests with one or more standard fertilizers of known characteristics. It is convenient to provide small, open-top bins for the tests. Typical test bins, designed to handle 400-600 lb (171-272 kg) of fertilizer, are pictured in figure 16. Walls and joints of these bins should be airtight so that moisture enters only through the exposed top surface of the material. The exposure conditions should be similar to those expected in actual bulk storage; if possible, the tests should be conducted in the actual intended storage building.

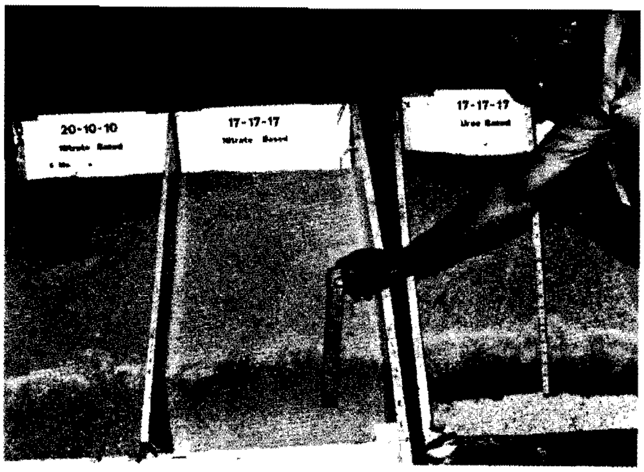


Figure 16. Small-Pile Exposure Tests of Fertilizers in Open-Top Bins.

Exposure periods of 1-3 months usually are sufficient to provide reliable comparisons of materials. Summer conditions are the most severe in most climates. Inspection involves cutting the pile vertically to expose a vertical section. The physical condition at various depths is observed and recorded. Samples are taken at several depths both in the moisture-affected portion and below the visible penetration of moisture. The samples usually are analyzed for moisture content and are checked for loss of granule hardness. The test has the advantage of requiring only simple equipment and of showing material behavior under the variable conditions of actual warehouse exposure. In areas where there are well-defined wet and dry seasons, it may be advisable to extend the test period through at least a portion of both seasons.

Protection in Bulk Storage

Fertilizers in bulk storage may require special protection from atmospheric moisture if one or more of the following conditions prevail:

1. The material is particularly hygroscopic, as indicated by the laboratory penetration test or the small-pile storage test.
2. The storage is in an area of high humidity.
3. The storage is for a long term.

For small piles (for example, 100-300 tons in a blending plant), covering the pile with polyethylene sheeting is a practical and effective method of excluding atmospheric moisture. For large piles, it usually is sufficient to provide a tightly closed storage building. However, the closure must be complete, and this frequently is a problem. The ultimate in storage protection is provision of a dehumidified building. Methods that have been used to lower relative humidity in storage areas include (1) heating of inlet air, (2) dehumidification by mechanical refrigeration, and (3) chemical absorption of moisture. The method employing mechanical refrigeration has been shown to be effective with a surprisingly small refrigeration requirement when applied to a reasonably tight building (61).

Drillability Tests

The term "drillability," as applied to fertilizers, first came into use in the early 1930s and at that time was used to denote the resultant of all the properties of a fertilizer that affect the ease and uniformity with which it will flow through a fertilizer drill (row applicator). Studies were made of the effects of such variables as hygroscopicity, particle size, specific gravity, moisture content, particle shape, angle of repose, and presence of conditioners; however, those studies were made almost exclusively with the nongranular-type fertilizers current at that time (62, 63, 64). With the advent of granulation in the early 1950s, it became evident that flowability of uncaked granular product was not a problem, except to the extent that exposure of hygroscopic granular products to humid atmosphere during handling or field application would impair flowability (65). Since that time, the use of drillability tests has been almost exclusively to determine the effects of humid exposure on flowability. In this work, the term "relative drillability" has been used to define the following ratio:

$$\frac{\text{(flow rate after exposure)}}{\text{(flow rate before exposure)}} \times 100 = \%\ \text{relative drillability}$$

The flow rates are determined in an actual row-type spreader with the same flow settings before and after humid exposure of the fertilizer.

A procedure for determining relative drillability of fertilizers was first described by investigators of the U.S. Department of Agriculture (65, 66). The same procedure, with some simplifications, was adopted also in early work by TVA (42). Both procedures employed a single-row applicator mounted in a stationary position but with the ground wheel driven by a motor at a constant speed to give a delivery rate typical of field application. The general procedure was as follows:

1. Determine delivery rate of dry, unexposed fertilizer.
2. Expose fertilizer to high humidity in shallow pans in a controlled humidity chamber for a measured time.
3. Measure delivery rate of exposed fertilizer with same drill setting and calculate "relative drillability."
4. Continue exposure and remeasure delivery rate for additional time periods until flow is seriously impaired.

The method has been useful chiefly for comparing the humidity resistance of a fertilizer to the resistance of standard fertilizers of known acceptability. It should be realized that the exposure used (shallow pans, high humidity) is more severe than is normally encountered in a careful field application. With proper care in the field, even highly hygroscopic materials such as ammonium nitrate or calcium nitrate are used successfully.

Laboratory Flowability Tests

The drillability test described above requires the use of relatively large quantities of fertilizer, a full-size fertilizer drill, and a humidity-controlled chamber of considerable size. Recently, however, a laboratory-scale test was developed by TVA investigators which provides a similar comparison of humidity effects on flow characteristics but requires only small samples (67). A photograph of the test apparatus used is shown in figure 17. In conducting a test, a 500-ml sample of the test fertilizer is first placed in a small (25-cm diameter by 15-cm depth), inclined, rotary pan that is equipped with shallow (1-cm) lifting flights. The entire pan and drive assembly is placed in a laboratory temperature-humidity chamber with horizontal airflow directed into the open face of the pan. A high relative humidity, for example 90%, is used. The pan then is rotated at 12 rpm, and measurement is made of the time during which the material remains free flowing within the pan. Free flow usually ends rather abruptly, and the end point, which is determined visually, is assumed to be the time at which flow of about 50% of the material is halted by stickiness. In addition to determination of free-flow time, the sample can be analyzed at the end of the test to determine the moisture content at which the product became nonflowable. Typical results obtained with several fertilizers in the test are shown in table 5. As with the drillability test, results of this test are relative, and standard fertilizers of known acceptability should be run as comparison standards. Results in table 5 show that knowledge of critical humidity alone is not sufficient to predict the persistence of flow under humid conditions. For example, prilled urea, with the relatively high critical humidity of 73%, showed the shortest flow persistence (9 minutes) apparently because of the low moisture-holding capacity (3.2%) of urea prills. However, moisture-holding capacity (as determined in the previously described absorption-penetration test) likewise was not a sufficient criterion, in itself, to predict flow persistence. The 19-19-19 urea melt-based NPK, in spite of high moisture-holding capacity (18.5%), became nonflowable in 20 minutes as compared with over 100 minutes persistence for four of the fertilizers tested.

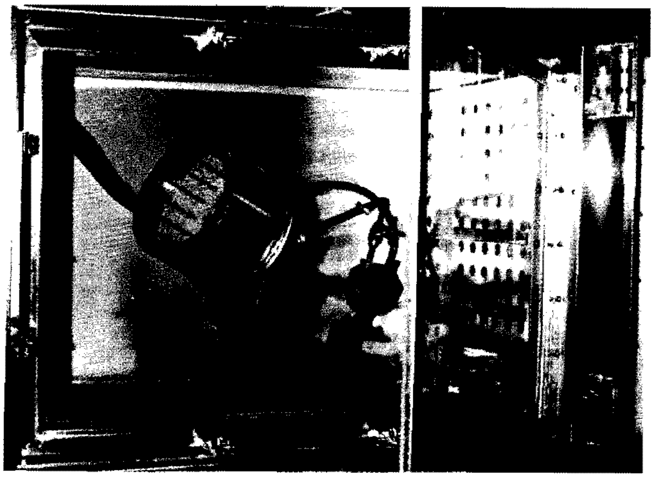


Figure 17. Laboratory Test to Determine Flow Persistence of Fertilizer During Humid Exposure.

Caking of Fertilizers

Fertilizers, between the time of their production and final application to the soil, must be stored, either in bulk or in bags. Storage times vary considerably, from less than a month to a year or more. It is essential that, during this storage, either the fertilizer remain completely free flowing or that "caking"

TABLE 5. RESULTS OF LABORATORY TESTS TO DETERMINE FLOW PERSISTENCE OF FERTILIZERS UNDER HUMID CONDITIONS (67)

Fertilizer Grade and Type	Critical Humidity, %	Moisture-Holding Capacity, %[a]	Minutes Flowable at 30°C, 90% RH
19-19-19 urea melt-based NPK	45	18.5	20
19-19-19 urea prill-based NPK	45	7.7	16
20-10-10 nitrate-based NPK	55	6.7	73
17-17-17 nitrate-based NPK	55	8.3	105
28-28-0 urea-ammonium phosphate	55	16.0	36
35-17-0 urea-ammonium phosphate	55	26.2	52
34-0-0 ammonium nitrate prills	59	2.1	11
13-13-13 sulfate-based NPK	70	11.0	156
11-55-0 ammonium polyphosphate (TVA)	70	7.9	164
18-46-0 diammonium phosphate	70	14.1	70-140
46-0-0 urea prills	73	3.2	9

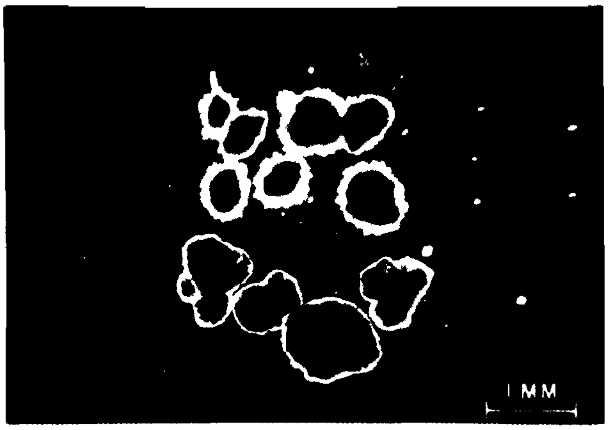
a. Determined in laboratory penetration test (see table 4).

(agglomeration or lumping) be so minimal that a small amount of normal handling will restore the original free-flowing condition. However, since the very beginning of the chemical fertilizer industry, problems with excessive caking in storage have been encountered frequently and have been the subject of much study and numerous publications.

The cause of caking of most fertilizers is the growth of crystal bonds between fertilizer particles (49, 68, 69). These crystals develop during storage either as a result of continuing internal chemical reactions or thermal effects that result in the deposit of crystals from minute amounts of salt solutions present in the fertilizer. A photomicrograph of crystals that developed on the surface of one granular compound fertilizer during 3 months of storage is shown in figure 18. Intergrowth of such crystals between granules, or between particles of a nongranular product, results in caking. The chemical composition of the bonding crystals usually is different in fertilizers of different formulations; a large variety of bonding compounds have been identified. A few instances have been reported of fertilizers in which particle bonding appeared to be by cohesive forces only, without observable crystal growth (70).

Contrary to a frequent misconception, caking in storage (bags or bulk) usually is not a result of the absorption of moisture during storage; the cause is much more likely to be the presence of excessive moisture left in the product during manufacture or any of several other factors that will be discussed. Fertilizer stored in modern, moistureproof bags is well protected from external moisture, yet caking in such bags is not uncommon. Likewise, fertilizer at the center of bulk storage piles is protected from external moisture by the surrounding fertilizer; yet, the most severe caking frequently is found at the center of piles. This is not, however, to minimize other undesirable effects of high humidity on bulk storage. Such high humidity will, as discussed earlier, cause wetting and caking of pile surfaces; with prolonged exposure, penetration of such surface moisture into some fertilizers can become quite deep. Also, conveying or otherwise handling fertilizers in a humid atmosphere prior to bagging or pile building can introduce moisture that later will promote caking.

Closeup of surface crystal growth responsible for caking during 3 months' storage



Effects of drying (lower set of granules) in reducing extent of caking-bond growth during storage

Figure 18. Photomicrographs of Granules of 12-12-12 Grade Fertilizer Made with Urea-Ammonia Solution—Photographs Made After 3 Months' Storage in Bags; Caking Bonds Identified as a Urea-Ammonia Chloride Complex (69).

Identification or review of factors that cause caking has been the subject of numerous publications (49, 68, 69, 70, 71, 72). Chief factors that can be controlled to reduce or prevent caking of fertilizers in bag or bulk storage follow.

Effects of Moisture Content

The amount of moisture allowed to remain in a fertilizer at the time of its manufacture has a great effect on its tendency to cake in storage. For most caking mechanisms, the presence of moisture, in the form of solution phase, is essential. The higher the degree of drying at the time of manufacture, the less active the caking mechanisms will be. The extent of drying required to effectively inactivate caking mechanisms varies rather widely with the composition and physical makeup of the fertilizer. Generally, those fertilizers that contain high proportions of nitrogen salts require a greater degree of drying. This is particularly true for fertilizers that contain ammonium nitrate or urea. Some very general guidelines on maximum product moisture content for granular fertilizers are tabulated below. These values should be used only in a general way because numerous processing variations alter the effects of moisture on storage and handling properties of a given fertilizer composition. The values given represent only "free water" content (nonhydrate water), such as is determined by 16-18 hours vacuum desiccation of a sample at 25°-30°C (procedure 2.013; Association of Official Analytical Chemists, U.S.A.). Results obtained by some other analytical methods, such as oven drying or use of Karl Fischer reagent, may include hydrate water which normally does not participate in caking processes.

Product Moisture, 0%-0.5%

* Ammonium nitrate
* Urea
* Ammonium sulfate
* Calcium nitrate
* Sodium nitrate

Product Moisture, 0.5%-1.0%

Mixed fertilizers with $N:P_2O_5$ ratios of
1:1 or higher that contain urea or
ammonium nitrate

Product Moisture, 1.0%-1.5%

Mixed fertilizers with $N:P_2O_5$ ratios
less than 1:1 that contain urea or
ammonium nitrate

Mixed fertilizers with $N:P_2O_5$ ratios
greater than 1:1 that contain no urea or
ammonium nitrate

Product Moisture, 1.5%-2.0%

Mixed fertilizers with $N:P_2O_5$ ratios
less than 1:1 that contain no urea or
ammonium nitrate

Product Moisture, Above 2.0%

Mixed fertilizers containing little or
no nitrogen

Superphosphates

Adherence to the moisture levels indicated above does not necessarily ensure good storage without other measures, as discussed below. Some high-nitrogen fertilizers, for example, ammonium nitrate, calcium nitrate, and some high-nitrogen NPK granulars, require the use of anticaking conditioners (coating agents) in addition to the high degree of drying indicated above. Use of conditioners, as discussed later, also can be used as a means of reducing the degree of drying required for some products.

Effects of Particle Size and Hardness

Production of relatively large fertilizer particles, with an absence of fines, reduces the number of contact points between particles and thus reduces caking. This reduced caking tendency was one of the major incentives behind the growth in the 1940s and 1950s of granular fertilizers in preference to powder or pulverized forms. Granular products generally require less complete drying and are less likely to require use of conditioners than are pulverized materials of the same composition.

Mechanical weakness of granules usually promotes excessive caking. Under the pressure of storage piles, weak granules tend to deform and form relatively large areas of contact between the granules. Also, fracturing of granules can form fines that promote caking. As mentioned in a previous section, a granule hardness (crushing strength of minus 7- plus 8-mesh granule) of 5 lb (2.27 kg) or more is desirable, and hardness of 3 is about the lower limit of practicality.

Effects of "Conditioners"

A fertilizer "conditioner" is a material added to a fertilizer to promote the maintenance of good physical condition (flowability) during storage and handling. Use of conditioner is essential with some high-nitrogen products but is not required with all fertilizers. Usually it is preferable to use other means, such as good drying, to avoid caking; the expense of purchasing and adding conditioner thus is avoided. Before the advent of granulation, when most fertilizers were of the pulverized type, the more popular conditioners were coarse-particle materials that functioned chiefly as "bulking" agents; these included such materials as vermiculite, perlite, cottonseed hulls, sawdust, corncobs, tobacco stems, rice hulls, peat, and others. With the advent of granulation, however, it became evident that these coarse-type materials are not effective anticaking agents in granular products; the most effective conditioners for granular products were found to be coating agents that will adhere to the surface of granules. Most conditioners now used on granular fertilizers are either very finely divided powders (dusts) that adhere to granule surfaces or are liquids that are sprayed onto the surfaces. The mechanisms by which these anticaking agents function are various. Inert powders such as diatomaceous earth (kieselguhr), clays, and talc function as mechanical barriers between granules and also serve to absorb, spread, and inactivate solution phase on granule surfaces. Where caking bonds do form, the presence of conditioner usually weakens the bonds, with the result that caking is less severe. Liquid conditioners usually function as crystal modifiers to inhibit or weaken crystal growth among the granules. Some solid inert conditioners are pretreated with chemical additives. With these products, the inert carrier serves to distribute a very small amount of chemical evenly over granule surfaces and also functions as a mechanical barrier and solution phase spreader. Contrary to a common misconception, most fertilizer anticaking agents (conditioners) do not function as moisture barriers or waterproofing agents. Most conditioned fertilizers, if exposed to humid atmosphere such as in an absorption-penetration test (see earlier section), will absorb moisture and be penetrated by moisture to fully as great an extent as unconditioned product. There are a few exceptions where conditioners, for example, wax-oil mixtures or plastic coatings, are designed specifically to improve the humidity resistance of hygroscopic products (73, 74, 75).

A few conditioners, classed as "internal" conditioners, are added into fertilizer formulations before granulation; these act internally, usually as hardeners or crystal modifiers, to improve storage properties. In the case of ammonium nitrate fertilizer, internal conditioners frequently are used to inhibit or modify the effects of crystal phase inversions that result from temperature cycling during storage; the inversion that occurs at 32°C (90°F), in particular, can cause uninhibited ammonium nitrate prills to shatter and cake seriously under cycling storage temperatures (76, 77, 78). In the case of urea prill or granule production, a popular current practice is the inclusion of 0.2%-0.5% of formaldehyde or urea-formaldehyde in the urea melt as a hardener and anticaking additive (79, 80, 81). Use of such additive obviates the need for coating agent. Fertilizer products made from wet-process phosphoric acids characteristically contain significant proportions of iron and aluminum phosphate impurities which have been shown to serve as effective internal anticaking conditioners in those products (82). The iron and aluminum phosphates are found in the products as amorphous "gels" that harden the products and apparently immobilize solution phase. Formation of the iron and aluminum phosphates under relatively high pH and low temperature conditions promotes the gel-type structure rather than crystalline forms (83); the latter are not believed to be beneficial to physical properties. Caking problems with some granular diammonium phosphates have been traced to the use of wet-process acids that were unusually low in iron and aluminum impurities.

Solid conditioning dusts in common use include diatomaceous earth (kieselguhr), kaolin clays, talc, and chalk. The proportions applied usually are in the range of 1%-4% by weight. The properties of these powder-type conditioners that are required for good anticaking action are not well defined; thus, actual use tests are the only reliable method of evaluation. Desirable properties do, however, include small particle size, good adherence to granules, and high moisture absorbency. Clay conditioners are extremely fine (90% < 10 µm, 50% < 1 µm) and thus usually have good adherence properties. Diatomaceous earths (kieselguhr) are coarser (90% < 20 µm, 50% < 3 µm) with the result that adherence is sometimes inferior;

furthermore, the sources of diatomaceous earth are not widespread, with the result that freight charges can be considerable. However, diatomaceous earth has superior absorption properties and is a very effective conditioner. It is sufficiently effective for use, even without organic additive, as a conditioner for ammonium nitrate, a product that has particularly demanding requirements for conditioner. Talc and chalk are less widely available; therefore, their use is rather localized.

In evaluating potential powder-type conditioners, it is advisable to first conduct an adherence test (see later section); powders that do not adhere well (about 85% or more) when applied in a well-designed coating drum are likely to result in dusty products and to have reduced anticaking efficiency. Proper sizing and operation of the coating drum are important (84). Powders found to have acceptable adherence should be subjected to use tests for anticaking action at various rates of application within the range of economic feasibility. Adherence of conditioners often can be improved by spraying the fertilizer with a small amount of oil (usually only 0.2%-0.5%) either before or after application of the conditioner. This is a common practice in Europe. Results are best with fairly viscous oil (25-100 centistokes) of high paraffin content. Less viscous oils are too easily absorbed into granules and also present volatility hazards. Use of oils on ammonium nitrate or high-nitrate products, however, is not allowable because of hazards of explosion or burning. However, some tests by TVA indicated that NP granules containing less than 60% ammonium nitrate were not sensitized by addition of oil at least up to 3% oil content (85).

Kaolin clays are widely available and are relatively inexpensive. When used alone (without organic additive), they usually are sufficiently effective for use on most NP or NPK granular fertilizers and on urea. Kaolins without organic additive are not normally considered sufficiently effective for use on ammonium nitrate or on some other high-nitrate products. Use of some organic additives in combination with kaolins, however, upgrades the kaolin sufficiently for use with these products; organically treated kaolin presently is a popular conditioner for ammonium nitrate (86). The organic additives are usually surfactants or hydrophobic amines; they can be applied separately to the fertilizer or preapplied to the kaolin (86, 87, 88, 89). There is some use of these and other organics also without kaolin or other solid coating agent.

Effects of Storage Temperature

High storage temperature increases the caking tendency of at least some fertilizers. For this reason, it is advisable to cool freshly made products adequately before storage in bags or bulk. The maximum advisable bulk-storage temperature for ammonium nitrate or granular mixed fertilizers containing ammonium nitrate is probably about 54°C (130°F). Urea-based mixed fertilizers made with unammoniated or partially ammoniated superphosphates likewise may, on the basis of work at TVA, have to be cooled to about this temperature to prevent hydrolysis of urea and resultant loss of P_2O_5 water solubility. Diammonium phosphate and granular sulfate-based or urea-ammonium phosphate products, on the other hand, usually need be cooled only to about 71°C (160°F). Prilled urea and granular urea also appear to be less sensitive than ammonium nitrate to storage temperature; storage up to 82°C (180°F) has in some cases caused no significant increase in caking tendency. These storage temperatures are for well-dried products; increasing moisture content of products would be expected to increase sensitivity to storage temperature. If product is to be bagged directly from production, cooling to at least 54°C (130°F) is advisable to avoid damage to bags.

Effects of Storage Pressure

If a fertilizer has a significant tendency to cake in storage, high storage pressure should be avoided, especially in long-term storage. Degree of caking frequently is quite dependent on storage pressure. Pressure can be limited by limiting the height of bag stacks or bulk-storage piles. A 20-bag stack is considered moderate in height. Pressure on the bottom bag of such a stack can be calculated by measuring the bearing area on the bag (contact area between bags) and dividing the weight of the stack by this area. In the case of a 20-bag stack of typical 50-lb (25-kg) bags, this pressure is about 4.0 lb/in^2 (0.28 kg/cm^2). Under a 20-bag stack of 50-kg (110-lb) bags, the corresponding pressure is about 6.4 lb/in^2 (0.45 kg/cm^2). Thirty- to forty-bag stacks are not uncommon (usually palletized) with some fertilizers of low caking tendency.

Average pressure on fertilizer at the base of a conical bulk storage pile of height "h" can be calculated to be hd/3, where "d" is the bulk density of the material. Assuming that pressure varies linearly from zero at the pile edges to maximum at the pile center[2], the maximum pressure in a pile would be 2hd/3. On this basis, for a material of 60 lb/ft^3 (961 kg/m^3) density, the relation of pile pressures to pile height and equivalent bag-stack heights would be as follows:

Pile peak height, ft	15	20	25	30	35	40
Pile peak height, (m)	(4.6)	(6.1)	(7.6)	(9.1)	(10.7)	(12.2)
Average pressure at base						
lb/in^2	2.0	2.8	3.5	4.2	4.9	5.6
(kg/cm^2)	(0.14)	(0.20)	(0.25)	(0.30)	(0.34)	(0.39)
Maximum pressure						
lb/in^2	4.1	5.5	7.0	8.3	9.7	11.1
(kg/cm^2)	(0.29)	(0.39)	(0.49)	(0.58)	(0.68)	(0.78)
Bag-stack height to give same maximum pressure,[a] No. of bags	22	30	38	45	52	60

a. Based on typical 50-lb (23-kg) bags.

Effects of Curing

Intentional aging of fertilizer in a storage pile prior to bagging or bulk shipment is referred to as "curing." In the manufacture of superphosphates, pile curing for about 30 days frequently is employed to allow continuation of acid-rock reactions and thus increase P_2O_5 availability, reduce free acid content, and improve physical properties (90). Curing is beneficial also to some granular mixed fertilizers as a means of reducing subsequent caking tendency (69, 72). The effect is especially pronounced with products formulated to contain appreciable amounts of superphosphates but is usually much less with ammonium phosphate-based products or with straight nitrogen fertilizers. In products that benefit from curing, chemical reactions that cause caking bonds apparently proceed to near completion during the curing period; the heat of reaction that is retained in the curing pile speeds the completion of the reactions. After bonds have been broken in reclaiming material from the curing pile, there is reduced tendency for additional bonding to develop.

Large-Bag Storage Tests

The caking tendency of a fertilizer can be evaluated reliably by a storage test, under pressure, in standard-size moistureproof fertilizer bags. Since the properties of the fertilizer, not those of the bag, are under test, the best bag available should be used and, if there is any doubt as to the moisture impermeability of the test bag, a polyethylene overbag should be used to afford essentially complete protection. Results of a storage test made under such conditions evaluate not only the bag-storage properties of the product but also its tendency to cake under pressure deep in bulk-

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[2] This assumption is not necessarily accurate but is believed to lead to conservative (more than actual) maximum pressure values.

storage piles. As was pointed out in an earlier section, fertilizer at the center of a bulk-storage pile is effectively protected from moisture intrusion by the surrounding material; thus, the environment there is similar to that in a moistureproof bag. Also, storage pressures in piles of moderate height approximate the pressures in bag stacks (see earlier section, "Effects of Storage Pressure").

The chief advantages of large-bag storage tests are the reliability of results and the limited need for specialized equipment. Disadvantages include the following:

1. The test is not an accelerated one; thus, it is of limited value for production quality control.
2. A relatively large amount of material is required.
3. A relatively large test area is required.
4. Building of bag stacks or otherwise applying pressure is labor intensive.
5. Intermediate inspections require considerable labor in disassembling and rebuilding stacks.

Reported procedures for carrying out bag-storage tests are generally similar. The following procedure currently is used by TVA and represents a simplification of a previously reported procedure (42).

1. The test is made in 50-lb (25-kg) size fertilizer bags of monofilm polyethylene with 7-mil wall thickness. The bags are of the valve-fill type. In some tests, overbags of 6-mil polyethylene are used to afford further moisture protection. Since test materials differ in bulk density, the weight of material used is adjusted to provide filling of the bags to their design volume.

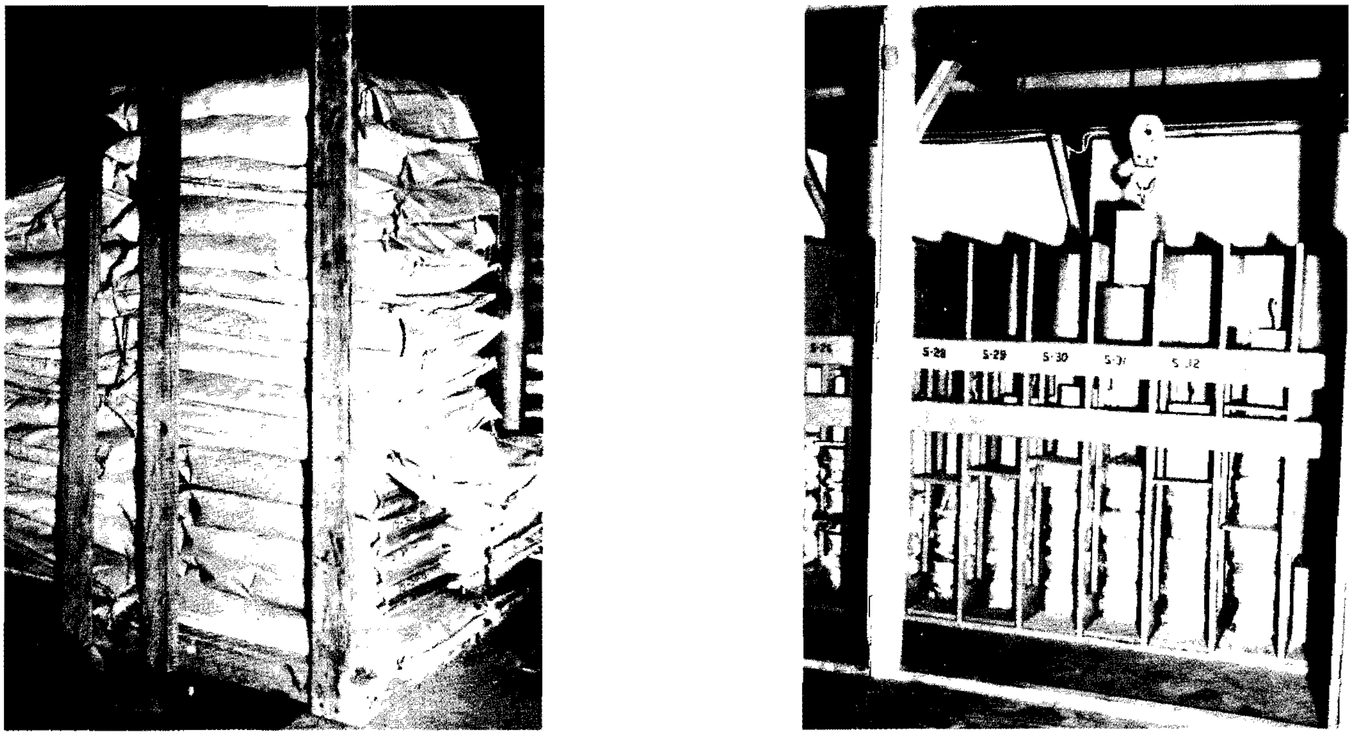
2. From one to five bags of the material to be tested are stacked vertically, and a 17- by 30-in (43- by 76-cm) piece of plywood is placed on the top bag. Then, ten 100-lb (45.4-kg) bags of sand (dummies) are stacked on this plywood board. The entire bag stack is made within a loose wooden framework to prevent tipping of the stack. The resulting pressure (3.5-4.0 lb/in^2) (0.25-0.28 kg/cm^2) on the test bags is equivalent to that at the bottom of a 20-bag stack of 50-lb (22.7-kg) bags. A photograph of bags under this test is shown in figure 19.

3. The storage tests are carried out in a large, unheated warehouse of hollow-tile construction with a concrete floor. Each test stack rests on a dummy bag placed on a wooden platform to isolate test bags from the floor. Windows and louvres of the building are kept open; thus, usual open warehouse conditions are duplicated. Since the fertilizers usually are in good moistureproof bags, the humidity entering through the open windows is not significant, but the open windows do serve to duplicate open-warehouse temperature fluctuations.

4. Inspections are made at intervals such as 1, 3, 6, 9, and 12 months. Products that develop any appreciable amount of caking in 1 month are very likely to develop more serious caking during longer storage. On the other hand, products that remain free of lumps during the first month will not necessarily remain free of serious caking during further storage. The procedure at the time of inspections is as follows:

    a. The upper 10 bags (dummies) are removed, and a test bag is inspected for "bag set" without moving it from its original position. The operator feels the bag and records bag set as none (0), light (L), medium (M), or hard (H). Bag set is not a reliable indication of degree of caking but is a factor in customer satisfaction with a product.

    b. The bag then is dropped once (on thin side) from a 3-ft height onto a concrete floor to simulate the action of normal handling. The bag then is cut open, and the material is



50-pound test bags under ten 100-pound bags of sand

3-pound test bags under 130-pound lead weights

Figure 19. Fertilizer Storage Tests in Large and Small Bags.

screened very gently (without lump breakage) to determine the proportion of plus 1/2-in (1.3-cm) lumps.

c. Hardness of the lumps is rated by crushing in the hand. Ratings of light (L), medium (M), or hard (H) are given. Light lumps are those that would easily be broken up by most application machinery. Medium lumps normally would not be broken by application machinery but could be crushed satisfactorily with some special treatment. Hard lumps normally are not acceptable for any use.

d. Results of the inspection are reported in an abbreviated manner to give bag set, percent lumps, and lump hardness. For example, a rating of M-10-L would indicate a medium bag set, 10% of plus 1/2-in (1.3-cm) lumps after the drop test, and a light hardness rating for the lumps.

It is not possible to give a universal criterion as to what degree of caking is tolerable since requirements differ widely in different areas and for different uses. Where machine application is employed, complete freedom from lumps is highly desirable, but a few (up to perhaps 15%) of only light lumps may be acceptable. For hand application, where labor is available and each bag can receive individual treatment, a higher percentage of lumps and the presence of lumps of medium hardness may not be considered intolerable.

Small-Bag Storage Tests

Some of the disadvantages of large-bag storage tests can be avoided by conducting the tests in small bags. Such tests can be made with smaller quantities of material, and the necessity for handling heavy test bags and dummy bags is avoided. Figure 19 shows a series of small-bag tests being carried out by TVA (42). In this test, bag size is about 3 lb (1.4 kg; filled size 12 x 7 x 25 cm), and pressure is applied by means of a 130-lb lead weight (59 kg). As in the large-bag tests, precautions are taken to ensure that the bags are impervious to moisture; a moistureproof bag is used and a polyethylene overbag is used as extra protection. Pressure in the test, as determined by the lead weight and the bearing surface area on the bags, is the same (about 4 lb/in^2) (0.28 kg/cm^2) as in the large-bag tests. As in the case of the large-bag test, this is not an accelerated test, and inspection periods of 1, 3, 6, 9, and 12 months are used. The storage location and the inspection and evaluation procedures are exactly as described above for large bags, except that use of two drops of the small bag prior to opening was found to give the better correlation with results in large bags. With this modification, the results in the small bags have been found to be a good indication of storage properties in large bags.

Because of the relatively small size of the small-bag test stacks, it is convenient to run special tests in controlled-temperature areas. Such tests have indicated that a constant elevated temperature (90°F; 32°C) gives a slight acceleration in caking over that resulting from ambient tests. However, the small difference probably does not warrant use of special temperature control in routine testing. Temperature cycling, likewise, was not considered useful.

Accelerated Caking Tests

Numerous tests have been devised to measure the caking tendency of fertilizers without waiting through long periods of storage. D. C. Thompson reported in 1972 that a literature review had revealed descriptions of 41 such tests (70). The incentives for such a test are obvious. With results obtainable rapidly, such a test could be used for production quality control or as a basis for acceptance or rejection of fertilizers in commerce. Also, obtaining results rapidly with small quantities of product would facilitate research study of factors that affect caking of fertilizers. Unfortunately, however, it appears that none of the procedures reported have been demonstrated to be fully reliable for application to a wide variety of fertilizers. As a result, there is no general acceptance of accelerated tests, and their use is limited mostly to research studies and to those quality-control applications in which empirical correlations can be made with properties of a specific product. For those uses, there apparently is considerable value in an accelerated caking test.

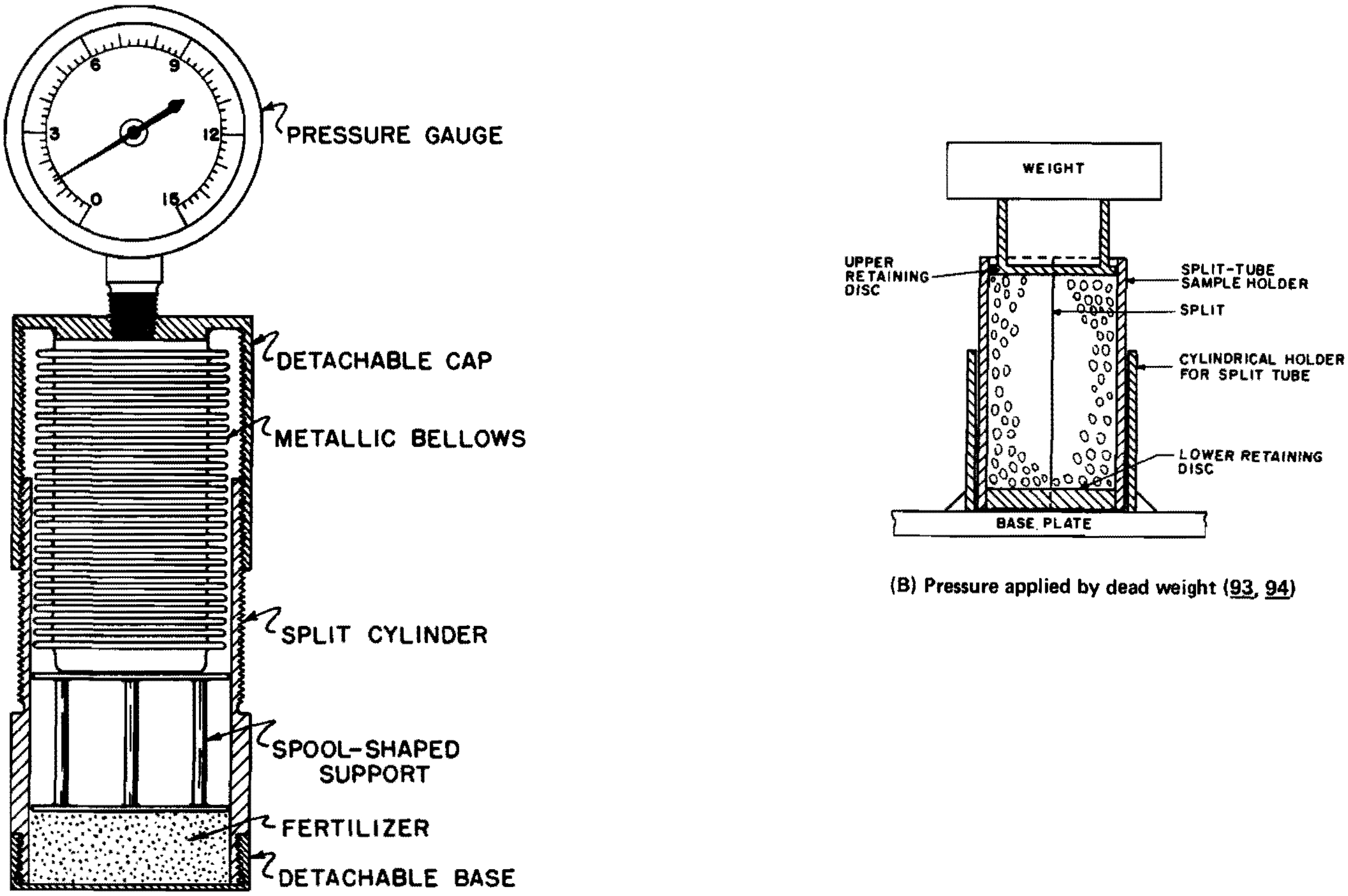
Essentially all accelerated test procedures involve the following basic operations:

1. Short-term storage of a small sample of fertilizer under pressure and other storage conditions that usually are more severe than in normal fertilizer storage and which are designed to encourage caking of the sample.

2. Sensitive measurement of the hardness of the formed cake.

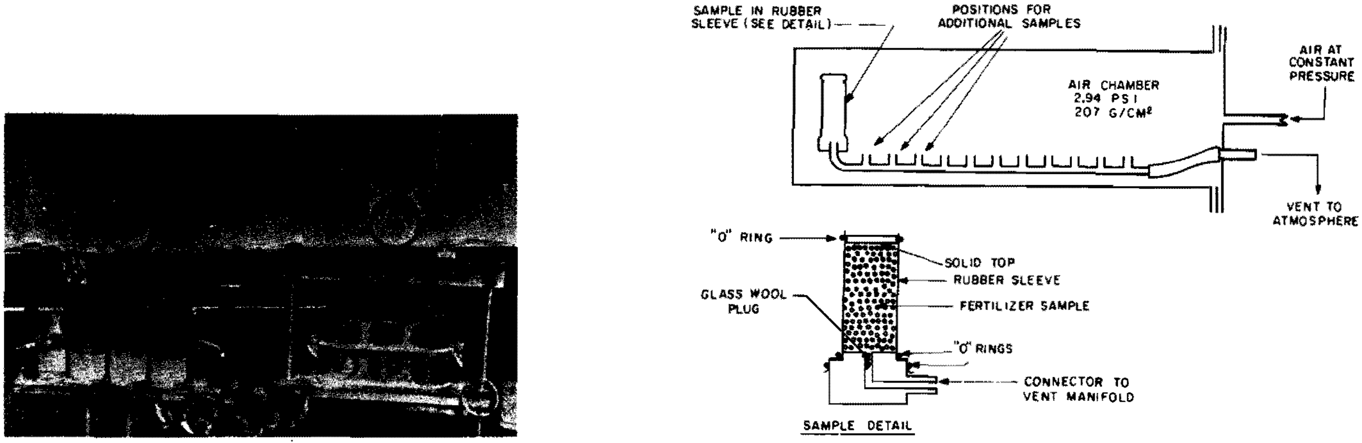
As pointed out by Thompson, the conditions used to promote caking of the sample should not deviate drastically from those encountered in actual storage (70). For example, some tests have been reported in which humid air is allowed to contact the sample during the period of cake formation. As mentioned previously, this condition does not prevail either in moistureproof fertilizer bags or within bulk-storage piles; thus, it is not a legitimate condition for a storage test. Results obtained in such tests would not be indicative of caking tendency under normal storage conditions; to be meaningful, accelerated caking tests should, like bag-storage tests, be carried out with the sample protected from ingress or egress of moisture. Conditions that have been used to accelerate the cake formation in protected samples include (1) higher than normal pressure, (2) higher than normal temperature, and (3) cycling temperature. Pressure increase probably is legitimate as a means of bringing the fertilizer granules into more intimate contact and thus promoting stronger cake, although, in some reported tests, pressure increase has been carried to the point that the crushing strength of granules was exceeded. Moderate elevation in temperature also would appear legitimate as a means of speeding caking reactions. Cycling of temperature, in limited unreported tests at TVA, has not effectively speeded caking of the fertilizers tested; furthermore, it has been observed that the temperature within bulk piles or large bag-storage areas normally shows little or no cycling. Even with application of the most severe conditions considered legitimate to promote caking, the caking process of some types of fertilizers cannot be speeded sufficiently to make an accelerated test useful. A typical example is urea, which usually will not form a significant cake in an accelerated test under legitimate test conditions. This natural slowness of some caking processes seems to be the main obstacle to development of a universally useful accelerated test.

Reported accelerated caking tests differ in the equipment and conditions used to form the fertilizer cake and in the equipment used to measure cake hardness. Several types of equipment used to form cylindrical cakes are illustrated in figure 20. Only tests in which cakes are formed under protected conditions are included. For the pictured tests, pressures applied ranged from about 0.2 kg/cm^2 (3 psi) to 1.7 kg/cm^2 (24 psi) (72, 86). Standard test periods ranged from 7 days to 28 days (41, 72). Details can be obtained from the indicated literature references. In all the tests illustrated, degree of caking was measured as the vertical force required to fracture the resulting cakes. In some other tests with cylindrical cakes, caking has been measured by the penetration of a needle-pointed penetrometer (87) or by the force



(A) Pressure applied by compression of air- or oil-filled bellows (41, 71)

(B) Pressure applied by dead weight (93, 94)



(C) Pressure applied by air to bellows of a standard "cement mold" test apparatus (86, 95)

(D) Pressure applied by air in vessel surrounding samples in thin rubber sleeves (72)

Figure 20. Some Methods Reported for Forming Fertilizer Cakes in Accelerated Caking Tests.

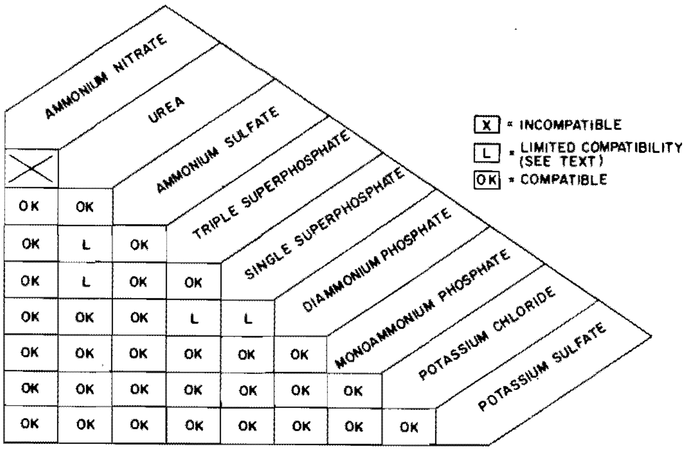
required for a small-diameter disc to penetrate and fracture a plug from the cake (70, 91). Another reported accelerated caking test involves the formation of a cake within two vertically stacked metal cylinders, and degree of caking is measured as the shearing force required to fracture the cake at the point of junction of the cylinders (92). Still another type of accelerated caking test involves applying pressure to very small plastic bags of the fertilizer and measuring the amount of caking by a standardized procedure (50, 86).

Chemical Compatibility in Blends

The first step toward making a bulk-blended fertilizer of good quality is choice of ingredients that are chemically compatible. Fortunately, there are only a few combinations of major fertilizer materials that may give trouble in this respect. Chemical incompatibility of materials may take the form of heat development in the blend, development of wetness, gas evolution, or caking. These types of incompatibility can best be detected in a large- or small-bag test (see preceding section); however, a simple "bottle test" is useful. In the bottle test, a freshly made blend is tightly capped in a 4-oz glass bottle, stored in a moderately heated cabinet (86°F; 30°C), and inspected after periods varying from 1 day to several months (96). Inspection reveals any wetting, caking, disintegration, or noxious gas formation.

Another type of incompatibility occasionally encountered is excessive lowering of critical humidity. As pointed out in a preceding section ("Critical Humidity"), the critical humidity of a blend of two materials is usually lower than the critical humidity of either material alone. If this lowering is excessive, the blend may be too hygroscopic for handling, even in only moderately humid atmospheres. Such is the case with mixtures of ammonium nitrate with urea, which have a critical humidity of only 18%. This type of incompatibility may not be detected in bag or bottle tests since air is excluded. To detect this type of incompatibility, the mixture should be subjected to a standard critical humidity determination (see previous section). In the absence of equipment for that type of test, a rough check for excessive hygroscopicity can be made by simply exposing a sample of the blend, in an open dish, to atmospheric air during a period of moderate humidity. If the blend is excessively hygroscopic, visible wetting usually will occur in a few hours. A standard material, of known hygroscopicity, such as ammonium nitrate, can be exposed simultaneously for comparison.

The chemical compatibility of some common fertilizer materials used in bulk blends is shown in figure 21. The only completely incompatible combination is ammonium nitrate with urea, as discussed above. However, combinations of urea with normal or triple superphosphates, which are given a "limited compatibility" rating in the figure, can be completely incompatible, depending on the water content (free water plus hydrate water) of the superphosphate (96). Cause of the incompatibility is a chemical reaction between urea and monocalcium phosphate monohydrate, the main constituent of superphosphate; this reaction releases water of hydration and causes severe stickiness. Mixtures of diammonium phosphate with superphosphates also are shown in the figure to be of limited compatibility because, in some long-term storage tests in bags, reactions between these materials have caused caking.



	AMMONIUM NITRATE	UREA	AMMONIUM SULFATE	TRIPLE SUPERPHOSPHATE	SINGLE SUPERPHOSPHATE	DIAMMONIUM PHOSPHATE	MONOAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE
UREA	X							
AMMONIUM SULFATE	OK	OK						
TRIPLE SUPERPHOSPHATE	OK	L	OK					
SINGLE SUPERPHOSPHATE	OK	L	OK	OK				
DIAMMONIUM PHOSPHATE	OK	OK	OK	L	L			
MONOAMMONIUM PHOSPHATE	OK	OK	OK	OK	OK	OK		
POTASSIUM CHLORIDE	OK	OK	OK	OK	OK	OK	OK	
POTASSIUM SULFATE	OK	OK	OK	OK	OK	OK	OK	OK

X = INCOMPATIBLE
L = LIMITED COMPATIBILITY (SEE TEXT)
OK = COMPATIBLE

Figure 21. Chemical Compatibility of Blend Materials (18).

Dustiness and Conditioner Adherence

Dustiness of fertilizer is a very undesirable property. In recent years, the problem has assumed increasing importance because of (1) the trend toward bulk handling, in preference to bags, and (2) present-day emphasis on ecology and clean occupational environment.

Granulation does much to reduce the dustiness of fertilizers but frequently does not completely solve the problem. Common causes of dustiness of granular products include the following:

1. Inefficient sizing (removal of fines).
2. Weakness of granules (degradation to form fines).
3. Poor adherence of anticaking conditioner dusts.
4. Formation of fine surface crystals on granules which subsequently abrade to form dust (see figure 18). The crystal formation may be caused by chemical reaction or by crystal growth during cooling in storage.

The problems of fertilizer sizing and granule hardness (items 1 and 2 above) were discussed in previous sections. Item 3, the problem of conditioner adherence, is discussed below. Chemical reaction and resultant surface dust formation (item 4), as a cause of dustiness, has been noted in the case of granular diammonium phosphate and in mixed fertilizers. Presently, the chief curative measure being employed is spraying of the products with a small proportion (about 0.5%) of petroleum oil to bind the dust to the granules.

Design of Conditioning Drums

Some fertilizers, for example prilled ammonium nitrate and some high-nitrogen granular products, require coating with small proportions (1%-4%) of finely divided conditioner "dusts" to prevent caking during storage (see earlier section). Commonly used dusts include diatomaceous earths, talc, kaolin clay, chalk, and organically treated kaolin or diatomaceous earths. Fertilizer dustiness frequently is a result of poor adherence of these dust-type conditioners to granule surfaces. One corrective measure that is employed is the use of a petroleum oil spray to enhance adherence of the conditioner (see a later paragraph); however, such addition of oil to ammonium nitrate or high-nitrate products is not permissible because of the explosion hazard of nitrate-oil mixtures. For such products, therefore, the solution to dustiness problems lies solely in (1) selection of a conditioner dust with good adherence characteristics and (2) application of the conditioner in a manner that will promote good adherence. A highly effective, and most commonly used, piece of equipment for applying conditioner dust is a nonflighted rotary drum (conditioning drum) in which the rolling and rubbing action of the granules promotes adherence of the conditioner. In studies of drums at TVA the action of particles in nonflighted conditioning drums was analyzed, and it was found that the degree of conditioner adherence was a function of the cumulative distance (K) through which granules were rolled in the drum (84). For application of typical kaolin clays, a roll distance of about 500 ft (152 m) ensured good adherence; whereas, with diatomaceous earths a roll distance of 1,000-1,200 ft (305-365 m) was indicated to be desirable. Equations were developed also that can be used for determining the drum size and operating conditions required to give desired roll distance (K) values. Based on those equations, the design chart shown in figure 22 was developed. The chart is useful for checking the adequacy of existing drums, as well as for design of new ones. If an existing drum is of different diameter: length ratio from that (2/5) on which the chart is based, the value for K obtained for that diameter drum from the chart should be adjusted in direct proportion to the actual drum length.

Measurement of Dustiness or Conditioner Adherence

A frequently reported method of measuring dustiness of fertilizers or conditioner adherence involves

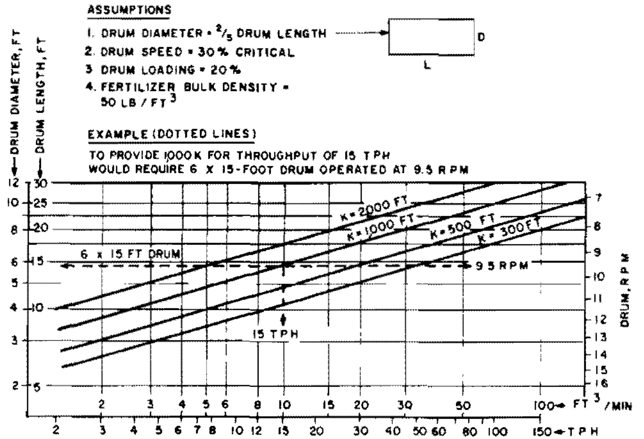
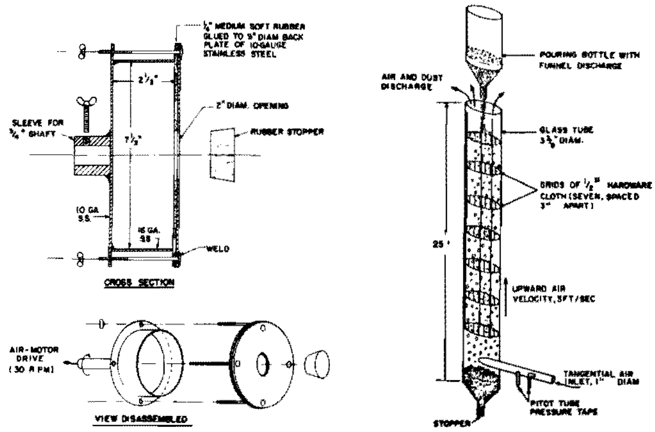


Figure 22. Size and Rotation Rate of Nonflighted Conditioning Drum Required to Give Granules Various Roll Distances (K).



Laboratory-Scale Conditioning Drum

Dedusting Tower for Measurement of Dustiness

Figure 23. Equipment for Measuring Fertilizer Dustiness and Conditioner Adherence.

simple screening over a fine screen, such as a 20- or 35-mesh, and weighing the amount of fine dust passing. However, in TVA studies of conditioner adherence, it was observed that the vibratory action of the screen wire against the fertilizer particles tended actually to compact some conditioners on the particle surfaces and thus give false high-adherence values. To obtain more realistic values, the dedusting tower shown in figure 23 was developed (41, 42). The tower is a glass tube 3-3/8 in (8.57 cm) in diameter by 25 in (63.5 cm) high fitted with seven removable trays of 1/2-in (1.27-cm) mesh screen. An airstream of 3 ft/second (0.91 m/second) velocity is passed upward through the tower while an accurately weighed 250-ml sample of fertilizer is poured downward. Loose dust is blown out the top. The dust loss is determined by weighing the sample before and after pouring. It was found that further dust loss approached zero after about six successive passes of a sample through the tower; therefore, a standard of six passes was adopted. Very reproducible values for conditioner adherence were obtained by this method. Some work was done also in which the exit dust was collected in a filter and weighed; this method was satisfactory also. The dedusting tower described should be usable also for determining the dustiness of unconditioned fertilizers. Some promising unreported work has been done also in which fertilizer samples were subjected to abrasion with steel balls in a small drum (see a previous section "Abrasion Resistance") and then passed through the dedusting tower to determine the amount of dust developed from abrasion.

Since it has been found (preceding section) that the degree of adherence of conditioners is dependent on the amount of rolling provided during the coating operation, it is important that a standardized coating procedure be used in the laboratory when comparing the adherence characteristics of various conditioners and that the amount of rolling be within the range that can be provided in plant conditioning drums. The following procedure was designed to meet these requirements (41).

Coating is done in a totally enclosed nonflighted rotary drum 7.5 in (19 cm) in diameter by 2.5 in (6.4 cm) long rotated on a horizontal axis. A sketch of this drum is included in figure 23. The removable end of the drum is considered an important feature because it provides a means for complete emptying without loss of loose dust. Flights were omitted from the drum because tests indicated that adherence is better without flights.

In conducting a test, a 250-ml charge of dust-free uncoated fertilizer is first weighed and placed in the drum; this provides a 14% loading of the drum by volume. Rotation then is adjusted to 30 rpm. As rotation continues, the desired weight of conditioner is charged quickly through the 2 in-diameter opening, which then is closed with the rubber stopper. Rotation is continued at 30 rpm for 15 minutes following addition of conditioner. Calculations which take into account the drum speed, diameter, and loading indicate that, with rotation time of 15 minutes, the average distance through which a granule rolls in the drum is about 700 ft (213 m). This amount of rolling was selected for the test because, with diatomaceous earth conditioners, it appeared rather critical. Less rolling caused significantly reduced adherence; whereas, additional rolling gave progressively smaller increases in adherence (84). With clays, the critical point was at approximately a 300-ft roll distance. A roll distance of 700 ft, as used in the test, is within the range reasonably attainable in properly designed plant-scale coating drums. At the end of the 15-minute coating period, the drum is stopped and removed from the drive shaft. The removable end then is turned upward, unbolted, and lifted off. The contents, including all loose dust, then are transferred quantitatively to a weighing jar and are weighed on an analytical balance in preparation for passage through the dedusting tower. Under the conditions of this test, a conditioner is considered excessively dusty if adherence is not at least 85%; adherence of 90%-95% is achieved with some fertilizer-conditioner combinations.

Another quantitative method reported for measuring the dust content of fertilizers involves fluidizing a 1.2-liter sample of the fertilizer with air in a vessel fitted with a porous bottom. Dust is carried out with the air and is collected in a glass-wool filter. Air velocity (1.3 m/second) is such that dust particles up to 200 μm in diameter are removed. Dust contents of the fertilizer were correlated with actual observed dustiness in bulk handling, as follows:

Analyzed Dust Content, mg/kg	Observed Dustiness in Handling
< 200	Little dust emission
200-500	Some dust emission
500-1,000	High dust emission
1,000-2,000	Very high dust emission
> 2,000	Extremely high dust emission

For some purposes, a qualitative evaluation of fertilizer dustiness is sufficient. The following procedure was found useful in work at TVA.

1. A 1-liter sample of fertilizer was placed in the bottom of an empty cylindrical fiberboard shipping drum, 1 ft in diameter by 2 ft high, and the cover was placed on the drum.

2. The container then was quickly inverted (180°) so that the sample dropped to the opposite end of the container.
3. After six such successive inversions, the cover was removed and the density of suspended dust in the drum was observed visually and was recorded. Shining a light beam through the atmosphere in the drum aided in the visual evaluation.

This procedure was useful in comparing various oil treatments for dust control. The oils were sprayed on fertilizer samples in a small rotary drum; then the treated samples were subjected to the dustiness test. After various periods of storage of the treated fertilizers, the dustiness measurements were repeated to determine persistence of the treatments. This dustiness procedure probably could be made quantitative by use of an opacity meter to measure dust cloud opacity in the fiber drum after the six inversions.

Use of Dust-Control Agents

It is preferable to produce nondusty fertilizer without use of special dust-control treatment. In many cases this can be done by proper attention to efficient screening, granule hardness, and proper selection and application of conditioner. However, when these methods fall short, it sometimes is necessary to resort to special antidust treatments. All such treatments known to be in use involve spraying the fertilizer with some liquid that will cause dust particles to adhere to granules or to agglomerate and thus not become airborne during handling. The most common liquids used are petroleum oils; proportions applied range from about 0.2%-2.0%. As previously mentioned, use of oils on ammonium nitrate or mixed fertilizers of high ammonium nitrate content is not allowable because of the explosion hazard. The most effective oils are ones with viscosities of at least 100 Saybolt seconds at 100°F (38°C) which is equivalent to 20 centistokes; somewhat higher viscosities (up to 500 Saybolt or 100 centistokes) often are preferable because of greater binding effectiveness and less tendency to be absorbed into granules during storage with resultant loss of effectiveness. Also, the more viscous oils have less tendency to penetrate and soften polyethylene fertilizer bags. No. 2 fuel oil, although widely available because of its widespread use as diesel fuel, is not desirable as a dust-control agent; its viscosity (about 5 centistokes) is too low, its high volatility presents a fire hazard, and it has been found to soften polyethylene bags. Oils of high paraffin content are particularly effective. Naphthenic-based oils, if used, require the use of special oil-resistant rubber belting on conveyors. Some petroleum companies market special lines of dust-control oils (97). Oils containing added amines are said to have enhanced dust-control properties.

The preferred method of application of oil or other liquid binder is by spraying onto a rolling bed of fertilizer, such as in a rotary coating drum or mixer. Alternate methods involve spraying in conveyors, on belts, or at other points where reasonable coverage of fertilizer can be obtained. In bulk-blending plants, the liquid can be applied through a spray nozzle or sparger in the mixer (98).

Liquids other than oils that have been used for dust control include lignin sulfonate liquors, liquid fertilizers, and water. These liquids are suitable if the water introduced does not cause caking during subsequent storage. They are frequently used in bulk-blending plants, where the fertilizer is intended for immediate application.

Melting Point

The melting point of fertilizers is of interest in connection with prilling or other melt-granulation processes in which a fluid melt is necessary. The melting point is also of interest in drying fertilizers that are granulated by other processes since it limits the maximum temperature in the dryer.

The melting point of pure compounds can be determined by standard methods and, in most cases, can be found in handbooks. However, impure materials and mixtures of compounds do not have definite melting points. TVA has adopted a method which is useful for determining approximate melting points of fertilizer granules (99). The method utilizes a Nalge-Axelrod apparatus which consists of a thick stainless-steel disk or block on which a single granule of fertilizer is heated slowly by a controlled electric element. The temperature of the disk is measured by a glass thermometer inserted in the block. The granule is observed through a 25-power microscope while the temperature of the block is slowly raised until a molten pool is seen forming around the granule. The melting temperature was determined on several granules of each material tested, and the values were averaged. A cross section of the melter is shown in figure 24.

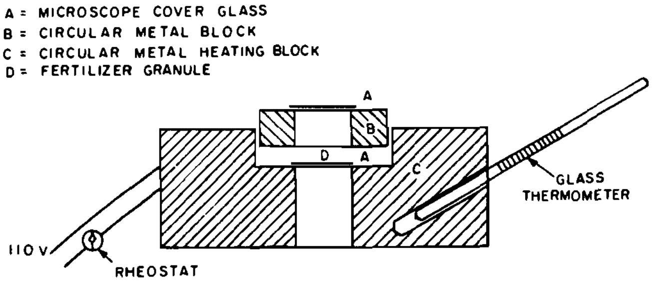


Figure 24. Melting Point Apparatus.

Table 6 shows melting points of several experimental fertilizer products and some pure fertilizer salts that have melting points in a range suitable for prilling or melt granulation.

Physiological Acidity and Basicity of Fertilizers

The use of fertilizers in agriculture often tends to change the pH of the soil. The physiological acidity or basicity of a fertilizer is a measure of the extent to which soil acidity or basicity is changed by the use of that fertilizer on crops. It is also called potential, residual, or equivalent acidity or basicity. Physiological acidity of a given fertilizer is commonly expressed in terms of the weight of calcium carbonate that would offset the effect of the fertilizer acidity on the soil; likewise, physiological basicity is expressed in terms of the weight of calcium carbonate that would have a similar effect on the soil.

The physiological reaction of fertilizer should not be confused with the chemical reaction. For instance, urea hydrolyzes in the soil to ammonia, thus raising the pH of the soil near the urea granule to as high as 9. However, the ammonia is oxidized in the soil under aerobic conditions, first to nitrite, then to nitrate. Most crops take up nitrogen mainly in the form of nitrate which leaves an acidic residue in the soil. Thus, all nitrogen in fertilizers is classed as acid-forming whether initially present in ammoniacal, nitrate, or organic form. However, only one-half of the nitrogen is assumed to be acid forming. This is an empirical factor based on agronomic experiments, which will be described later.

The effect on soil pH of a single year's application of fertilizer at normal rates is small and usually

TABLE 6. MELTING POINTS OF SOME FERTILIZER PRODUCTS

	Nominal Grade	Melting Temperature, °C
Urea-ammonium phosphate	21-42-0	153
Urea-ammonium phosphate	25-37-0	141
Urea-ammonium phosphate	29-29-0	145
Urea-ammonium phosphate	32-22-0	135
Urea-ammonium phosphate	36-18-0	130
Urea-ammonium phosphate	25-15-15	133
Urea-ammonium phosphate	17-27-17	143
Urea-ammonium polyphosphate[a]	22-44-0	123
Urea-ammonium polyphosphate[a]	30-30-0	126
Ammonium polyphosphate[a]	15-60-0	150
Ammonium nitrate	33.5-0-0	167
Urea	46-0-0	136
Ammonium phosphate nitrate	30-10-0	152
Ammonium phosphate nitrate	25-25-0	153
Nitrophosphate	26-13-0	148
Nitrophosphate	20-20-0	152
Sodium nitrate[b]	16-0-0	308
Potassium nitrate[b]	13-44-0	333
Calcium nitrate (tetrahydrate)[b]	12-0-0	43
Sulfur[b]	-	120

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a. Products with 30%-50% of P_2O_5 in the form of polyphosphates.

b. Melting points for pure compounds from Chemical Engineers' Handbook, J. H. Perry, ed., third edition, 1950.

negligible; however, the cumulative effect of many years of application of an acid-forming fertilizer can decrease the soil pH to the point that crop production is seriously impaired unless the acidity is corrected by application of limestone or other basic materials. On the other hand, the use of acid-forming fertilizers on alkaline or calcareous soils may be helpful, although the effect of normal fertilizer applications on soil pH usually is small in a single year. Thus, a quantitative measurement of the acidity or basicity of fertilizers is useful to inform farmers of the magnitude of the probable effect of fertilizer use on soil pH. Also, in some cases, it enables manufacturers to formulate neutral fertilizers, for example, by addition of limestone. Some states of the United States require that fertilizers be labeled "acid-forming" or "nonacid-forming." However, it is usually more economical to apply limestone directly to the soil at intervals of several years, when needed, rather than to incorporate it in compound fertilizers.

Methods for Determining Acidity and Basicity

Quantitative evaluation of acidity or basicity of fertilizers is based on the work of Pierre (100). The main acid- and base-forming elements are:

Acid-Forming Elements	Equivalent Acidity (-) or Basicity (+), kg of $CaCO_3$ per kg of Element
S	-3.12
Cl	-1.41
P	-1.62
N	-1.79
Base-Forming Elements	
Ca	+2.50
Mg	+4.12
Na	+2.18
K	+1.28

In the case of all of the elements except nitrogen and phosphorus, the factors are based on straight stoichiometry. For example, the molecular weight of $CaCO_3$ is 100, and the equivalent weight of sulfur, assuming that it forms sulfate, is 32. Therefore, the equivalent acidity would be 100/32 = 3.125. In the case of monovalent elements, the equivalent weight of the element is twice the atomic weight. For example, the equivalent weight of potassium is 2 times 39.1 = 78.2; the calcium carbonate equivalent is 100/78.2 = 1.28.

In the case of phosphorus, neutral salts are those in which one of the three hydrogen ions of phosphoric acid is neutralized (monocalcium phosphate or monopotassium phosphate, for example). In the case of nitrogen the acidity is based on the empirical factor developed by Pierre (101). Thus, the acidity or basicity of many fertilizers can be calculated from their chemical analysis.

An analytical method was developed by Pierre and later adopted, with some changes, in the United States by the Association of Official Agricultural Chemists (AOAC), particularly for compound fertilizers (100, 102). The procedure consists of determining the total nitrogen content which is multiplied by the factor mentioned above (-1.79) to determine acidity due to nitrogen. In a separate determination, a weighed sample of the fertilizer is mixed with a specified amount of sodium carbonate solution and a reducing agent (carbon black), and the mixture is evaporated to dryness in a beaker and then ignited in a muffle furnace to 575°-600°C. This eliminates nitrogen compounds. The residue is treated with a measured excess of hydrochloric acid and then filtered. Next, the solution is back-titrated with sodium carbonate solution to a pH of 4.3, using a mixed indicator of methyl orange and bromocresol green. The acidity or basicity of fertilizer (other than that due to nitrogen) is calculated by the difference between the titration value as compared with a blank determination. The net acidity is the algebraic sum of the acidity due to nitrogen and that determined in the above procedure.

The AOAC method involves a correction for citrate insoluble P_2O_5 which is assumed to be unaltered phosphate rock (102). The basicity of an amount of tricalcium phosphate equivalent to the citrate insoluble P_2O_5 in the sample is subtracted from the value obtained by the analytical procedure. Thus, the basicity of straight Tennessee phosphate rock (33.8% P_2O_5) as determined by Pierre was plus 56 kg of $CaCO_3$ per 100 kg of rock. A typical value for phosphate rock with the AOAC correction applied is plus 10 (Farm Chemicals Handbook). The correction is based on the assumption that the reaction of phosphate rock in most soils is too slow to have much effect on soil pH. This assumption may not be valid for strongly acid soils and for the more reactive rocks. As mentioned in chapter XII, the liming effect of phosphate rock warrants further study.

Table 7 shows the acidity or basicity of some common fertilizer materials. Values for pure compounds were calculated, and values for most commercial compounds were determined either by Pierre's original method or the AOAC modification (100). Sources of these values are: Farm Chemicals Handbook (1977 edition), Commercial Fertilizer Yearbook (1970 edition), and Sauchelli's Manual on Fertilizer Manufacture (Third Edition, 1963).

TABLE 7. EQUIVALENT ACIDITY OR BASICITY OF SOME FERTILIZER MATERIALS

	Equivalent Acidity (-) or Basicity (+)	
	kg of $CaCO_3$/ kg of N	kg of $CaCO_3$/ 100 kg of Material
Pure Materials[a]		
Ammonia, 82.2% N	-1.8	-148
Urea, 46.6% N	-1.8	-84
Ammonium nitrate, 35.0% N	-1.8	-63
Ammonium sulfate, 21.1% N	-5.3	-112
Ammonium chloride, 26.1% N	-5.3	-139
Monoammonium phosphate, 12.1% N, 61.7% P_2O_5	-5.3	-65
Diammonium phosphate, 21.2% N, 53.8% P_2O_5	-3.5	-74
Monocalcium phosphate, 56.2% P_2O_5	-	0
Dicalcium phosphate, 52.2% P_2O_5	-	+37
Tricalcium phosphate, 45.6% P_2O_5	-	+64
Commercial Products		
Ammonium phosphate-sulfate, 16% N, 20% P_2O_5	-5.3	-85
DAP, 18% N, 46% P_2O_5	-3.5	-64
Sodium nitrate, 16% N	+1.8	+29
Potassium nitrate, 13% N, 46% K_2O	+2.0	+26
Calcium nitrate, 15% N	+1.4	+20
Superphosphate, 16%-48% P_2O_5		approx. 0
Phosphate rock, 33.8% P_2O_5		+56[b]
Bone meal, 34.5% P_2O_5		+61
Potassium chloride (all grades)		0
Potassium sulfate (all grades)		0
Kieserite and other magnesium sulfates		0
Gypsum		0
Calcitic limestones		+80 to +95
Dolomitic limestones		+90 to +100
Borax		+55
Calcium metasilicate, 48% CaO		+86[a]
Fused calcium magnesium phosphate, 20.2% P_2O_5, 32.1% CaO, 19.4% MgO		+91[a]
Rhenania phosphate, 28.0% P_2O_5, 40.2% CaO, 16.8% Na_2O		+79[a]
Sulfur, 100% S		-312[a]
Pyrites, 50% S		-156[a]

a. Calculated from analysis.

b. The value given for phosphate rock is that obtained experimentally by Pierre using the analytical procedure outlined previously. The effect of phosphate rock in neutralizing soil acidity is slow except on strongly acid soils, and it has practically no effect on neutral or alkaline soils. In the AOAC method the basicity of the citrate-insoluble fraction of the rock, calculated as tricalcium phosphate, is subtracted from the value found by analysis.

Table 7 shows that ammonium sulfate, chloride, and phosphate are more strongly acid forming per unit of nitrogen since the acidity due to nitrogen is augmented by the acidic anion. Ammonia, urea, and ammonium nitrate are intermediate; their acidity is only that due to their nitrogen content. Sodium, potassium, and calcium nitrates are basic since the acidity due to the nitrogen is more than offset by the basicity of the cation.

Some Limitations of Acidity-Basicity Ratings

Pierre described in detail his experiments on the effect of nitrogen fertilizers on soil acidity (101). The experiments were conducted mainly with Cecil clay loam (an Alabama soil with an initial pH of about 6) in greenhouse tests with a series of four crops. The conclusion that nitrogen in fertilizers is acid forming to the extent of one-half of the stoichometric equivalent amount of nitric acid is an empirical one and may not hold for all soils and crops. For instance, in rice culture in flooded soils, ammoniacal nitrogen placed in the anaerobic soil zone is not nitrified and is taken up in the ammoniacal form by the rice plant, presumably without increase of soil acidity. Also, the amount of nitrogen lost by leaching, runoff, volatilization, and decomposition is subject to wide variations and presumably would have some effect on the extent of the development of soil acidity.

In Pierre's greenhouse experiments there was no leaching. However, determination of soil acidity was made both on washed and unwashed soil. The results with washed soil were used as a basis for the ratings given in table 7 since they were considered more representative of field conditions where the amount of rainfall is sufficient to leach soluble materials into the subsoil, and, in fact, these determinations did agree well with some field experiments. The effect on acidity was much greater with unwashed soil, particularly for ammonium salts such as ammonium sulfate. In the case of arid climates where the amount of rainfall or irrigation is insufficient to remove soluble fertilizer residues from the soil, it seems possible that the effect of both nitrogen and other fertilizers on soil acidity might be quite different.

Pierre also noted that the effect on soil pH depended strongly on the base exchange capacity of the soil although the rating in terms of calcium carbonate equivalent was about the same.

Thus, while the results of Pierre's study have correlated well with field tests in the eastern part of the United States and in England, their application to other climates, soils, and agricultural systems may not be quantitatively exact.

Salt Index

It is well known that a high concentration of soluble salts in soil solutions can cause injury or death to plants or prevent germination of seeds. The extent of injury is believed to be related to the osmotic pressure of the soil solution.

Under normal conditions, uniformly distributed fertilizers at the usual application rate will not cause concentrations high enough to damage plants. However, localized application in contact with the seed or in bands near the seed or near growing plants may cause damage, depending on the placement, rate of application, and supply of soil moisture.

The salt index of fertilizer salts and compound fertilizers is an index of the extent to which a given amount of various fertilizers increases the osmotic pressure of soil solution. The index was developed by Rader, et al., of the U.S. Department of Agriculture (103). The index is useful in selecting or formulating fertilizers for special placements (combine drilling, band placement, "pop-up," side dressing, etc.). It may also be of interest in soils where the salt concentration is already high or in areas subject to drought when the soil solution becomes more concentrated because of dry conditions. The osmotic pressure of fertilizer solutions for foliar application is also of interest, but in this case the solution is not in contact with the soil. Therefore, the "salt index," as determined by Rader, is not quantitatively useful for determining the suitability of a solution for foliar application. Direct measurement of osmotic pressure of water solutions would be more suitable for this purpose.

Method of Determination

In Rader's studies, several soils and several rates of application were used. However, for determination of the salt index, a single soil (Norfolk sand) having a specified moisture content was used, and the fertilizers to be tested usually were applied at a single rate. It was demonstrated that the increase in osmotic pressure was proportional to the application rate; therefore, measurements made at one rate could be converted to another by a simple calculation.

In brief, the method consisted of mixing the air-dried soil with the fertilizer or salt to be tested, usually in the proportion of 1 part by weight of fertilizer material to 1,000 parts by weight of soil. The soil was then sprayed with water to moisten it to 75% of its field capacity moisture equivalent (5.1% in the case of Norfolk sand) after which it was stored in a closed container for 5 days at about 5°C. After 5 days the soil was allowed to return to room temperature and was then packed in a cylinder. The soil solution was then displaced from the soil. Determinations of conductivity and freezing points were made on the soil solutions. The osmotic pressure was calculated from the depression of the freezing point. The increase in osmotic pressure was obtained by subtracting the osmotic pressure of solution from untreated soil. The salt index was expressed as the relative increase in osmotic pressure as compared with that obtained with the same weight of sodium nitrate. Table 8 shows the results obtained with common fertilizer materials, as reported by Hardesty (104). Hardesty has also shown how the salt index of compound fertilizers can be calculated from their formulation (104).

TABLE 8. SALT INDEXES OF SOME FERTILIZER MATERIALS

Materials and Analysis	Salt Index--Basis: Sodium Nitrate = 100 Per Equal Weights of Materials	Per Equal Weights of Primary Plant Nutrients[a]
Nitrogen		
Ammonia, 82.2% N	47.1	9.5
Ammonium nitrate, 35.0% N	104.7	49.4
Ammonium sulfate, 21.2% N	69.0	53.7
Ammonium nitrate--limestone, 20.5% N	61.1	49.2
Calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$, 11.9% N	52.5	76.8
Calcium cyanamide, 21.0% N	31.0	24.4
Sodium nitrate, 16.5% N	100.0	100.0
Urea, 46.6% N	75.4	26.7
Nitrate of soda potash, 15.0% N, 14.0% K_2O	92.0[b]	52.3
Urea-ammonium nitrate solution, 32% N	74.2[b]	38.3
Phosphate		
Normal superphosphate, 20% P_2O_5	7.8	6.4
Concentrated superphosphate, 45% P_2O_5	10.1	3.7
Concentrated superphosphate, 48% P_2O_5	10.1	3.5
Monoammonium phosphate, 12.2% N, 61.7% P_2O_5	29.9	6.7
Diammonium phosphate, 21.2% N, 53.8% P_2O_5	34.2	7.5

(Continued)

TABLE 8. SALT INDEXES OF SOME FERTILIZER MATERIALS (CONTINUED)

Materials and Analysis	Salt Index--Basis: Sodium Nitrate = 100 Per Equal Weights of Materials	Per Equal Weights of Primary Plant Nutrients[a]
Potash		
Potassium chloride, 60% K_2O	116.3	32.0
Potassium chloride, 63.2% K_2O	114.3	29.8
Potassium nitrate, 13.8% N, 46.6% K_2O	73.6	20.1
Potassium sulfate, 54% K_2O	46.1	14.1
Monopotassium phosphate, 52.2% P_2O_5, 34.6% K_2O	8.4	1.6
Manure salts, 20% K_2O	112.7	93.0
Manure salts, 30% K_2O	91.9	50.6
Sulfate of potash-magnesia, 21.9% K_2O (langbeinite)	43.2	32.5
Miscellaneous		
Dolomite, 20% MgO	0.8	-
Magnesium oxide, 100% MgO	1.7	-
Gypsum, 32.6% CaO	8.1	-
Calcium carbonate, 56.0% CaO	4.7	-
Calcined kieserite, 33.5% MgO	38.7	-
Epsom salts, 16.4% MgO	44.0	-

a. Based on plant nutrients shown in column 1.
b. Calculated.

Significance of Results

The osmotic pressure was always lower in soil solution than when the same amount of salt was dissolved in the same amount of water in the absence of soil. This was particularly true of phosphates and is probably related to reactions of phosphates with soils that remove some of the soluble materials from solution. Table 9 shows osmotic pressures of water solutions of a few fertilizer salts as compared with soil solutions for two soils treated with the same salts. The data also show the large difference in osmotic pressure of soil solution for different soils, which is largely due to the difference in moisture-retention capacity of the soils. Each soil was moistened to 75% of its moisture equivalent which was 5.1% for Norfolk sand and 21.9% for Hartsells silt loam.

TABLE 9. OSMOTIC PRESSURE INCREASES IN SOIL SOLUTION COMPARED WITH SOLUTIONS OF SALTS IN WATER ALONE

Salt Applied[a]	Osmotic Pressure, Atm Norfolk Sand Soil Solution[b]	 Norfolk Sand Water Alone[c]	 Hartselle Silt Loam Soil Solution[b]	 Hartselle Silt Loam Water Alone[c]
$(NH_4)_2SO_4$	8.14	10.38	1.71	2.89
$NaNO_3$	11.92	12.38	2.68	3.16
KCl	13.49	14.39	2.79	3.54
$NH_4H_2PO_4$	4.04	9.21	0.30	2.54
$Ca(H_2PO_4)_2.H_2O$	1.82	5.28	0.19	1.44
$NaH_2PO_4.H_2O$	4.27	8.81	0.52	2.18

a. Applied at the rate of 1 kg per 1,000 kg of soil.
b. The Norfolk sand contained 5.1% moisture, and the Hartselle silt loam contained 21.9%. These moisture levels corresponded to 75% of field capacity for each soil.
c. The amount of water used in the "water alone" experiments was equal to that present in the tests with soils.

Usefulness of the Salt Index

It is emphasized that salt index values are useful only for comparison of one fertilizer with another; the amount of fertilizer that may be safely applied depends on the placement, type of soil, moisture conditions, and crop as well as the salt index. In addition, injury to crops can be caused by effects other than salt concentration. For instance, ammonia released from urea or diammonium phosphate in the soil adjacent to seedlings may have a phytotoxic effect. In case of soils already high in chloride, the addition of chloride (KCl, for example) may cause an adverse effect due to excessive chlorides.

The salt index is particularly useful in selecting fertilizers to be applied with or very near the seed. This placement often results in high agronomic efficiency, provided the amount and kind of fertilizer used does not cause injury due to salt concentration. Thus, selection of a fertilizer with a low salt index per unit of nutrient is best for this purpose.

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PART FIVE

PLANNING AND ECONOMICS

XXIII Pollution Control and Other Environmental Factors

Introduction

In the present chapter, pollution control aspects of fertilizer plants are described. In 1974 UNIDO, responding to numerous requests, held an expert group meeting in Helsinki on "Minimizing Pollution from Fertilizer Plants." A report (Document ID/140) summarized the conclusions and recommendations of the meeting. More recently, following the Lima Declaration and Plan of Action on Industrial Development and Cooperation at the Second General Conference of UNIDO, a series of consultations on the development of the fertilizer industry were held in Vienna. The request to summarize the pollution control aspects of fertilizer plants and guide the developing countries to protect their environment was repeated at the First Consultation Meeting on Fertilizer Industry held in January 1977.

UNIDO responded to these requests by preparing monograph No. 9 of the Fertilizer Industry Series, titled "Guide to Pollution Control in Fertilizer Plants." The present chapter is drawn mainly from that publication. It summarizes the guidelines without going into case histories or details for solving pollution control problems associated with the fertilizer industry.

Pollution control standards are not uniform from one country to another, and there is seldom any agreement within any country as to whether standards that have been set are too lax or too stringent. Therefore, description of standards that have been set up in individual countries does not constitute a recommendation for universal use. In setting up standards, due consideration should be given to the cost: benefit ratio and the particular circumstances which apply to each project.

In general, standards should be set to achieve the following purposes:

1. Protect the health of workers in the plant and of the people in the community by avoiding harmful concentrations of known pollutants in the atmosphere in and surrounding the plants.
2. Avoid damage to crops and other vegetation.
3. Prevent deterioration of the quality of water in streams, lakes, estuaries, or harbors and protect other industries and people who use the water.
4. Maintain aesthetic values that are essential to pleasant surroundings and to the attraction of tourists.

When establishing itself, the fertilizer industry in any of these countries must make sure to safeguard the environment and be a "good neighbor."

In the past in both developed and developing countries, damaging errors have been made during the establishment of fertilizer production facilities. Human lives have been lost; vegetation has been killed together with marine and fresh water fauna. It is to avoid a repetition of these mistakes that the environmental considerations for the fertilizer industry are summarized for future guidance.

This chapter first outlines the main types of chemical gaseous and liquid or aqueous effluents that originate in fertilizer plants. In many cases when corrective steps are taken to reduce or completely eliminate the gaseous effluents by scrubbing, aqueous effluents are produced with varying concentrations of the contaminants. Unless economical recovery is available to recycle these effluents in the process stream, steps have to be taken to neutralize their impact on public receiving waters. This study, therefore, gives an account of the measures taken at the production facilities of nitrogenous and phosphate fertilizer industries to prevent or minimize their impact on the environment. The disposal of gypsum and other solids, such as those from potash processing plants, is also briefly described.

The site selection criteria for a new grassroots plant and a guide to engineering contractors' specification to enable effective in-plant control of effluents are summarized. A description of appropriate surveys to measure the environmental impact of fertilizer plants is included to guide policymakers and investors in establishing a new industry.

Gaseous Effluents

Most of the processes used for the manufacture of fertilizers discharge gaseous effluents. By far the largest source of these is the combustion of fossil fuels used in the manufacture of ammonia in some countries of the world. However, combustion gases do not pose a pollution problem unless they contain excessive amounts of impurities or particulates. Other effluents from process streams include oxides of sulfur, oxides of nitrogen, and compounds of fluorine for which there is insufficient economic and political incentive for further processing and recovery. The resulting air pollution can have serious effects on human health and on animal and plant life. However, this is predominantly a local problem which can be solved by industry.

Ammonia

When gaseous ammonia is discharged from an operating plant, it is more likely due to some spills from faulty equipment or an operating problem. Because of its alkaline properties, high concentrations of ammonia will affect the mucous membranes of the nose, throat, and eyes, as well as attack the skin. The odor threshold concentration is between 18-35 mg/m^3. Exhaust gases containing ammonia are normally scrubbed, and the resulting scrubber liquors are recycled to the process or discharged to the plant sewers. In some cases, it may be necessary to treat the scrubber liquor to remove ammonia before discharge, as discussed later under liquid effluents. If vented to the atmosphere, gaseous effluents containing ammonia can form smog if they are allowed to combine with acidic gaseous effluents vented from other fertilizer processes located in the same complex.

Ammonia is also likely to occur in effluents from downstream processing plants that produce urea, ammonium nitrate, ammonium phosphate, and compound fertilizers. If present in significant amounts it is usually recovered by scrubbing with water or acidic liquors and recycled.

Nitrogen Oxides

Oxides of nitrogen are discharged from ammonia oxidation processes, such as nitric acid plants or ammonium nitrate and NPK plants, using the nitrophosphate route. The oxides (NO_x) are mostly NO, NO_2, or N_2O_4; the latter is the unstable byproduct of oxidation. Both NO and NO_2 can be harmful to people, plants, and animals and can produce smog by photochemical reaction in the atmosphere.

The toxic action of nitrogen oxides causes an irritation of the respiratory tract and can, in mild forms of poisoning, cause vomiting and inhibit the bloodstream in carrying oxygen. The exposure threshold limit value (TLV) for nitrogen oxides (as nitrogen dioxide) is the concentration of 9 mg/m^3. At this concentration exposure for 8 hours/day over a 5-day working week can be tolerated without adverse effects. Damage to certain vegetation can occur after 1 hour of exposure to 1 mg/m^3. The exact value, of course, is dependent on humidity, species, and other ambient conditions (1).

The vented tail gas from nitric acid plants consisting of both NO and NO_2 (calculated as NO_2) spreads pollution from fertilizer plants to the surrounding areas. Technology to reduce tail-gas emission rates in various degrees is available to meet the various emission standards proposed or adopted by several industrialized countries. Both the investment and operating costs of these control processes are increasing as lower emission standards are being enforced in some developed countries. The following table illustrates emission standards for nitric acid plants (2):

Country	Emission Rate kg of NO_2/ton of Product (100% Acid)	mg/m^3 of Tail Gas[a]
United States	1.5	450
France	3.3	1,000
Federal Republic of Germany (according to type of plant)	N.D.	1,000-1,600
United Kingdom (as NO_x) (colorless plume)	N.D.	2,000

a. Volume calculated for "normal" conditions, 0°C and 1 atm pressure (1 mg/m^3 of NO_2 = about 0.48 ppm by volume).

In nitric acid plants having no air pollution abatement systems, the concentration of nitrogen oxides in the tail gas can be as high as 6,000 mg/m^3. Numerous methods have been developed and are in use for removing nitrogen oxides from the tail gas. These methods include catalytic reduction by hydrogen, ammonia, or methane; absorption with molecular sieves; scrubbing with urea solution or alkaline materials; and extended absorption. The latter method, which in effect increases the recovery of nitric acid by additional absorption capacity, seems to be gaining favor in most countries.

Nitrogen oxides are also evolved in the treatment of phosphate rock with nitric acid to produce nitrophosphate fertilizers and may require scrubbing to prevent atmospheric pollution.

Sulfur Oxides and Sulfuric Acid Mist

The main source of sulfur dioxide or trioxide as a gaseous effluent from fertilizer plants originates in the captive sulfuric acid plants associated with the manufacture of phosphoric acid. Most phosphate fertilizer complexes have one or more captive sulfuric acid plants. Practically all modern sulfuric acid plants use the contact acid process. Sulfur is burned and the gases containing SO_2 are passed over a catalyst (see chapter X11). The hot gases of sulfur trioxide are subsequently absorbed in absorption towers to form 98^+% sulfuric acid, H_2SO_4. Sulfuric acid plants, particularly since the advent of larger plants, are known to have caused widespread damage to vegetation and to have caused serious pollution problems in areas near production plants, thus resulting in complaints from the public.

Airborne effluents from absorption tower stacks often contain acid droplets of 100 μm down to well below 1 μm which become difficult to remove. These droplets form a mist even after passing through the drying tower of a plant in which sulfuric acid is circulated to reduce the residual water vapor to give an H_2SO_4 mist level above normally acceptable stack exit levels (3).

At first, "wire-mesh" entrainment separator pads were installed in drying towers. Later fiber mist eliminators and "Brink" eliminators using low gas velocities (5-10 m/min) were used to remove all particles above 9 μm and 99% of those of smaller size. Electrostatic precipitators requiring relatively high capital investment cost but lower energy input have also provided an efficient way to eliminate this source of pollution.

To reduce sulfur dioxide emission from sulfuric acid plants, recently double catalytic conversion and double absorption systems have been used (see chapter XII). Alternatively, scrubbing systems are widely used in some countries to remove SO_2 from tail gas. The tail gases can be scrubbed with a solution or slurry of an alkali (lime, soda ash, or ammonia). For example, scrubbing with ammonia solution yields ammonium sulfite-bisulfite. This solution, when acidulated with sulfuric acid, releases SO_2 which, in turn, can be recycled to the sulfuric acid process, leaving the ammonium sulfate solution as a fertilizer material for conversion to fertilizer production.

Concentrations of sulfur dioxide in excess of 27 mg/m^3 are known to be a strong irritant, and the maximum safe concentration for industrial hygiene exposure generally is considered to be half this value. Concentrations of measured urban or city smog seldom exceed 3 mg/m^3 of SO_2 and generally are associated with smoke from power-plant stacks (1).

Plant life, particularly the more sensitive species, can be damaged by a single exposure concentration of 0.4 mg/m^3. Continuous exposure can affect certain plants at even lower concentrations. The U.S. Environmental Protection Agency (EPA) has proposed the following National Ambient Air Quality Standards for limiting sulfur dioxide concentration in ambient air (4).

Sulfur Dioxides	Primary[a] (μg/m^3)	Secondary[b] (μg/m^3)
Annual arithmetical mean	80 (0.03 ppm)	
Maximum 24-hour concentration[c]	365 (0.14 ppm)	
Maximum 3-hour exposure		1,300 (0.5 ppm)

a. Primary standard for public health protection.
b. Secondary standard for protection of public welfare.
c. Not to be exceeded more than once per year.

Monitored airborne sulfur dioxide emitted by industry is known to have traveled over distances of 1,000 km or more, under certain weather conditions, before reaching ground level. Emission standards for sulfuric acid plants now call for (2):

United States	A maximum of 2.0 kg SO_2/ton[a] of product 0.075 kg acid mist/ton[a] of product (10% opacity)
Federal Republic of Germany	A minimum of SO_2 conversion efficiency of 99.5% A maximum of 0.4 kg SO_3/ton[a] of product
United Kingdom	An overall conversion efficiency of 99.5% No acid mist

a. Metric tons.

In fertilizer plants that burn high-sulfur coal or fuel oil for generation of process steam or electricity, sulfur oxides in the flue gases may exceed permissible discharge levels. In some countries, dispersal through tall stacks may be an acceptable way of controlling ambient concentration. In other cases, scrubbing the flue gas to remove most of the sulfur oxides may be necessary. Several scrubbing processes are available that use lime, limestone, sodium carbonate, or ammonia as the scrubbing medium.

Gaseous Fluorides

In the manufacture of phosphate fertilizers, various fluorides are released in processing the phosphate rock. Gaseous fluorides are considered among the most hazardous pollutants.

Phosphate rock usually contains between 3% to 4.5% of fluorine by weight. In processing this rock to produce phosphoric acid, large quantities of fluorides are released in the acidulation reactors, in the acid concentration plants, and in production of superphosphates. The fluorine in vent gases from the reaction system of a wet-process phosphoric acid plant is mainly in the form of silicon tetrafluoride (SiF_4), since the highly reactive fluorine combines immediately with the available silica contained in the reaction slurry. However, when the rock has a low silica content, hydrogen fluoride (HF) may also be present.

The reactor fluorides are usually scrubbed with water or dilute concentrations of fluosilicic acid. The SiF_4 rapidly hydrolyzes to fluosilicic acid. There is sufficient information available today from standard phosphoric acid plants to make a fluorine material balance for the battery-limits production facilities. Various wet-scrubbing equipment is available. Some of this equipment provides for the recovery and concentration of fluosilicic acid up to and above 20% concentration, a saleable product that can be used for the production of synthetic cryolite, aluminum fluoride, and various fluosilicates. If there is no market for these byproducts, the scrubber effluents have to be neutralized with limestone or lime, generally in two stages, to permit discharge into public waters. Multistage liming has proven to be costly in terms of operational expense.

Gaseous fluorine compounds are also evolved in the production of nitrophosphates and single or triple superphosphates and are controlled by scrubbing. Superphosphates in storage buildings continue to evolve fluorine gases which may cause a health hazard to workers. In some cases, ventilation of the storage building may be a satisfactory solution, but in some countries, removal of the fluorine from the air exhausted from the building may be required. Another source of atmospheric pollution by fluorine gases may be evaporation from gypsum ponds or acidic scrubber liquor ponds. This source has not been fully evaluated.

Atmospheric fluoride damage to vegetation and animals is much more widespread than it is to man. The first sign of chronic fluorosis in man is mottling of the teeth and later ossification of the ligaments. Exposure of workers to fluorides in industry has caused an accumulative effect. Urinalysis of plant operators is usually recommended at regular intervals. Most plants are able to maintain an atmosphere where fluoride concentration is below 10 mg/m^3. Some artificial cryolite plants have measured fluoride concentration up to 30-40 mg/m^3. Threshold limit value (TLV) of industrial exposure to hydrogen fluoride for daily intake has been calculated at 5-6 mg/m^3 (5). The basis was hydrogen fluoride or other fluorides in gaseous form. Most plant workers have other inputs of fluorides, such as drinking water and food. To provide a reasonable margin of safety, 2 mg/day of fluorides ingested from the air has been recommended as the maximum (1).

Vegetation is more sensitive to exposure than animals or human beings are. Fluoride concentrations as low as 0.015-0.04 mg/m^3 will damage gladioli and some pine and fruit trees. If adequate monitoring instruments are not available, industrial sites should use garden plots to assess the pollution by fluorides of areas in and surrounding the plant (1).

Animals, such as cattle, are known to be affected by concentrations of fluoride in excess of 30 mg/m^3. Here again, they have other intakes of fluoride such as that from phosphate dust settling down on foliage and fodder. Cattle can extract the fluorine from particulate phosphate and contract osteosclerosis.

Mist, Fumes, and Dust

Pollution in mist and fumes originating in sulfuric acid plants has already been discussed. Fertilizer plants producing mixed granular NPK, MAP, or DAP fertilizers from feedstocks of phosphate rock, phosphoric acid, and/or ammonia, nitric acid, and sulfuric acid produce gaseous effluents containing particulate matter mixed with vent gases from their reactors. Prilling towers for ammonium nitrate and urea have increasingly caused concern in areas surrounding the manufacturing facilities.

In fertilizer plants manufacturing single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP), and diammonium phosphate (DAP), as well as NPK, all solid materials handling equipment, including screens, is normally exhausted by induced air. If it is dry the fine dust can be collected by a duct system and passed through bag filter equipment which will eliminate 99% of the particulate matter. More difficult is the control of particulate matter or dust from granulators, dryers, and coolers in which the moisture and the temperature of the gas and its particulates vary. To reduce the discharge from these sources, high-efficiency cyclones are normally installed which remove most of the larger particles. To prevent condensation of the wet gas upon cooling, the cyclones must be insulated and, in many cases, the equipment is heated externally to maintain the gas temperature above dew point. Most of these particulate materials are recovered and returned to the various process systems of the plant. The use of wet scrubbers is increasing in granulation plants. The scrubber liquor is recycled to build up its concentration and then returned to the granulator. When the gas being scrubbed contains ammonia, phosphoric or sulfuric acid is added to the scrubber liquor to maintain a near-neutral pH. Feedstock-handling bins such as for phosphate rock, potash, etc., can be equipped with individual bag filters to return the pure raw material to its own storage bin.

For those NPK plants that have their own reaction systems, such as most nitrophosphate plants, the fumes vented from the processes are usually scrubbed and concentrated in order to return them as a dilute slurry to the "wet section" of the reaction system.

The dust and fumes from prilling processes have presented a major problem in recent years. The volume of air or gas involved is usually very large. Very recently, after considerable research and pilot-plant testing, suitable fume abatement systems have been developed (1, 4, 6).

Ammonium Nitrate

Emissions from ammonium nitrate plants originate from three main sources--neutralization, evaporation, and the prill tower. Fumes from the neutralization and evaporation processes are normally scrubbed in wet scrubbers; their volume is relatively small. The concentration is increased by adding the fines separated by screens. Blowdown from the recirculating scrubbing solution is returned to the system. Most of the particles from the prill tower are less than 1 µm in size. Knowing the prill surface temperature and the dissociation pressure of ammonia and nitric acid, we can calculate the rates at which the ammonia and acid will diffuse into the air and thereby determine the minimum potential amount of fume formed in the prilling towers (normally 0.25 kg/ton of prilled AN). Recent developments point to technology incorporating a duct collection system in series with a "Brink" filter system in which actual emission rates were reduced to meet the regulations for mass emission and opacity of less than 0.5 kg/ton (6).

Urea

The major air pollution concern in a urea plant is urea dust in the exhaust of the prilling towers. From a 1,000-tpd urea plant between 400,000-500,000 m^3/hr of hot air is vented to the atmosphere. Dust-removal systems using wet scrubbing are well known to have reduced the dust content from an average of 500-1,000 mg/m^3 from the tower exit down to 200-300 mg/m^3. These impinger-type baffle-plate devices are easily applied to the natural draft prilling towers. The urea dust particles are very small (less than 10 µm); therefore, dry cyclones are not effective for high-efficiency removal. Improved dust-removal systems developed more recently reduce the urea dust content to less than 30 mg/m^3 or 0.3 kg/ton of product in the vent gases from the prill tower (4).

Discharge limits of particulate matter vary among the developed countries and within industrial districts of a single country. In the Ruhr area of the Federal Republic of Germany, 100 mg/m^3 from vent stacks between 90-100 m high was the specified maximum limit until quite recently.

Recently, several new ammonium nitrate and urea plants have used granulation rather than prilling. The main purpose was to improve the size and strength of the product, but less difficulty in controlling fume and dust is also an advantage. Wet scrubbers or bag filters provide adequate dust control (7).

In most cases it is realized that older plants will face problems in meeting some of the new regulations. In all cases, however, it is emphasized that construction permits to build new plants will only be granted if the designers guarantee that the plant will perform as designed and that the gaseous effluents will meet the applicable local standards. It is recommended that in developing countries where such local standards have, in many cases, not been adopted, the guidelines given in this chapter be used when new fertilizer plants are planned.

Liquid Effluents

Aqueous or liquid effluents from fertilizer plants are usually of smaller volume compared to those that are vented to the atmosphere. Naturally, if pollution abatement systems adopt wet-scrubbing systems to reduce air pollution, the contaminants which are eliminated from the gases remain and are concentrated in the solutions or scrubbing liquor. Unless these contaminants are concentrated or transformed into a recovery for the process or a saleable byproduct, they present a disposal problem as liquid waste. For this reason, each case has to be examined in its own environment, not losing sight of its socioeconomic aspects, before the best practical methods are adopted for elimination of a contaminant. In other words, the most economical method is not necessarily the best one to solve a problem in a fertilizer plant in the long run. However, the method which minimizes total societal costs and maximizes total benefits is a desirable one at any time.

Nitrogen Fertilizers and Intermediates

Ammonia--Liquid effluents from an ammonia plant may contain ammonia from various sources such as condensation of excess steam used in the reformer. The presence of ammonia in waste water streams is undesirable because it increases the biological oxygen demand (BOD).

In some plants in the United States, this effluent is raised to a pH higher than 10 and then stripped with steam in a tower. This, of course, can only be done in an area where the air pollution created by the vent gases is considered less significant. The process involves stripping the condensates containing ammonia with steam which removes volatile ammonia and carbon dioxide. Stripped water is then passed to an ion exchanger where heavy metal ions can be replaced by ammonium ions. The water purified in this manner is suitable for boiler feedwater. Steam stripping can reduce the ammonia (N) content to a nominal level of 20-25 g/m^3 (perhaps as low as 10-15 g/m^3), but a nitrogen level of about 40 g/m^3 is more common. At elevated pressure (5 atm) cationic resins to keep the carbon dioxide in solution have also been used for cleanup of condensate waters--the resin can be regenerated with acid to produce an ammonium salt which is returned to the fertilizer process stream.

In ammonia plants where methylamines (MEA) are used for removal of carbon dioxide, condensates usually contain organic impurities. Even so, the use of the ion-exchange resin treatment was investigated. The cationic-exchange resin was regenerated with dilute sulfuric acid--the ammonium sulfate formed was returned to the process stream. The concentration of ammonia leaving as an aqueous effluent is subject to legal restrictions in many countries. Aqueous ammonia, as well as MEA, is harmful to fish life and can remove fish scales by destroying the mucous protective layers. In the United Kingdom a limitation of 10 g/m^3 of ammoniacal nitrogen has been applied on occasion (2). A number of states in the United States have set a limitation of 1.5-2.5 g/m^3. Ammonia plants using feedstocks and processes other than natural gas or naphtha are likely to produce condensates containing organic substances. Their effluent will have a biological oxygen demand (BOD), as well as a chemical oxygen demand (COD). These effluents have to be collected and treated according to the BOD, or COD load in an activated sludge or similar treatment plant before discharge to a public receiving water. The removal of ammonia by biological processes is achieved by first oxidizing it to nitrate and then denitrifying it (by the addition of methyl alcohol as a source of carbon) to nitrogen gas. Some plants dispose of waste water containing ammonia by using it in the irrigation of crops such as bermuda grass. The liquid effluents from the manufacture of urea contain ammonia, carbon dioxide, ammonium carbonate, and urea. These waste liquids stem from the process of urea solution concentration where, by flash evaporation, the pressure is reduced, producing a condensate. In some processes, pump-seal leakage contributes ammoniacal waste water to the process effluent.

The major decomposition products of urea are ammonia and carbon dioxide. They can be returned to the process or stripped to the atmosphere. According to the U.S. EPA guidelines, effluents from plants not prilling urea may contain up to 0.075 kg (maximum daily value) and 0.0375 kg (average of 30 days) of organic nitrogen per metric ton of urea product (4).

Urea plant designers have designed a system of wet scrubbing for prilling towers using forced draft. While this process supposedly reduces the urea content in the vent gas to 6-12 mg/m^3, an aqueous waste water is produced which has to be recycled to the vacuum concentrator and concentrated in order to recover urea. From a 1,000-tpd plant vacuum system, liquid condensate effluent containing 1,000-2,000 g/m^3 of urea and up to 50,000 g/m^3 of ammonia is produced at the rate of 20-25 m^3/hr. Ecological problems created by this continuous effluent range from ammonia toxicity, on the one hand, to eutrophication of receiving water from both ammonia and urea as nutrients stimulating the algae growth. The preferred treatment is hydrolysis followed by distillation from which the treated condensates or tail discharge of the distillation unit emerge at 50 mg of ammonia and 200 mg of urea per liter of solution which is recycled to the process (8).

Ammonium Nitrate (Including Nitric Acid)--Facilities for the manufacture of ammonium nitrate normally include a captive plant for nitric acid at the same site. Nitric acid plants do not have any continuous aqueous effluents. The nitric acid plant uses large amounts of cooling water for its heat exchanger equipment--contamination from cooling water discharge is dealt with later. Intermittent acidic discharges from pumps and equipment can be collected in a floor sump and neutralized before discharge.

The manufacture of ammonium nitrate entails the neutralization of the nitric acid with ammonia. This process is normally controlled by pH, and the reaction is exothermic. The vapors discharged from the ammonium nitrate solution carry ammonium nitrate and water vapors which, upon condensation, result in polluting effluent. The fumes are normally scrubbed in a wet scrubber. The scrubber solution is too dilute for economic recovery; however, its concentration can be increased by adding screened fines and dust collected from the prilling plant section and returned batchwise by pumping it to the neutralizer. Alternatively, after ion-exchange treatment the scrubber solutions can be recycled to the cooling tower.

Ammonium Sulfate--Ammonium sulfate is manufactured by neutralizing sulfuric acid with ammonia. It is an exothermic reaction from which the vapors are usually scrubbed and in a once-through system contain 10-100 mg/m^3 of ammonia which can be sewered (except in the United States); however, the scrubbing liquors can be recirculated and gain enough in concentration to be eventually returned to the process. With the demand for high-analysis N fertilizers, the ammonium sulfate market was greatly depressed in developed countries. This is not the case for developing countries, especially those engaged in the cultivation of rice.

Phosphate Fertilizers

Phosphate fertilizers marketed can be classified in two major categories--those which contain only phosphates by processing phosphate rock to increase the soluble P_2O_5 concentration, such as single superphosphate (16%-22% P_2O_5), or those using phosphoric acid in the manufacture of triple superphosphate (40%-49% P_2O_5). The manufacture of the former normally entails a sulfuric acid plant while the latter entails both a sulfuric acid and a phosphoric acid plant, usually as captive acid plants. Mixed phosphate fertilizer plants will manufacture various NP or NPK formulations, including MAP and DAP, by ammoniation of phosphoric acid or alternatively using one of the nitrophosphate routes where the rock is acidulated with nitric acid and ammonia and/or potash is added later in reaction systems.

Phosphoric Acid--The majority of the phosphoric acid today is manufactured by use of the "wet process" in which phosphate rock is reacted with sulfuric acid in a reactor. Since this is an exothermic reaction, the classical processes employ a vacuum cooler to maintain a controlled temperature of 80°C. These coolers normally operate by using a barometric condenser system producing a liquid effluent containing P_2O_5 and fluorine in the form of fluosilicic acid. Effluents containing fluorine and P_2O_5 are also obtained from the reactor scrubbing system, the gypsum filter vacuum pumps, and the phosphoric acid concentration or evaporation system. In some plants these effluents, together with slurried gypsum, are discharged to a lagoon or pond from which the clarified acidic liquors are recycled to the plant for cooling or scrubber water. Many plants recover fluosilicic acid for sale from the more concentrated streams (usually from acid concentration).

Plants located in industrial areas or where land is not available cannot use the pond method of disposal and are forced to neutralize the effluents with lime in two steps. The latter also applies to any effluent that overflows from ponds.

Sulfuric Acid--Captive sulfuric acid plants for the manufacture of fertilizers are part of a complex in which phosphoric acid or ammonium sulfate is manufactured. Aqueous effluents from the sulfuric acid plant can originate from spills, leaking pumps, or flanges. There should be no continuous discharge of acidic effluent from a well-operated and maintained sulfuric acid plant either as effluents or in the cooling water discharged.

Single and Triple Superphosphate--Aqueous effluents from single and triple superphosphate plants originate from gas scrubbers that are installed for the materials handling equipment and dens. The vent gases containing silicon tetrafluoride and phosphate dust are scrubbed with water or solutions of fluosilicic acid. If the fluosilicic acid cannot be marketed because of the relatively high P_2O_5 content which could make it unsuitable for processing into saleable products, the liquid effluents are treated with lime, yielding impure calcium fluoride as a byproduct. In the hydrolysis of silicon tetrafluoride (SiF_4) to fluosilicic acid (H_2SiF_6), silica (SiO_2) is formed as a byproduct. The silica generally deposits itself on the equipment and associated piping which could cause the system to be plugged if regular maintenance is not performed. Solution concentrations from 15% to 25% fluosilicic acid have been produced in multistage gas-scrubbing systems (4). These solutions are then sold for further processing. Gas scrubbing using cyclonic or floating bed systems has been used in connection with green triple superphosphate curing dens from which large volumes of gases containing relatively small concentrations of silicon tetrafluoride are removed. Scrubbers having low-pressure drop and which consume very little energy for the induced draft fans are preferred by the fertilizer industry.

Compound and NPK Fertilizers--Liquid effluents from granular and complex NPK fertilizer plants generally result from scrubbing equipment. In nitrophosphate plants having wet reaction systems, the phosphate rock is reacted with nitric acid and phosphoric acid and neutralized with ammonia in such plants. The aqueous effluents, spills, and washings are usually collected in floor sumps and slowly returned to the system in order not to dilute the resulting slurries before they are granulated. In some plants, the dust collected from the granulation section cyclonic collectors is added at the same time, thus increasing the solids concentration in the liquid wastes which otherwise would hardly warrant economic recovery for this waste stream.

Boiler and Cooling-Tower Effluents

Boilers and cooling towers are generally found in most fertilizer complexes as auxiliary facilities.

Boiler Water Effluents--All boilers must be cleaned both before and during operation. Acid and alkaline solutions, as well as special detergents, are used as cleaning agents and are periodically discharged as waste. These wastes are generally acidic and contain hydrochloric acid, acetic acid, potassium borate, ammonia corrosion inhibitors, detergents, and phosphates. In addition, all boilers must be protected from scaling and corrosion during operation as a routine matter. These wastes are generally alkaline and contain trisodium phosphate, sodium carbonate, sodium hydroxide, sodium sulfite, sodium nitrate, and detergents. The cleaning waste waters result from cleaning the boiler tubes and boiler drum surfaces at infrequent and generally unpredictable periods during the year. On the other hand, boiler blowdown waste waters occur regularly, usually one or more times daily. It is recommended that both the acid-cleaning waste and the alkaline blowdown waste be discharged to holding basins, neutralized, and discharged slowly, uniformly, and proportionally into the greater volume of cooling water being discharged continuously into a receiving water. Periodically settled scale and solids should be removed from the holding basin.

Waste Waters from Cooling Towers--Fresh water is usually used to condense the turbine exhaust steam from the plant power station. This water is normally cooled in a cooling tower before it is discharged. The nature and extent of the problems connected with the discharge of cooling waters vary, depending upon the location, the availability, and type of waterway into which the liquids may be discharged.

For coal-fired steam plants about 3,300 kcal of heat must be dissipated by means of this cooling water for every kWh of electricity generated. The temperature of the cooling water discharged is often 5°-8°C higher than the temperature of the water in the receiving stream. In addition to heat these waters often contain small amounts of residual chlorine to control bacterial slime growth; algicides, such as copper sulfate to control algae growth (especially used when cooling towers are exposed to natural light); and sometimes corrosion inhibitors, such as chromium or sodium sulfite. Remedial measures to be used by fertilizer plants include (1) elimination of the once-through type of cooling by tower recirculation and/or reuse of these cooling waters, (2) use of spray ponds or heat dissipation systems (artificial recreational lakes or underground heating pipes), (3) elimination of chromium and/or other toxic metals for corrosion inhibition, and (4) protecting the cooling water from exposure to or contact with any type of foreign contaminants.

Potash

The disposal of liquid wastes arising from the processing of potash has become a concern more recently with the opening of new mining and processing facilities in developed countries.

The mined potash ore, after being crushed, screened, and milled, is separated from the salt crystals and other impurities in specially constructed flotation cells using strong brine as the dispersing medium. High-grade potash ore from sylvinite deposits contains about 20%-30% K_2O (32%-48% KCl); the remainder is salt and other impurities. Commercial-grade potash contains about 60%-61% K_2O.

If seawater is available for preparing the brine, the salt content of the effluent can rise about seven times in concentration compared with that of water. The main disposal problem lies in achieving rapid dilution of the concentrated effluents to below the toxicity level. It has been found that if the salinity of the diluted effluent falls to within 2 parts/1,000 of the ambient level within 30 m of the discharge point, that is with tidal excursions providing a 100:1 dilution, no detectable buildup occurs from one tidal cycle to the next (9).

The discharge of effluents into rivers by inland processing plants still poses a problem in developed countries and is under scrutiny by the regulating authorities at this time. Disposal of waste salts in piles is feasible in some locations where space is available and rainfall is light (see chapter XVIII).

Solid Wastes

The safe disposal of solid wastes or byproducts from fertilizer plants has been a problem particularly in developed industrial areas. Phosphogypsum is by far the largest byproduct in the manufacture of "wet-phosphoric" acid.

Gypsum

The safe disposal or, alternatively, the recovery of byproduct phosphogypsum from wet phosphoric acid plants has become of concern due to the construction of larger phosphoric acid plants in the last decade. For every ton of P_2O_5 produced, 5 tons of phosphogypsum byproduct must be disposed of.

In countries where land is relatively cheap and available, the gypsum cake from the filter is mixed with water and discharged as a slurry to a gypsum pond or lagoon. The lagoon can be several hectares in size and is dyked to retain the gypsum product from the plant over a 5- to 7-year period of operation. The gypsum ponds, of course, receive acidic slurries from the plant. The calcium sulfate and calcium fluorides settle and eventually fill the pond. Care must be taken to prevent ground water contamination due to seepage from the pond. In areas where the rainfall is heavy and evaporation losses relatively low, pond water overflows have to be neutralized with lime to prevent contamination of the receiving waters.

Phosphoric acid plants located on ocean shores usually discharge their slurried gypsum waste into the sea. Gypsum is soluble in seawater and is rapidly dissolved where the tidal currents are strong. Ocean disposal of gypsum has also been practiced by inland plants that dispose of their gypsum by special bottom-unloading barges or ships. Many plants premix seawater with gypsum. About 100 tons of seawater per ton of gypsum is required for rapid dissolution. Gypsum is also soluble in fresh water. It is also permissible to discharge gypsum to rivers where the amount is relatively small in relation to the stream flow. The solubility of gypsum in seawater is 3.5 g/liter as compared with about 2.3 g/liter for fresh water.

Recovery of gypsum for cement, building blocks, and plaster boards, as well as the recovery of SO_2 from calcium sulfate, has been practiced by several fertilizer manufacturers in landlocked countries, where the lack of other disposal methods proved this process economical.

When gypsum recovery is needed, the residual P_2O_5 content in the gypsum waste must be reduced in most cases, and for this reason two-stage hemihydrate-dihydrate phosphoric acid processes are favored even over the straight dihydrate process since the residual P_2O_5 content is normally lower. Several developing countries are now interested in acquiring this type of technology, and those that must import sulfur hope to recover the SO_2 for their sulfuric acid plants (4, 10, 11, 12).

Market conditions for the recovered byproducts will determine in each case the economic viability and specific process to be adopted.

Calcium Nitrate and Calcium Carbonate

Calcium nitrate byproduct is obtained from the ODDA-type nitrophosphate process after the reacted slurries have been cooled in order to increase the water solubility of the final NPK product. The calcium nitrate crystallized out in these slurries is removed by centrifuges, granulated, and dried to be sold as a low-nutrient fertilizer (15% N and 27% CaO) or converted to calcium ammonium nitrate (20%-26% N).

Calcium carbonate is obtained in some plants upon converting the calcium nitrate byproduct of the ODDA process by ammoniation and the addition of carbon dioxide. Unless this calcium carbonate is reused in the manufacture of calcium ammonium nitrate, it is separated by filtration from the process and is used for neutralizing other plant wastes. Alternatively, it has to be sold as a commercial product or disposed of otherwise (13).

Arsenic Trioxide

Another solid waste is produced in Vetrocoke (potassium carbonate) processes for eliminating carbon dioxide in the manufacture of ammonia. The volume of this waste is small and the sludge contains 20% As_2O_3. At present, these wastes are sometimes dumped into the sea as a means of safe disposal. It can create problems by killing the fish if concentrations are high at the discharge point.

Spent Vanadium Catalyst

The disposal of spent vanadium catalyst from sulfuric acid plants cannot be overlooked because of the high toxicity of the vanadium compounds. A 1,500-tpd sulfuric acid plant can produce about 20 m^3 annually which is removed usually during the annual maintenance shutdown. In some cases spent catalyst has been buried underground in locations where it could not affect ground water.

Trends in Pollution Control and Legislation

Developed Countries

The rapid post-World War II industrialization demanded increased pollution control and a policy based on legislative regulation of industry. Economics demanded the increase in size of the manufacturing facilities, and their impact on the environment was, in many cases, overlooked by the planners. Until legislation was enforced by the authorities in developed countries, fertilizer plants exercised only the discipline of in-plant control. This resulted in accidents producing atmospheric pollution in many industrial areas and contamination of public receiving water which became "open sewers," killing fish and fauna.

In the United States, the Environmental Protection Agency (EPA) was created by the Federal Government. In the United Kingdom, the alkali inspectors were reinforced to handle the problems within the framework of "Common Law." Similar regulating authorities today exist in most developed countries having either a so-called "Clean Air Act" or standards for water quality for their public receiving waters. A fertilizer industry located on the shore of a river or the sea has an equal right and obligation as any other riparian to use the facilities in such a way that its neighbors downstream or on the seashore have access to the same quality and quantity of water as it possesses. Under legislative inspection and controls, inspectors can impose fines for negligence and even close down an operation to prevent harm to the environment.

Developing Countries

The fertilizer industry is often the first large-scale industry to be established in developing countries with primarily agricultural economies and indigenous raw materials. Very often skilled labor is not available and has to be trained to operate the production facilities. Planners are preoccupied with the rapid completion of the new facilities, and personnel training is aimed at bringing the production facilities on stream as quickly as possible. Considerations of possible damage to the environment by misoperation of the plant are overlooked, and the rules of safety and good housekeeping are ignored. It is only by strict discipline and good supervision from the very start of the operation in the plant that this can be prevented. This is an aspect which should not be overlooked by management of developing countries and which can have serious sociological repercussions.

When a developed country establishes a new fertilizer plant, its choice of location may not always be close to the source of raw materials or, alternatively, close to the marketing area. Very often the availability of skilled labor, a harbor, or an existing transportation network can influence the final decision. Mobility of labor is normally, however, assumed to exist. In a developing country with a growing infrastructure, very often mobility of labor cannot be counted on. No sooner does construction of a plant or operation of a new facility start than villages or communities in the immediate surroundings are established for the workers. The lack of public transportation or the relative cost of it forces the creation of communities in the immediate vicinity of the plant. Thus, the community welfare and environment become the responsibility of the industry that provides for the operating personnel's livelihood. If the environment deteriorates because of atmospheric pollutants being discharged from the plant or if the availability of potable water decreases as a result of contamination from the plant, difficulties in labor relations will very probably occur. Such difficulties are certainly not in the interest of management, and they hamper the implementation of a viable project. Inevitably, they lead to considerable problems for all concerned. For this reason legislative enactment of pollution constraints paves the way for preventive measures which will guide and protect both employees and management in the next decades of industrial development.

UNIDO's Role

To avoid the pitfalls which have often occurred in developed countries and to guide the new industries to be built in developing countries, UNIDO's role is to technically assist the management of the industries in the planning stage. Impartial adjudication among government, investors, and planners of fertilizer plants to be situated in new locations can save much trouble for all the parties in their joint endeavor.

Establishing a "Grassroots" Plant in a Developing Country

In selecting a "grassroots" site in a developing country, environmental considerations are very often overlooked. This has resulted in the destruction of a fishing industry in harbors or crops in areas surrounding fertilizer plants. Plant sites are normally chosen to be close to the source of raw materials--regardless of whether they are natural gas or phosphate rock. Fertilizer is a bulk product, and all export-oriented plants are either located near an existing harbor area or on navigable rivers. In too many cases political considerations have overridden sound assessment of the impact of fertilizer plants on their surroundings. For example, a harbor authority wants to locate the industry next to its harbor which has been used up until then only for fishing and recreational purposes. Needless to say, both the fishing and tourist industry suffer. In another case, a pharmaceutical industry wants to locate adjacent to a fertilizer plant under construction. Even if the latest technology for fume abatement and dust removal is used in the fertilizer plant, the two industries are not compatible neighbors.

Guide to Engineering Contractors' Plant Specifications

The choice of a process for producing the fertilizer is important from the point of view of environmental impact. Although most of the fertilizer processes to be established in developing countries are classical and have been well tried in developed countries, many contractors overlook the environmental considerations for locations where no legislative constraints exist. To prevent this, the contractors bidding for such facilities should be required to submit in their proposals the quantitative and qualitative details for both atmospheric and aqueous effluents leaving the plant. These specifications should include such information as temperature of the used cooling water leaving the plant, etc. Contractors should be given specifications on effluent discharge limits in their invitation to bid. They should specify the type and performance of all equipment which they intend to install for reducing the pollution of the atmosphere as well as receiving waters.

Material Balances--The contractor is normally required to provide a flowsheet of the process and a piping and instrumentation (P and I) diagram with his proposal. It is uncommon for a material balance flowsheet showing plant losses or effluents to be a part of this proposal unless it is requested by the tender specifications. It is highly recommended that in the future this information be included as part of the proposal in order to enable the assessment of the probable impact that the new plant can have on its environment.

In-Plant Control for Gaseous and Aqueous Plant Effluents--The establishment of in-plant effluent control is essential to a well-operated fertilizer plant. The gaseous discharges should be sampled on a regular basis in the same way as the process streams for control purposes as a matter of routine. The aqueous effluents discharged should be sampled continuously within the plant limits. Whenever possible, continuous recording analyzers should be installed. In every plant, spills and outages occur because of either human error or equipment failure. Often these spills cause considerable yield loss and present great dangers to the receiving waters as well as surrounding environment. As a precautionary measure to contain and confine the inadvertently discharged hazardous spills, impounding basins can be constructed within a plant's fenced-in property, providing an opportunity to neutralize acid spills before discharge of the contaminants to public waters. This is, of course, not practical for atmospheric effluents. While dilution of these effluents, particularly in windy regions, can be expected to be greater, their effect on the surroundings of the plant can be equally dangerous. The installation of wind vanes, coupled with recording instruments, can determine the direction in which the contaminants will travel after discharge.

The construction of vent stacks of sufficient height will assist dispersion of these pollutants. When a plant is constructed, all vent stacks should be built sufficiently high to safeguard the immediate vicinity of the plant. Maximum ground concentration of a contaminant can be calculated for any point source release using the Bosanquet Pearsons diffusion model method (14, 15). This empirical method without accurate meteorological data, however, only provides for an approximation. As a rule, maximum ground concentrations are found at 10 stack heights downwind from a chimney for SO_2 and lighter aerosols discharged. The collection of meteorological data, such as barometric pressure, rainfall, etc., is useful in assessing the responsibility of damage. Dust collectors located in strategic areas surrounding the plant are particularly useful in connection with fertilizer plants. These should be installed before a fertilizer plant is established to measure the "base level" of dust in the area and act as a measure of the impact of this industry after commissioning, as well as during continuously sustained operation.

Environmental Surveys

Before Breaking Ground--In the 1950s, during the post-World War II industrialization and reconstruction period, when many developed countries discovered new markets for industry, enlightened companies took care to establish industry in primarily rural areas prior to breaking ground. Many factors influenced the choice of site, but one major one which was not overlooked was the environment.

Legislative controls and constraints were not identified quantitatively. The basic principle of common law as a "good neighbor" was the guiding policy.

New industry established itself in an area for the following basic reasons:

1. Marketability of its products;
2. Availability of raw materials at optimal prices;
3. Availability of sufficient skilled labor;
4. Good communication with other centers of activity for their business;
5. Congenial environment for employees and communal activities.

The emphasis for the last item (item 5) has gained in importance since those days. The natural waters--rivers or sea--were provided by nature for most "grassroots" sites; this was to be respected as a public domain to be shared with communities that had equal riparian rights with industry. The needs of the industry were easily established by the planners from surveys in the area. Whether it was a river or sea, the environmental considerations were taken into account, and the existing flora and fauna in the rivers or sea were determined (16). Specialists, such as biologists and agronomists, were contracted for surveying the area. Plankton counts were made for the water upstream and downstream of the proposed site, mainly to establish the natural habitat and ambient conditions. This scientific approach established the base-level data and, in some cases, pinpointed the level of existing influences of a polluting nature that might eventually disturb or augment dangers to the environment by establishing a new industry. The surveys were normally conducted by independent academic institutions under contract. They provided important information to industrial management and, at the same time, by virtue of local publicity, established public confidence. Many community residents were suspicious of the new neighbors in spite of the increased employment opportunities and financial benefits that were expected (17).

After One Year of Establishing Industry--As everyone knows, establishing a new industry, in many cases in virgin rural areas, is plagued with many teething problems. When new technologies are introduced and unskilled labor is trained, many mishaps occur. With skilled supervision and adequate training of the new employees, within 1 year these problems can sort themselves out and productive operations of the industrial plant can be normalized.

At this point it is important for the management of a company to plan a program to determine the impact, if any, that the company's operations have had on the environment. This study should be done irrespective of whether or not any legislative authorities are demanding data on the company's operations.

The survey of river or ocean fauna and the quality of waters, including plankton, pH, temperature, BOD, COD, and dissolved oxygen, has to be established upstream and downstream of the riparian-established industry. The dispersion of aqueous plant effluents, including cooling waters, should be examined. Their impact must be measured quantitatively not only within the plant boundaries but also in the immediate area. This self-discipline is the core to guide industry even before any governmental legislation and constraints are introduced with penal codes to punish offenders. The management of industry (whether in developed or developing countries) should establish this discipline at the very start of operations, and it involves in every case training and encouragement of employees to maintain and observe the guidelines.

This pollution control must be the responsibility of the management, and it should not be restricted to liquid effluents from the fertilizer plant. Gaseous effluents, which emanate from a fertilizer plant, should also be monitored. Using garden plots that are placed in strategic locations with respect to the prevailing wind conditions in the area and planting crops that are sensitive to the pollutants from the plant provide a measure of the pollution and safeguard the agricultural or forested area surrounding the plant. Mobile air-sampling stations equipped with sulfur dioxide and oxide of nitrogen analyzers operating 24 hours/day can provide quantitative analyses for this purpose. The investment is relatively small; the annual operating expense approximately equals the expense for equipment. The socioeconomic benefits for both industry and the community can easily outstrip and justify the expense in the long run without even trying to establish a cost:benefit ratio by simply calling it "goodwill expense" (18).

Economic Aspects of Pollution-Control Costs

The assessment of the costs of pollution-control measures in fertilizer plants has always been difficult to quantify. It is certain that when a new industry is established, it is more economical to incorporate in the beginning all the necessary abatement equipment to meet the requirements and local standards. Any changes to be made to existing plants will always entail higher investment costs and in some cases loss of production. Only in cases where recovery of byproduct from a fertilizer plant can be achieved economically, can one arrive at a cost:benefit ratio. In an expert group meeting of UNIDO, the general consensus of the participants was that the cost:benefit considerations must be evaluated in a different manner in developing countries from those in developed countries (4). Only if a minimum degree of uniformity in equipment specification is assumed, can any meaningful, though rough, calculation of worldwide capital expenditures for fertilizer manufacture pollution control be made in the next decades. Assuming a growth rate of approximately 9% per annum for the fertilizer industry, the total expenditure on a worldwide basis for air and water pollution control in the fertilizer industry through 1980 could approach \$3-\$5 billion (\$3,000-\$5,000 million) (4).

It is not unusual in a developed country to spend 15%-18% of the total capital investment on pollution-control equipment. The Fertilizer Institute has estimated that operating costs of pollution-control equipment have added about \$3.30/mt of N and P_2O_5 in the United States (19).

In the United States, Federal standards are based on the "best available technology." The disadvantage of this approach is that it does not permit assessment of a cost:benefit ratio. Also, it does not take into account location factors or the scale of operation. For example, a 20-tpd sulfuric acid plant must conform to the same standards as a 2,000-tpd plant. Moreover, the "best available technology" is likely to change as new technology is developed; thus, planning is difficult. In addition to Federal standards, states, counties, and municipalities may impose other controls.

In most European countries, there is a tendency toward a more flexible approach, often permitting consideration of plants on an individual basis (19). For example, Norway, Sweden, and Spain have no general statutory emission limits, but permissible limits are established for each plant separately. Permissible discharges into rivers may vary depending on the characteristics of the river. Some countries have different standards for different types of plants.

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XXIV Planning for the Development of a Fertilizer Industry

Introduction

The need for sharply increased production and use of fertilizers in developing countries has been pointed out in chapters II and III. This need arises from the need to increase agricultural productivity to meet the growing needs for food and fiber and to increase export of agricultural products to earn foreign exchange.

Many countries that have relatively little experience will be building new fertilizer production facilities, and others that have some experience will be expanding production and use manyfold. It is obvious that success of these undertakings will depend on how well they are planned.

"Developing countries" include a wide range in size, population, agricultural potential, degree of development, raw material resources, and other factors. Thus, it is quite impossible to set forth any development plan that will be useful to all countries. The aim of this chapter is to suggest some general guidelines and to point out some pitfalls in planning for a fertilizer production and distribution system. Primary emphasis will be placed on planning to supply the domestic needs of a country or region, but some attention will be given to planning for export of fertilizer raw materials, intermediates, and products.

Two prerequisites to good planning of a fertilizer industry are (1) an accurate assessment of the country's present and future needs and (2) a detailed knowledge of its resources including particularly raw materials that can be used for fertilizer production and infrastructure needed for development of the industry. Unfortunately, these two prerequisites are often difficult to define with any degree of certainty.

Estimates of Demand and Requirements

It may be assumed that a country's government will have some goals for its agriculture, including supplying enough food crops of appropriate types for nutrition of its estimated future population; supplying nonfood needs such as rubber, cotton, wool, hemp, etc.; and producing cash crops for export of products for which the country has natural advantages. Some approximation of the amount and kinds of fertilizers needed to achieve these goals usually can be formulated, provided sufficient agronomic information is available. The fertilizer requirement is only one factor in attaining goals of agricultural production (see chapter III); thus, the reliability of the estimate will depend on how accurately other requirements are estimated and how well the plan, as a whole, is carried out.

Government estimates of requirements or goals tend to be optimistic for they reflect what the government hopes to achieve rather than that which realistically can be expected. In planning fertilizer production, it may be better to rely on estimates of effective demand, unless the excess production can reasonably be assumed to be absorbed by exports.

A difficult problem that sometimes is not fully appreciated is the estimation of the kind of fertilizer needed in the future. Usually there are data available on the response of major crops to each of the primary nutrients and sometimes to the secondary nutrients. However, with continued fertilizer use of one or two nutrients, other nutrients may become more and more deficient. For instance, developing countries often start fertilizer use with straight nitrogen because the economic response to this element is greatest. After several years of nitrogen fertilization, the soil supply of phosphorus (for example) is exhausted to the point that response to nitrogen falls off. When both nitrogen and phosphorus are used for several years, other elements (such as K, S, Zn, or Mg) may be the limiting factors. These needs can and should be anticipated as far as possible on the basis of soil analyses and crop requirements or on the basis of long-term test data, if available.

The choice of kind of fertilizer should be made with due regard to the prospective cost. For example, if ground phosphate rock is 80%-90% as effective as triple superphosphate but costs only half as much, the ground rock may be the better choice. If sulfur is likely to be needed, it may be economically preferable to supply it as single or enriched superphosphate, ammonium sulfate or sulfate-nitrate, ammonium phosphate-sulfate, or compound fertilizers in which the sulfur content can be varied to suit agronomic needs. The choice often may be influenced by the raw material and other resources available. Thus, when phosphate rock and a source of magnesium are available together with low-cost hydroelectric power or fuel, fused calcium magnesium phosphate may be a good choice, especially if its magnesium content and liming value are agronomically useful. The advantages of ammonium phosphates have been pointed out in chapter XVII. In summary, the choice of type of fertilizer should be made by cooperation among agronomists, engineers, and marketing specialists with a view to determining the most economical means for supplying all needed nutrients at the farm level while making the best use of the country's resources. The resulting decision may involve some compromise between agronomic effectiveness and cost or between production and distribution costs.

Marketing

Marketing, including distribution, regional and local storage, and retail sales of fertilizers, is a very important part of planning which is often given insufficient attention. Too often it is assumed that if an adequate amount of fertilizer is produced it will somehow find its way to the farms. A detailed discussion of marketing is beyond the scope of this manual and could well be the subject of another manual.

Many developing countries have very poor transportation systems which are already overtaxed. In some inland countries or remote regions of large countries, the cost of transportation far outweighs the cost of fertilizer production. In such cases small local plants using local resources may be the best choice.

For instance, in China, numerous small local nitrogen and phosphate plants help supply the needs of many districts and thus ease the stress on the transportation facilities. A recent paper has suggested that small local nitrogen plants might be more economical than large ones in some cases when all costs are considered (1). In any case it should be evident that emphasis should be placed on minimizing delivered cost rather than on minimum cost at the factory.

For marketing the output of a large plant, it is of vital importance to develop a logistics system that will ensure that fertilizer of the right kind is available to farmers in the right amount and at the right time. To plan such a system it is first necessary to estimate the requirements of each region and district in detail, including kinds of fertilizers required, quantity of each, and the time when each is required. When this information is at hand, a system of regional and district distribution centers can be set up with adequate storage facilities at each center and retail outlets can be identified or established. Transportation of fertilizers to the distribution centers must be planned and scheduled to make the most efficient use of existing facilities and to provide new facilities when necessary.

Natural Resources

A detailed inventory of a country's natural resources is helpful in planning a fertilizer industry. Unfortunately, most developing countries and many developed countries have incomplete knowledge of their mineral resources. Since thorough exploration of mineral resources is very expensive, it is not surprising that very little is known about the mineral content of much of the earth's crust. Naturally, much of the exploration has been aimed at finding the most valuable materials. Many of the fertilizer raw materials have relatively low value on the world market but might be quite valuable to a country that is planning a fertilizer industry. Phosphate rock, for example, is not easily recognized by the casual prospector and until recently was not valuable enough to stimulate intensive exploration. Pyrites and coal are more easily recognized but not valuable enough to warrant extensive exploration unless well located and of good quality. Even natural gas has not been looked for extensively except in consuming areas; most of it has been found while looking for oil.

While short-term plans must be based on currently known resources, each country should make long-range plans to gather as much information as possible about its mineral resources. Natural resources other than mineral resources that may be useful include hydroelectric potential, water supply, and waterways or harbor sites that can be used for transport of raw materials and products.

Types of Fertilizer Production Facilities

The first decision in planning a fertilizer industry is whether a new plant should be built, and, if so, what kind. Realistic estimates of present and future market demand or requirements are needed as a basis for this decision. If the intention is to export part of the production, an analysis of world or regional supply and demand is needed to determine to what countries the product could be sold competitively and what the market is likely to be in those countries. In considering exports it would be well to make some inquiries, perhaps at government levels, to determine the plans and policies of prospective importing countries. Such data are needed to establish that importation is likely to be acceptable to the importing country. Some sort of a trade agreement might be mutually beneficial.

When fertilizer production is planned for domestic use only, the type of facilities may depend on the estimated market. General guidelines, to which there may be many exceptions, follow. If the market is less than 5,000 tpy of fertilizer, it is unlikely that any facilities can be justified other than those required to receive and distribute bagged fertilizers. For market volume between 5,000 and 25,000 tpy, facilities for receiving bulk fertilizers for bagging may be considered. Also in this range, a small bulk-blending plant could be considered if special formulations are needed that cannot be imported except at a much higher price than the ingredient materials.

If demand is between 25,000 and 100,000 tpy, bulk-blending or granulation may be considered. In the case of a granulation plant, imported intermediates such as phosphoric acid, powdered monoammonium phosphate, ammonia or ammoniating solutions, potash salts, and urea may be used; and local production of superphosphate may be considered if either sulfuric acid or phosphate rock or both are available.

In the range of 100,000 to 300,000 tpy, basic manufacture of some types of fertilizers may be considered if the raw material situation is favorable. If total demand is above 300,000 tpy, basic production of ammonia, urea, and phosphoric acid may be considered, but the mere fact that prospective demand is sufficient to utilize the production of a full-scale plant is no guarantee that the project will be economically justifiable. For instance, if a country has neither phosphate rock nor sulfuric acid, it may not be economical to manufacture phosphoric acid unless an economical supply of these materials is ensured. Likewise, when a country has no economical indigenous supply of ammonia feedstock, basic production of ammonia and nitrogen fertilizers may be uneconomical in comparison with importation. On the other hand, for inland countries where importation is very expensive and when raw materials are available, relatively small plants often can be economically justified. For these reasons each situation must be considered separately; there are likely to be many exceptions to the general guidelines given above.

When production is planned mainly for the domestic market, the planning should be closely integrated with the plans and goals of the agricultural and industrial sectors. Reliable, realistic estimates of future needs become extremely important. If this demand is overestimated, the plant will be too large, and the production cost will be high because of underutilization of capacity. If the estimated demand will support an economical scale of production in the more distant future (10-20 years), it may be better to include construction of a plant in long-term rather than short-term planning.

The choice of product or product mix is an important one. Previous chapters have discussed some factors that should be taken into account in selecting a nitrogen or phosphate fertilizer. The proper choice is not a simple one for it should take into account not only the prospective cost of production but also the cost of distribution and the agronomic effectiveness of the products for the intended uses. The agronomic effectiveness depends, among other things, on how the farmers will use the products. While farmers' methods can be changed by education, it should not be assumed that they will use each product in the most effective way unless some effective program is planned to achieve this result.

In most cases, it is likely to be advisable to produce several grades of compound fertilizers for use on various crops and soils as a basal application plus straight nitrogen fertilizers for supplemental application during the growing season. The alternative of marketing straight fertilizers for separate application by farmers can be acceptable in some cases, but the problems of farmer education and timely distribution are likely to be greater.

In many situations it will be advantageous to produce and/or market different types of fertilizers to supply the needs of different crops or regions or to take advantage of local situations. For instance, urea may be preferable for rice, ammonium sulfate for tea, and ammonium nitrate for wheat, depending on soil characteristics, farmer practices, etc. Anhydrous or aqua ammonia may be well suited for use on large farms or plantations but impractical for use on small farms. Ground phosphate rock may be the most economical for use on some acid soils while soluble phosphates are preferable for neutral or calcareous soils. Potassium chloride is usually the best choice for most situations, but nonchloride sources of potash may be better for some crops (tobacco, potatoes, and grapes) or for use in areas where a harmful accumulation of chloride is likely. The extra expense (if any) of supplying different products for diverse needs must be balanced against the expected benefits.

Sometimes part of a country's needs may be supplied in local regions by low-analysis products that are less expensive in that region such as ground rock from local deposits, ammonium chloride or ammonium sulfate byproducts from a local industry, or low-analysis potash salts from local brines or ores. The concept of making maximum use of local resources has been well developed in China and serves to minimize transportation problems, especially for the more remote areas.

Development of the Marketing and Distribution System

The marketing and distribution system is fully as important as the production system and should receive equal attention. Planning of the two systems should be closely integrated. Sometimes the close coordination can best be done by making a single organization responsible for both. In other cases the marketing system may be more effectively integrated with agricultural production organizations which also plan the marketing and distribution or export of farm or plantation products. Regardless of the type of marketing system selected, it should be closely integrated with plans for the fertilizer supply (by manufacture or import).

The marketing system will usually include physical facilities for storage of fertilizers in regional, district, and local warehouses. Where existing transportation is inadequate, the marketing system also may need to include transport facilities such as trucks, barges, or railcars. These facilities may also be used for carrying grain or other agricultural products to the market. One of the most pressing problems in many developing countries is improvement of the infrastructure, especially transportation facilities--railroads, highways, waterways, harbors, etc. Such facilities are vital for marketing of fertilizers as well as marketing of the increased agricultural production and development of the country as a whole. It seems futile to build large fertilizer plants when the infrastructure is inadequate to distribute their production. Development of the infrastructure may well be such an enormous job that the building of numerous smaller plants would provide a more economical and practical alternative in some cases.

Government Policies

The establishment of an effective fertilizer production and marketing system in most developing countries is not likely to succeed unless the government assigns it a high priority and adopts policies to expedite its development. This should be done in those countries that have good agricultural potential, particularly if food supply is a problem. A recent IFDC report examines the role of government policies in promoting an efficient fertilizer industry (2). A brief summary of the report has been given in chapter II.

Government Legislation and Regulations

Most governments in developed countries and in some developing countries have established laws and regulations to specify and enforce quality standards of fertilizers to ensure that products of satisfactory quality are available to farmers and that the farmers know what they are buying and get what they pay for. An FAO publication, "Fertilizer Legislation," discusses the subject and gives some examples (3). Most of the regulations are concerned with such subjects as adherence to guaranteed analysis within specified limits of tolerance, guaranteed weights, identification of sources of products, specification of what grades may be sold, what nutrients may be claimed, and specification of methods of sampling and analysis. Most laws also specify penalties, such as fines or revocation of licenses for failure to conform to specified standards. Most developed countries do not attempt to specify the physical properties of fertilizers since farmers can judge for themselves whether the physical quality is suitable for their purpose, and if they are dissatisfied they can buy from another source. In some developing countries farmers often may not have a choice, and governments may choose to specify some minimum standards of physical condition to ensure that the product is usable.

In any case it is important that governments set up and enforce regulations to protect farmers and honest merchants against fraudulent practices and inferior products and to provide adequate information about the quantity and quality of fertilizers and their nutrient content. The regulations should not be so restrictive as to preclude sale of low-cost products such as basic slag or ground phosphate rock; however, full information as to their value should be required.

Plant Location

Selecting a location for fertilizer production facilities is important and sometimes not given sufficient consideration. The usual aim is to select a location that will result in the lowest average cost of the products, delivered to retail outlets. There may be other social or political objectives such as increasing employment in a depressed region. Also, on a national basis plant locations within a country are likely to be preferred for reasons of national security, foreign exchange saving, and increasing employment. These are all valid objectives and must be given due but not excessive weight lest the product cost be so high that farmers cannot afford to use it.

In general, high-analysis products preferably are produced near the source of raw material; whereas, low-analysis products are produced in consuming areas. A classic example is that high-analysis phosphates (TSP, DAP, etc.) usually are produced in a large plant near a source of one or both of the raw materials (phosphate rock and sulfur) while low-analysis products (single superphosphate) are more likely to be made in small plants in consuming areas. The reason, of course, is to minimize total transportation costs. Likewise, ammonia plants based on natural gas are likely to be located reasonably near the source of the gas, although transport of the gas by pipeline is sufficiently economical to permit some latitude in selecting plant location. The alternative of transporting the ammonia by pipeline is attractive except when urea is the desired end product. Coal-based ammonia plants usually should be reasonably near the coal mine, but ammonia plants based on naphtha or fuel oil usually are near an oil refinery. Compound fertilizer plants based mainly on imported materials often are located at a port. When based on domestically produced intermediates, they are often located near the source of the intermediates, although there are many cases in which they are advantageously located in market areas.

The alternative of small plants located in consuming areas versus a single large plant should be considered in countries where transportation facilities are poor or inadequate. It is obvious that the large plant, if operated at or near full capacity, will have the lower production cost and consumers located near it will benefit. However, it is not easy to calculate which alternative will have the lower average delivered cost, particularly when the distribution system will require extensive infrastructure improvements at enormous cost. Such infrastructure improvement may be far beyond the capability of many developing countries in the foreseeable future, and it is difficult to decide what portion of the cost should be allocated to fertilizer distribution.

It is probably fair to state that the case for small ammonia-urea plants or small ammonia plants with other end products has not been given as much consideration as it deserves, particularly for remote regions or large countries with difficult transportation problems. Too often planners accept without question that there is an economic minimum scale such as 1,000 tpd for an ammonia-urea complex and that smaller plants cannot be considered. The small local plant concept could become more attractive if a standard design were developed and spare parts made widely available.

In addition to transportation of raw materials and products, numerous other factors must be considered in selecting a plant site. Most plants require a large amount of water of reasonable purity, and a dependable supply is very important. Prevention of pollution (see chapter XXIII) must be considered; the problem can be minimized by selection of a site where disposal of effluents and solid waste is least expensive. Space for lagoons to treat liquid effluents may be needed. Some wastes can be economically and safely disposed of in the sea or large rivers (with suitable precautions to prevent local accumulations).

Site preparation expense can be minimized by selecting a reasonably level location with firm soil and subsoil, but sometimes other factors outweigh this advantage, thereby necessitating extensive site preparation. Availability of a supply of local labor with suitable skills or aptitude for training is an important factor. In this connection selection of a site in an area where employees will enjoy living is important. If a plant must be built in a remote area or a hostile environment such as a desert, jungle, or cold region, much extra expense will be involved in creating comfortable living conditions, and usually much higher salaries and wages will be required to attract and keep a competent work force.

The character of the infrastructure has been mentioned in connection with transportation--roads, railroads, waterways, harbors, airports, etc. These facilities, or the lack of them, will have an important effect on construction costs. Also local service facilities such as a dependable source of electricity, for example, can help.

Regional planning can reduce construction, production, and distribution costs substantially. Country boundaries seldom coincide with logical economic regions, and few countries have the facilities to be fully self-sufficient.

In many cases the plant location may be influenced by the location of other industries. There are numerous cases in which other industries can supply materials for fertilizer production and vice versa. For instance, smelters may supply sulfuric acid for phosphate fertilizer or ammonium sulfate production; oil refineries may supply ammonia feedstocks; byproduct ammonium sulfate may be available from numerous other industries; and ammonium chloride fertilizer can be produced profitably as a coproduct with soda ash. Likewise, ammonia or urea is useful for production of plastics and synthetic fibers; methanol production can be integrated with ammonia production; and byproduct gypsum from phosphoric acid production can be used as a cement additive to control set time. Aside from exchange of materials, these are advantages arising from grouping industries in an industrial complex in that numerous items of infrastructure and heavy equipment can be shared.

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XXV Economics of Fertilizer Manufacture

In the preceding chapters, the economics of production of major fertilizer products has been discussed, and illustrative estimates of capital investment requirements, production costs, and gate sale prices have been given. The purpose of the present chapter is to bring this information together in a single chapter for convenience and to combine some of the information into groups of processes (complexes) in which the product of one process becomes the raw material of the next one. An example is an ammonia-urea complex or a sulfuric acid-phosphoric acid-diammonium phosphate complex.

Assumptions for Plant Cost Estimates

As explained in chapter VI, there are three common types of plant cost estimates--battery limits, turnkey, and project. The battery-limits cost usually can be determined with a fairly good degree of precision once the process is identified and a site selected. In this chapter, the battery-limits cost in an industrial location in a developed country will be the basis for estimating plant costs. In many cases the cost data are for the U.S. Gulf Coast area where there is a high concentration of both phosphate and nitrogen plants. However, some of the data are from European sources. In these cases the fluctuating value of the dollar against European currencies introduces an additional factor of uncertainty. Most of the cost data are for 1977 or 1978 although some are for 1976. Some of the data for 1976 and earlier years have been escalated to 1978 levels using the CE Plant Cost Index which is published in each issue of Chemical Engineering.

To arrive at a total plant cost, the battery-limits cost is multiplied by a factor of 1.5 except as otherwise noted. This is a "turnkey" plant cost for a developed country. This value is used in production cost estimates for calculating capital-related production costs. It normally includes all supporting and auxiliary facilities necessary for plant operation in a developed country. It also includes storage facilities for a normal supply of raw materials and intermediate products but not for a finished product. For example, phosphoric acid, sulfuric acid, nitric acid, and ammonia are assumed to be intermediate products which will be used onsite for further processing. However, the cost of storage terminal facilities for receiving or shipping ammonia and phosphoric acid are discussed separately in chapters VII and XIII, respectively. The turnkey plant cost does not include sufficient storage for raw materials that must be imported in large ships nor does it include port facilities.

In this chapter no attempt will be made to estimate a total project cost or the cost in a developing country. However, the effect of increased capital cost on production cost is estimated. Some items that the estimates do not include are:

1. Escalation of costs beyond 1978;
2. Interest on capital during construction;
3. Feasibility studies;
4. Training programs and other startup expenses;
5. Contingencies;
6. Electric power generation, except in the case of ammonia plants based on coal or heavy fuel oil;
7. Emergency electric-generating facilities to serve as backup for regular power supplies;
8. Import taxes or custom duties;
9. Any unusual expense to ensure water supplies such as dams, reservoirs, long pipelines, or desalination of sea water;
10. Infrastructure such as housing, roads, or railroads outside the plant; harbor improvement; piers; jetties; airport facilities, etc.;
11. Unusual site preparation expenses; and
12. Working capital.

For finished products such as urea, AN, DAP, and TSP, the cost of storage is calculated as a separate item based on capacity for 45 days' production for bulk storage and 10 days' production for bagged product. The assumed cost of bulk-storage facilities is $40/ton without humidity control and $50/ton with humidity control. Urea, ammonium nitrate, and any fertilizer containing a high percentage of these materials are assumed to require dehumidified storage although in some climates it may not be necessary. The cost of storage for bagged product is calculated on the basis of $75/ton of capacity including bagging facilities. Both bulk and bagged storage costs include the cost of conveying and handling equipment to move the product in and out. Any storage requirement beyond that described above is assumed to be a part of the marketing and distribution system and usually will be located in regional or district distribution centers.

An example of some of the extra investment costs that may be included in a total project cost for a developing country may be helpful. The example project consists of a 1,000-tpd natural gas-based ammonia plant and a 1,725-tpd urea plant in a nonindustrial location. If such a facility were built in an industrial location in a developed country, the estimated turnkey cost, based on data in chapters VI and XI, would be:

	$ Million
Ammonia plant	75.0
Urea plant	40.2
Storage facilities	5.1
Total	120.3

The estimated project cost for the proposed plant in a remote location in a developing country is $313 million. Of this total about $145 million seems to be directly related to construction of the plant and its auxiliary and supporting facilities. Some of the cost items in this proposal that either would not be encountered in a typical project in a developed country or would be much lower are listed below:

	$ Million
Harbor, breakwater, and pier	31
Water supply line (25 km)	6
Housing colony	14
Ocean freight and local handling	12
Physical contingency	18
Provision for escalation during construction (42 months)	53
Interest during construction	13
Preoperational expense	7
Initial working capital	8
Total	162

It is evident that a plant in a developing country may cost two to three times as much as a similar plant in a developed country for a variety of reasons that will be discussed in chapter XXVI. Sheldrick, in a paper prepared for the FAO Commission on Fertilizers, estimated that the total plant cost for a 1,650-tpd ammonia-urea complex would be $150 million in a developed country, $230 in a developing country with fairly good infrastructure, and $320 million in a remote location.[1] The most important reasons for the difference seem to be the increased requirements of infrastructure and offsite facilities and the longer construction time with accompanying escalation and interest costs. The long construction time in a developing country is very costly, especially in countries where the inflation rate is high. In a developed country, a major new plant usually can be completed in 18 months; whereas, as much as 4 years may be required in a developing country. In the above example the provision for escalation during construction is $53 million, and the interest during construction, even at the low rate of 4%/year, is $13 million. Some possible means for decreasing these costs will be discussed in chapter XXVI.

In addition to the cost of long construction periods, there is the possibility that the process and equipment may become at least partially obsolete before it is finished. An ammonia-from-coal project is likely to take 7 years from process selection to operational status. During this time process improvements (or discovery of natural gas) may make the plant noncompetitive.

It should be noted that none of the capital and operating costs in this manual include the costs of a marketing and distribution system. This cost is likely to vary widely from one country to another and, in some cases, may approach the cost of the production facilities. Distribution costs are not within the scope of this manual; a useful recent publication on this subject is "Fertilizer Marketing" by K. Wierer and J. C. Abbott, FAO Marketing Guide No. 7 (1978), published by the Food and Agriculture Organization (FAO).

Assumptions for Production Cost Estimates

The following simplified assumptions are made to arrive at comparative estimates for production costs:

Capital-Related Costs

Capital-related costs are calculated on an annual basis as a percentage of the total plant cost as follows:

Depreciation (15 years)	6.67%
Interest	4.0 %
Taxes and insurance	2.0 %
Maintenance (materials and labor)	5.0 %
Total	17.67%

The interest rate is assumed to be 8% applied to one-half of the capital as an average over a 15-year period, since the depreciation allowance decreases the capital investment to zero in 15 years.

To arrive at a gate sale price, 10% return on the total plant cost is added which includes provision for income tax. This may be regarded as a 20% pretax return on the average investment over a 15-year period.

No estimate of working capital is made, and hence no interest on working capital is included. However, 5% is added to the production cost of all final products and some products that may be used as intermediates for "administrative and miscellaneous costs" which should be adequate to include interest on working capital. In production cost estimates involving plant complexes, this 5% is added only to the final product.

All capital-related charges are assumed to be constant on an annual basis, and therefore their cost per ton of product will vary with the annual production (capacity utilization).

It is recognized that more sophisticated methods for calculating capital charges or profitability would be preferable for a specific project, but for a generalized comparison these refinements are not warranted.

Capacity Utilization

It is assumed that full capacity utilization is attained when the annual production of a plant is 330 times its rated daily capacity. An allowance of 35 days for scheduled maintenance or other delays is considered normal. Although some plants attain 100% capacity utilization according to this definition and some exceed it, a capacity utilization of about 90% is more typical of average results in developed countries when market conditions are not limiting. Accordingly, most of the production cost estimates assume an annual production equivalent to 300 times the daily capacity or about 90% capacity utilization (actually 90.9%). Illustrations are given of the effect of percentage capacity utilization on production cost.

Labor-Related Costs

The average direct cost of operating labor including working-level supervision is assumed to be $8/man-hour. (Maintenance labor is included in maintenance as a capital-related cost.) Labor rates are likely to be lower in some developing countries, but a larger number of workers may be used, and indirect costs may be higher. Overhead costs and fringe benefits are assumed to be 100% of direct labor costs. The cost of chemical control is assumed to be 20% of direct operating labor. Thus, total labor-related costs are assumed to be 220% of $8 or $17.60/man-hour. Labor-related costs are assumed to be constant on an annual basis (330 times daily cost) and hence variable per ton of product. In comparing plants of different

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[1] W. F. Sheldrick, "Investment and Production Costs for Fertilizers," Paper No. FERT 79/4 presented at the 5th Session of the FAO Commission on Fertilizers, Rome, January 22-25, 1979.

capacities, labor-related costs are assumed to vary with the 0.6 power of capacity on an annual basis.

Raw Material Costs

The costs of raw materials are calculated per ton of product with allowance for recovery factors in accordance with the best available process information. In addition, 1% or 2% apparent loss in processing is assumed which may be partly a mechanical loss or overage in analysis (for example, urea may contain 46.2% N rather than the assumed 46.0%). Current world market prices are used for raw materials or intermediates (such as ammonia) when such information is available, except as otherwise noted.

Utilities

Unless otherwise noted, assumed utilities costs are:

Electricity	\$0.027/kWh
Steam	\$4.00/ton
Cooling water	\$0.01/m^3 on a once-through basis
Boiler feedwater	\$0.26/m^3
Fuel oil (for drying)	\$0.01/thousand kcal

It should be noted that the utility costs are in part covered by capital-related costs associated with auxiliary and supporting facilities. Such facilities include, for example, water purification, steam generation, and distribution facilities for these services. Thus, the costs listed above are not comparable with utility costs at battery limits which is a basis commonly used in many other estimates. For example, when the process requires a steam supply, the capital and maintenance costs of a steam generation unit are included in "capital-related costs," thus the \$4/ton charge for steam includes only fuel costs and labor-related costs.

Byproduct steam is credited to the process at \$4/ton when the process is considered separately. However, the value of byproduct steam (or electricity) depends on what use can be made of it. In a plant complex containing a sulfuric or nitric acid plant, byproduct steam from one unit usually is used in other units either for heat, mechanical energy, or generation of electricity for plant use.

In a few instances there may be excess steam available as, for example, when a sulfuric acid plant is separated from the industry it supplies. In such cases it may be difficult to find a profitable use for the steam.

Other Costs

Catalyst costs are based on an average replacement cost not including the initial charge. Likewise, costs for absorbents (such as CO_2 removal absorbents) and recycled chemicals or solvents are based on replacement costs. Miscellaneous supplies are usually assumed to amount to \$0.50 or \$1.00/ton of product depending on the complexity of the process except when there is information to indicate that a different value should be used. Administrative and miscellaneous costs are taken as 5% of other production costs as explained under "capital-related costs."

Cost of Bags

The production cost estimates given in this manual usually are for bulk products, but in some cases the estimated cost of bagged product is also given by adding \$12/ton to cover the cost of bags and labor for bagging. The cost of bags varies widely depending on their quality, size, etc. The \$12 allowance is intended to apply to strong, weatherproof bags of 50-kg capacity. For example, a woven polypropylene bag with a polyethylene liner may cost \$0.60 for a 50-kg bag (\$12/ton) in the United States. The cost would vary with the thickness of the polyethylene liner. Also, the size of the bag, which depends on the bulk density of the material to be bagged, has some effect. Since polyethylene and polypropylene are produced from naphtha or light oil feedstocks, their cost depends on the feedstock cost. It is reported that bags similar to those described above can be manufactured in a southeast Asian country at about half the U.S. cost (\$0.30/bag) with indigenous feedstock.

Double bags with woven polypropylene or jute outer bag and a polyethylene or other moisture-proof inner bag are usually required for overseas transport or for transport within a developing country involving several steps of manual handling. Lower-cost single plastic film bags are commonly used in developed countries with automatic palletizing and mechanical handling. On the other hand, farmers in developed countries often prefer smaller bags (50 lb or 25 kg); thus, the cost of bags per ton of product is increased.

Various schemes have evolved for bulk handling and transport or for transport in returnable containers including bags of 0.5- or 1.0-ton capacities designed for mechanical handling. These various systems for handling and distributing fertilizer are obviously important to the marketing and distribution system and should be discussed in detail in another publication.

Process Requirements

The assumed raw material and utilities requirement for the processes considered in this chapter are shown in table 1. The values chosen are, in most cases, a compromise among several reported values. Naturally, the raw materials and utilities consumptions vary, depending on the efficiency of the plant and its operators, the quality of the raw materials, etc. Also, there are compromises and tradeoffs--efficiency versus capital requirements, high recovery versus high production rate, steam versus electricity, etc. Thus, the values given in table 1 should be considered illustrative and probably typical of good design and operation but not necessarily the most efficient.

Nitrogen Fertilizers

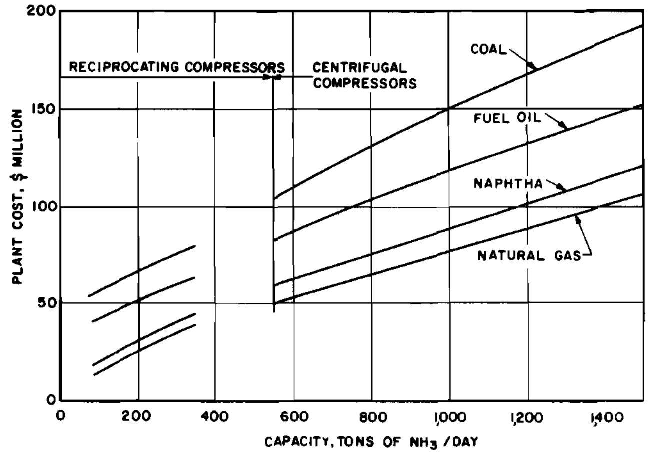
Ammonia

Estimated turnkey ammonia plant costs as affected by scale of operation and type of feedstock are shown in figure 1. The estimates are for an industrial location in a developed country. Costs for natural gas-based plants with capacities of 550, 1,000, and 1,360 tpd are considered the most reliable. Costs for smaller plants, 100 to 350 tpd, are less reliable since few have been built. Costs for 1,000-tpd plants using naphtha, heavy oil, and coal were obtained by multiplying the cost of the natural gas-based plant by a factor which was selected after reviewing several estimates and reports. For oil- and coal-based plants, costs for capacities in the range of 550 to 1,500 tpd were assumed to vary as the 0.6 power of capacity. The costs of naphtha-based plants in this range were obtained by applying a factor (1.14) to the cost of natural gas-based plants. In the range, 100 to 350 tpd, costs of plants using naphtha, oil, or coal were estimated by multiplying the cost of natural gas-based plants by factors of 1.14, 1.6, and 2.0, re-

TABLE 1. TYPICAL RAW MATERIAL AND UTILITY REQUIREMENTS PER TON OF PRODUCT

	Raw Materials							
	Kind	Quantity, ton	Supplies, $[a]	Steam, ton	Electricity, kWh	Cooling[b] Water, m^3	Boiler Feed Water, m^3	Fuel, 1,000 kcal
Ammonia	Natural gas	36 GJ	1.75	in balance	33	220	2.3	included in raw materials
Urea, prilled 46% N	NH_3 CO_2	0.575 0.760	2.33	1.2	125	70	-	-
Nitric acid, basis 100% HNO_3	NH_3	0.288	1.85	-0.4	9.5	87	8.5	-
Ammonium nitrate, 34% N	HNO_3 NH_3	0.773 0.210	1.50	0.2	20	8	-	-
Sulfuric acid, 100% H_2SO_4	S	0.34	0.50	-1.2	35	26	1.3	-
Phosphoric acid, basis/ton P_2O_5	Phosphate rock[c] H_2SO_4	3.22 2.78	1.00	1.9	150	150	-	-
Triple superphosphate 0-46-0	Phosphate rock[c] Acid P_2O_5	0.40 0.345	-	0.02	40	-	-	125
Diammonium phosphate 18-46-0	Acid P_2O_5 NH_3	0.47 0.224	-	-	30	-	-	125
Monoammonium phosphate 11-55-0	Acid P_2O_5 NH_3	0.56 0.137	-	-	30	-	-	125

a. Includes catalysts, chemicals, conditioners, etc.
b. Once-through basis.
c. Phosphate rock assumed to contain 33% P_2O_5.



Basis: Industrial location in developed country, Turnkey costs = battery-limits cost plus 50%.

Notes: The most reliable data are for natural gas-based and naphtha-based plant with capacities of 550, 900-1,140, and 1,360 tpd. Data for smaller plants and other feedstocks are more speculative because few such plants have been built.

Figure 1. Estimated Turnkey Plant Cost for Ammonia Plants as Affected by Capacity and Feedstock.

spectively. Little confidence should be placed in these values, but these are believed to be of the right order of magnitude.

In figure 1, a straight line is shown to represent costs for naphtha- or natural gas-based plants. However, if the curve were fitted to available data, it would be slightly concave because of greater experience in the 900- to 1,100-tpd range and consequent availability of standard designs. It is likely that costs for plants larger than 1,360 tpd would be substantially higher than indicated by extrapolation of the line in figure 1 because of the need for developing new engineering designs and using nonstandard equipment. However, a 2,000-tpd plant consisting of two 1,000-tpd trains should cost somewhat less per ton of capacity than a single 1,000-tpd plant because of lower nonbattery-limits costs.

There has been much less experience with plants using partial oxidation of coal or oil. Therefore, the curves for these were assumed to follow the 0.6 power (a more or less normal relationship for single-train plants), and the resulting curves are slightly convex. For reasons discussed previously, total plant costs in developing countries are likely to be higher than those indicated in figure 1.

The assumed heating values of ammonia feedstocks that were used in production cost estimates are tabulated below:

Feedstock	Low Heating Value	
Natural gas	8,015 kcal/m^3	33.56 GJ/1,000 m^3
Naphtha	10,556 kcal/kg	44.20 GJ/ton
Heavy fuel oil	9,722 kcal/kg	40.71 GJ/ton
Coal	6,333 kcal/kg	26.52 GJ/ton

The "low heating value" in the above tabulation is the heat of combustion not including the heat of condensation of water vapor in the combustion products, which cannot be usefully recovered in ammonia production processes. The heating value for natural gas is approximately that of methane (measured at 20°C and 1 atm); natural gas often contains higher hydrocarbons which increase the heating value per unit volume.

The total requirements for fuel and feedstock per ton of ammonia that were used in the present calculations are:

		Energy Equivalent	
	Requirement	Million kcal	GJ
Natural gas	1,073 m^3	8.6	36.0
Naphtha	0.89 ton	9.4	39.4
Heavy fuel oil	1.00 ton	9.7	40.7
Coal	1.97 ton	12.5	52.3

The fuel and feedstock requirements are for ammonia plants with good heat and energy recovery facilities, particularly for natural gas- and naphtha-based plants. In areas where low-cost fuel is available, it may be economical to use simpler, less efficient equipment at the expense of increased fuel and feedstock consumption (see chapter VI). All ammonia plants are assumed to be self-sufficient in steam and mechanical power. In the case of oil- and coal-based plants, a steam-generating plant is assumed to be part of the battery-limits ammonia plant: its capacity is assumed to be sufficient to supply all of the steam and power (mechanical or electrical) required by the process.

The estimated production cost of ammonia as affected by scale of operation and type of feedstock is shown in figure 2 assuming coal at $25/ton, oil at $80/ton, and natural gas at $0.053/m^3. The calculations for this figure were based on tables 7, 8, 9, and 10 of chapter VI. The figure indicates that 1,000 tpd may be near an economic optimum size for a single-train natural gas-based plant. However, multitrain plants (two, three, or more 1,000-tpd trains) presumably would produce ammonia at a lower cost although the increased cost of marketing the product over a wider area would have to be considered. In the cases of oil- and coal-based plants, the estimated production cost decreases with capacity up to and perhaps beyond 1,500 tpd.

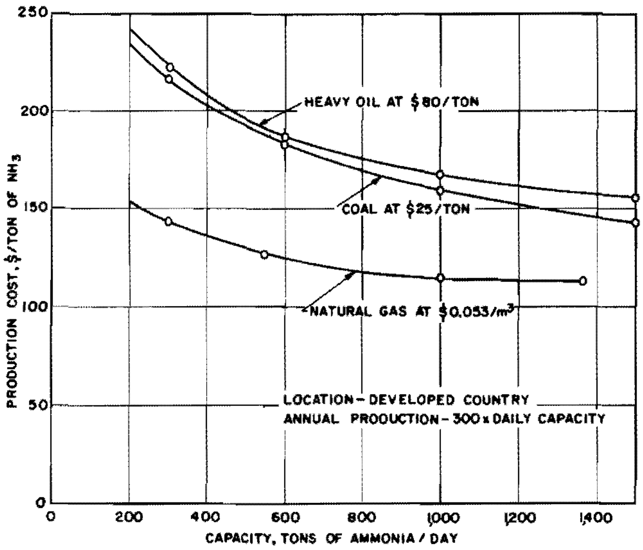


Figure 2. Effect of Type of Feedstock and Plant Capacity on Production Cost of Ammonia.

The effects of the cost of natural gas and of the capital cost of the plant on production cost and gate sale price of ammonia are shown in figures 3 and 4 which are identical with figures 9 and 10 of chapter VI and are reproduced here for convenience. Likewise, the effects of cost of natural gas, naphtha, heavy oil, and coal on production cost and gate sale price of ammonia is shown in figures 5 and 6, corresponding to figures 11 and 12 of chapter VI.

Figure 7 shows the effect of capacity utilization on the estimated production cost of ammonia plants using natural gas, naphtha, heavy oil, and coal as feedstock and fuel. Previous graphs have been based on an annual production of 300 times rated daily production. In figure 7 annual capacity is assumed to be 330 times daily capacity, a common assumption. It is quite possible to exceed 100% of rated annual production based on this definition, either by achieving more than 330 on-stream days per year or by producing more than the rated daily capacity or both. Ammonia plants often are designed to have some excess capacity as a margin of safety to ensure meeting guaranteed rates. The data for figure 7 were based on the "base cases" given in chapter VI and were calculated by assuming that the capital-related and labor-related costs were constant on an annual basis while all other costs were constant per ton of product.

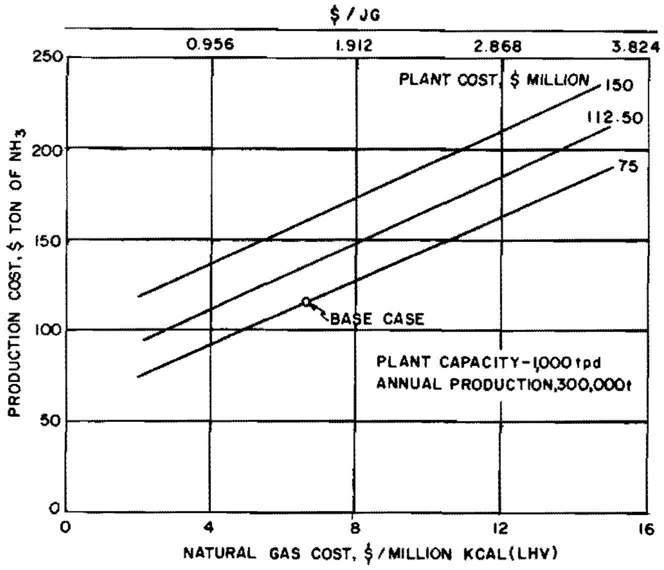


Figure 3. Effect of Plant Cost and Natural Gas Cost on Production Cost of Ammonia.

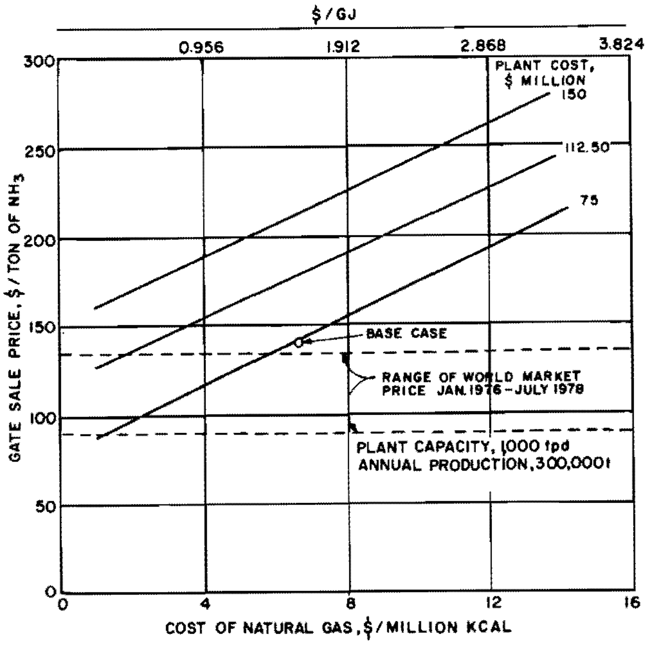


Figure 4. Effect of Plant Cost and Natural Gas Cost on Gate Sale Price of Ammonia.

As indicated in figure 7, operation at 60% capacity would increase the production cost in a natural gas-based plant by about $29/ton as compared with operation at 100% capacity ($140 versus $111/ton). Low capacity utilization would have a greater effect with other feedstocks. For instance, in a coal-based plant the production cost would be about $149/ton at 100% capacity as compared with $214/ton at 60% capacity, a difference of $65/ton. In a developing country, high capacity utilization is still more important because of the higher plant investment. Moreover, the effect of low capacity operation on the cost of urea in a urea-ammonia complex would be still greater

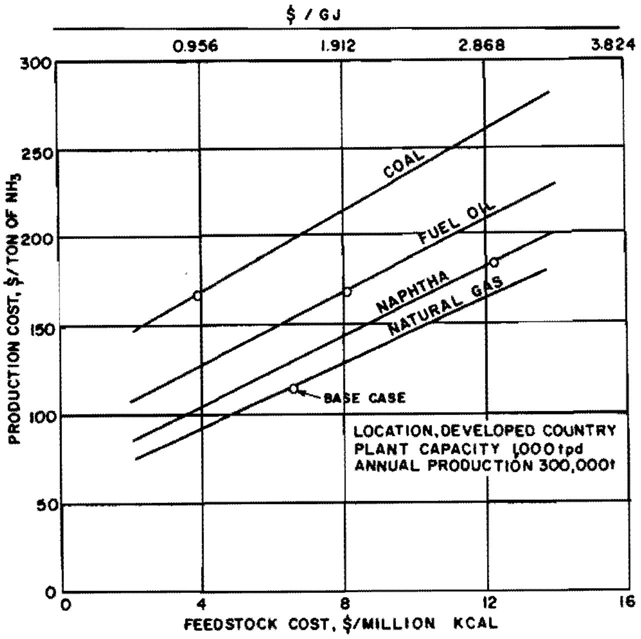


Figure 5. Effect of Price and Type of Feedstock on Production Cost of Ammonia.

since the capital-related costs of urea production would also be increased.

Urea-Ammonia Complexes

In many developing countries ammonia is used solely for production of urea; therefore, it is appropriate to consider the economics of such urea-ammonia complexes. The investment cost for such complexes is based on estimates in previous chapters.

Turnkey Investment Costs of Ammonia-Urea Complexes, $ Million (Estimated for a Developed Country)

Ammonia capacity, tpd	300	550	1,000
Urea capacity, tpd	522	956	1,739
Investment, $ million			
Ammonia	35.0	52.5	75.0
Urea	19.5	31.0	40.2
Product storage	1.5	3.0	5.1
Total	56.0	86.5	120.3

The production cost and gate sale price are calculated as in previous chapters except that the 5% administrative and miscellaneous cost is not added to the ammonia production cost, but it is added to the urea production cost (the final product). The results of these calculations are shown in figure 8 and in the following tabulation for operation at 90.9% capacity (300 times daily capacity).

Urea capacity, tpd	522	956	1,739
Production cost, $/ton of urea			
Ammonia, 0.575 ton	78.29	70.47	63.06
Operating costs	43.19	36.92	31.01
Subtotal	121.48	107.39	94.07
Adm. and misc. cost, 5%	6.07	5.37	4.70
Total production cost	127.55	112.76	98.77
10% ROI	35.76	30.18	23.06
Gate sale price	163.31	142.94	121.83

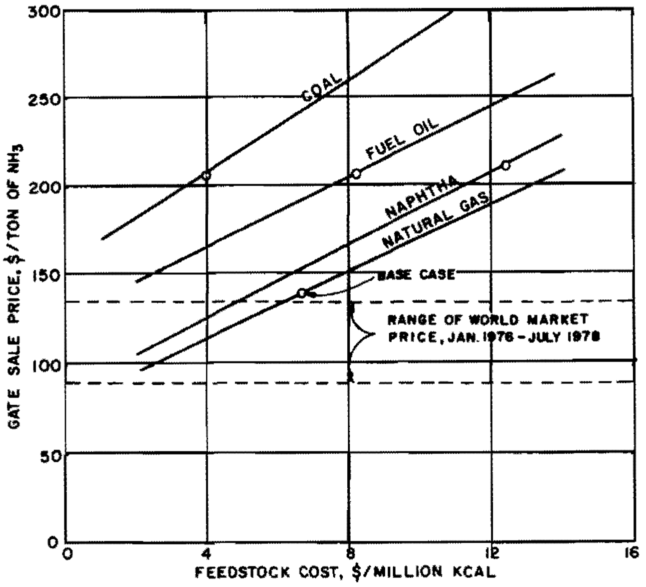


Figure 6. Effect of Type and Price of Feedstock on Gate Sale Price of Ammonia.

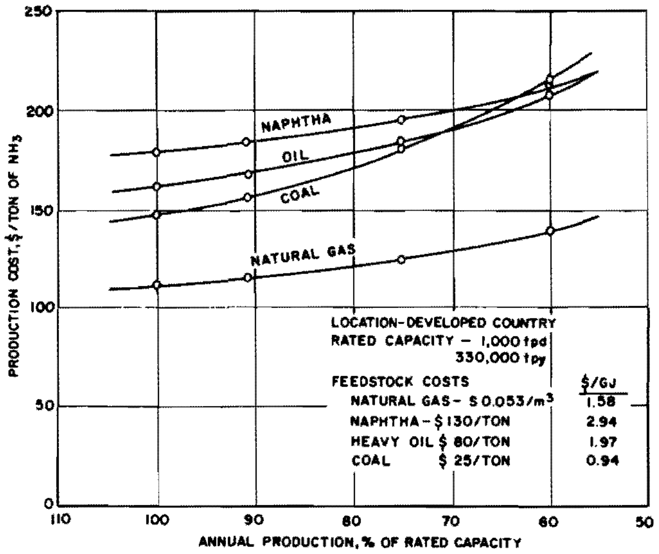


Figure 7. Effect of Capacity Utilization and Type of Feedstock on Estimated Production Cost of Ammonia.

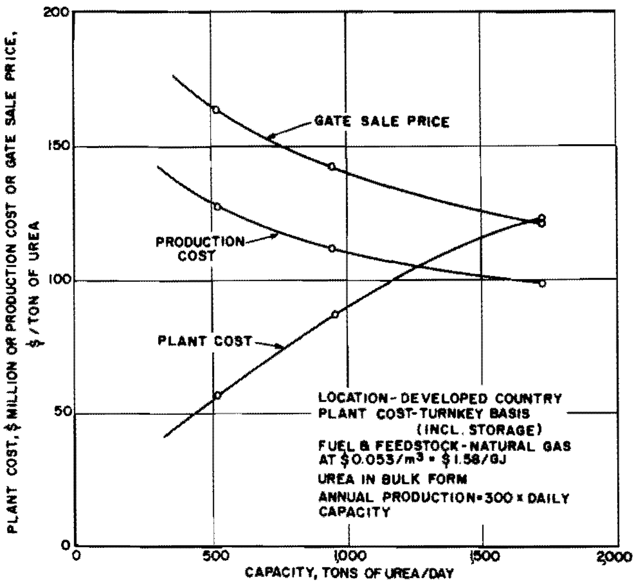


Figure 8. Plant Cost, Production Cost, and Gate Sale Price for Urea Produced in an Ammonia-Urea Complex as Affected by Capacity.

The effect of cost and type of feedstock on the gate sale price of urea produced in a 1,739-tpd ammonia-urea complex is shown in figure 9. The gate sale price is the production cost plus 10% return on investment. The lower portion of the figure shows estimated costs (prices) for an industrial location in a developed country, and the upper portion shows estimated prices in a location where cost of constructing the plant is 50% higher, which may be the case in some developing countries. The figure shows that urea costs in a developed country would be about the same ($161-$162/ton) for plants using coal at $0.94/GJ, oil at $1.97/GJ, and naphtha at $2.94/GJ. (These were the values selected for the base cases in chapter VI). Natural gas cost would have to rise to $3.50/GJ to bring the urea cost to a comparable level. Where natural gas costs are high, it may be advantageous to use a lower cost fuel for part of the requirements. For example, steam required in the urea plant can be generated in a coal-fired boiler.

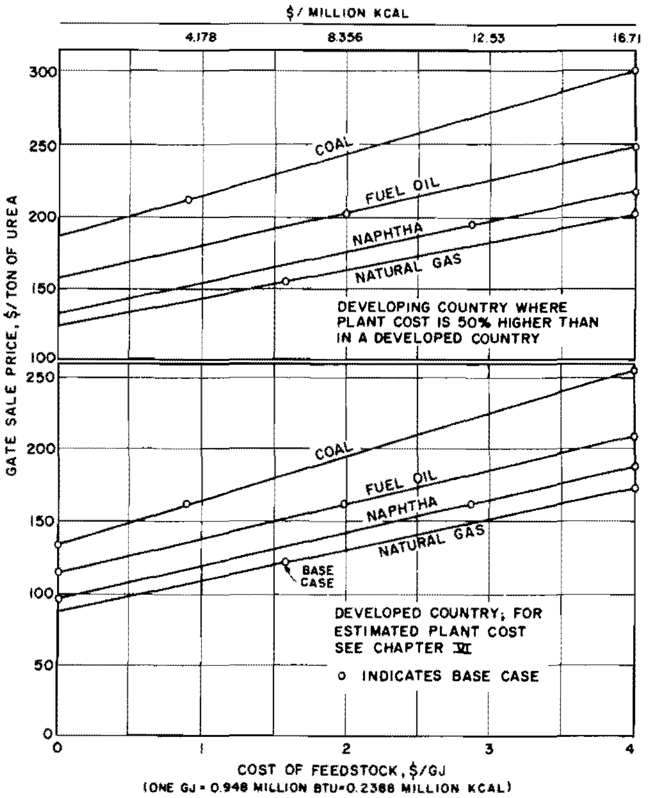


Figure 9. Effect of Type and Cost of Feedstock on Gate Sale Price of Bulk Urea in Developing and Developed Countries (Urea-Ammonia Complexes Producing 1,739 tpd; 521,700 tpy).

For high-cost plants (developing countries), all costs are higher, and coal is relatively less favorable; it gives the highest cost of the base cases.

In some developing countries, natural gas is available at costs in the range of $0.30-$0.60/GJ; resulting urea costs should be $130-$136/ton. The same cost is attainable in a developed country with gas costing $2.0-$2.3/GJ. Thus, the advantage of low-cost gas may be offset by the capital charges resulting from high plant costs. The above comparison does not apply to all developed or developing countries; it is intended only to indicate the effect of plant investment costs which may vary widely in countries that are more or less arbitrarily classified as developed and developing.

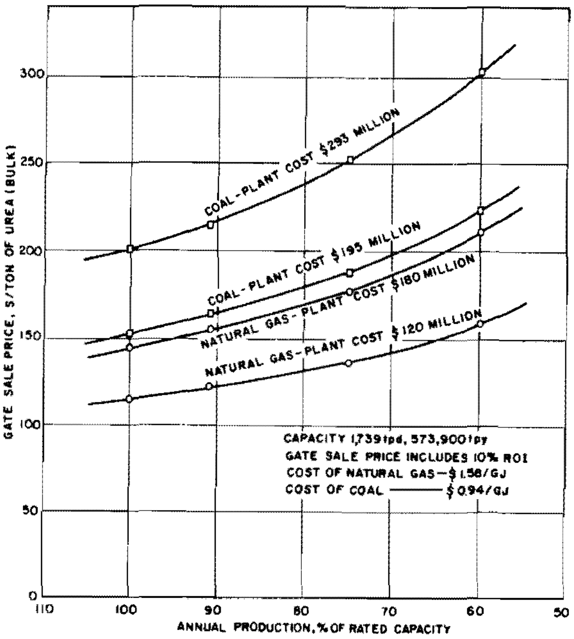


Figure 10. Effect of Plant Cost and Capacity Utilization on Gate Sale Price of Bulk Urea in a Urea-Ammonia Complex.

Figure 10 shows the effects of capacity utilization and plant cost on gate sale price of urea that is produced in 1,739-tpd ammonia-urea complexes using natural gas or coal feedstock. For natural gas-based complexes the estimated cost is $120 million in a typical developed country and $180 million (50% more) in a developing country location. For coal-based complexes the estimated plant costs are $195 and $293 million. The figure shows the drastic effect of low capacity utilization on urea costs, especially for complexes with high capital cost. In this connection, the world average capacity utilization for nitrogen fertilizer plants is about 90% for developed countries and 70% for developing countries, according to World Fertilizer Situation and Outlook, a publication (March 1979) by IFDC and TVA.

The combined effects of low capacity utilization and high plant cost can be particularly disastrous for a coal-based plant. A 60% capacity utilization rate would result in a gate sale price of $304/ton of bulk urea for the plant with the higher capital cost, whereas, in the case of the lower cost plant operated at 90% capacity, the urea price would be about $165/ton. The cost of feedstock (coal) is only $28/ton of urea; therefore, even if coal costs were reduced to zero, the economics would be unfavorable in locations where the plant cost is high and capacity utilization is low.

For natural gas-based complexes, the cost of natural gas (at $1.58/GJ) is $32.70/ton of urea. In some developing countries where low-cost natural gas is available, the cost per ton of urea may be as low as $10. However, the combined effect of low capacity utilization and high capital cost can more than offset this advantage. For example, if the gas costing $0.48/GJ is used in a $180 million complex at 70% capacity utilization, the estimated gate sale price would be about $165/ton. This price could be equaled in a developed country location ($120 million complex) with 90% capacity utilization with a gas cost of about $3.65/GJ or a naphtha cost of $3.00/GJ (see figure 9). This example illustrates the difficulty of realizing the potential advantages of low-cost natural gas in remote locations, particularly when there is little or no domestic demand for nitrogen fertilizer and the product must be shipped to other countries.

The importance of improving capacity utilization can be illustrated by the incremental cost of additional production. For example, if a $293 million coal-based plant is operating at 70% capacity, the estimated gate sale price is $267/ton of urea (figure 10). If capacity utilization can be increased without capital expenditure, each additional ton of urea would cost only about $42. This incremental cost is the cost of the additional feedstock, utilities, and supplies. In the natural gas-based complex, the incremental cost is about $46/ton of urea with gas at $1.58/GJ or $23 with gas at $0.48/GJ.

Urea is almost always produced in a complex that contains an ammonia plant which supplies the two essential raw materials, ammonia and carbon dioxide. However, in many cases urea is not the only product of the complex; part of the ammonia may be sold as such or converted to other nitrogen fertilizers or compound fertilizers. In such cases it is of interest to calculate the cost of urea production separately. Process requirements were discussed in chapter IX, and the economics of urea production was discussed in chapter XI. Figures 11, 12, and 13 show the estimated capital cost of urea plants and the production cost and gate sale price of urea as affected by scale of operation and ammonia cost. These figures are the same as figures 1, 2, and 3 of chapter XI and are reproduced here for the reader's convenience. For discussion see chapter XI.

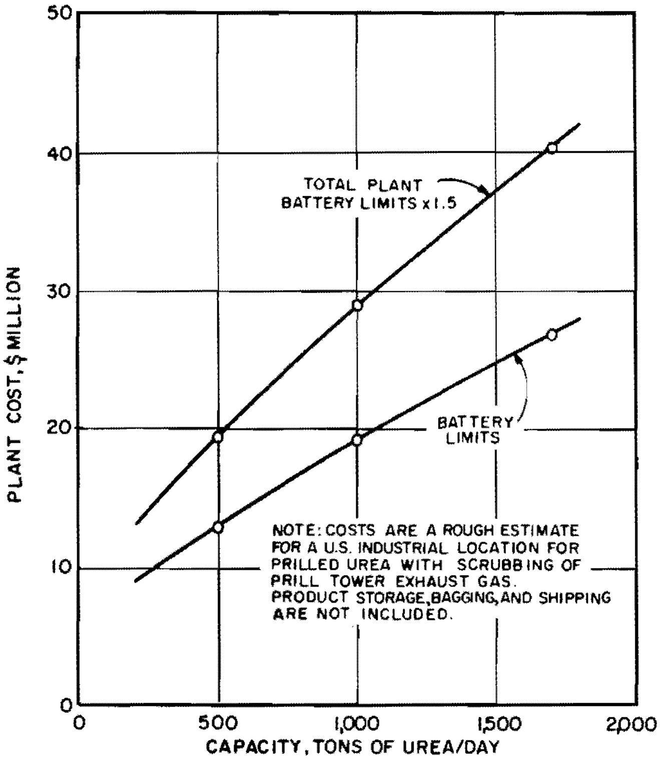


Figure 11. Estimated Cost of Urea Plants as Related to Capacity.

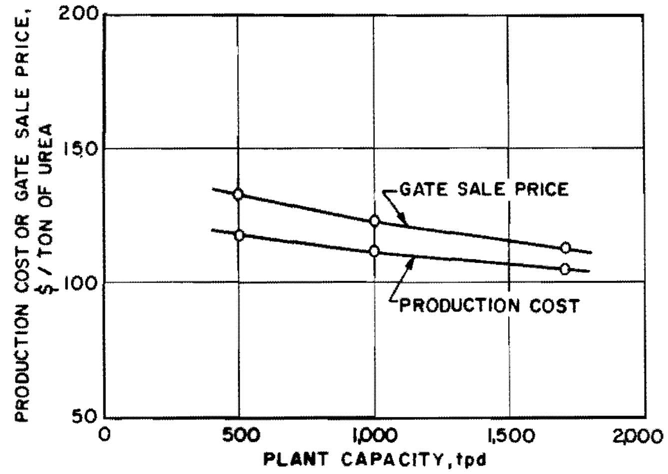


Figure 12. Effect of Plant Capacity of Production Cost and Gate Sale Price of Urea (Developed Country, 90% Capacity Utilization, Ammonia Cost—$120/ton).

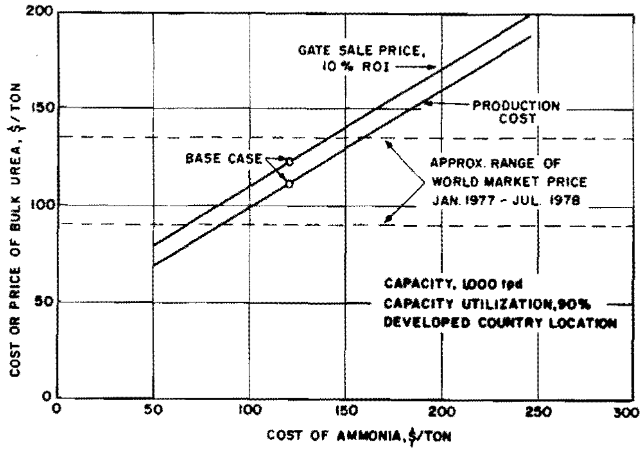


Figure 13. Effect of Ammonia Cost on Production Cost and Gate Sale Price of Urea.

Nitric Acid and Ammonium Nitrate

Ammonium nitrate is almost always produced in a complex containing a nitric acid plant since transportation of nitric acid is uneconomical because of its low concentration (about 13% N for 58% HNO_3). Unlike urea, the complex does not necessarily contain an ammonia plant, and in many cases ammonia is transported to the plant site from distant sources. Ammonium nitrate also may be produced as a coproduct with nitrophosphate as discussed in chapter XV. Figures 14, 15, and 16 (identical with figures 4, 5, and 6 of chapter XI) are reproduced here for convenience and show estimated nitric acid plant costs and production costs and ammonium nitrate production costs.

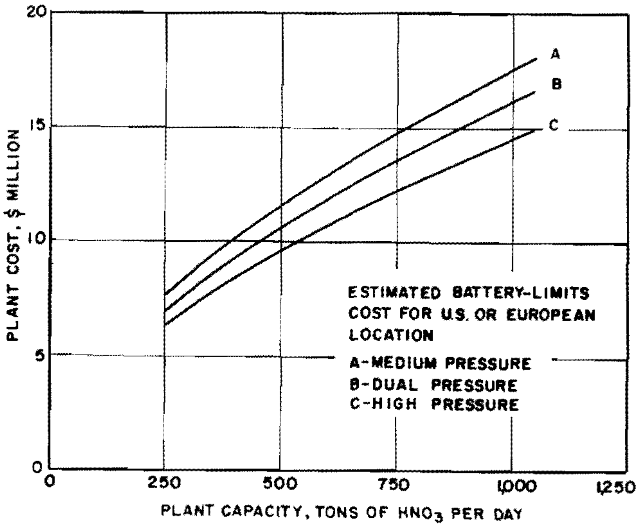


Figure 14. Effect of Type of Process and Plant Size on Cost of Nitric Acid Plants.

The estimated capital investments for turnkey nitric acid-ammonium nitrate (AN) complexes are tabulated below and shown in figure 17:

Capacity, tpd of AN (34% N)	323	647	1,353
Capacity, tpd of HNO_3	250	500	1,070
Capital investment, $ million			
HNO_3	9.75	14.60	23.00
AN	8.13	11.66	17.50
Storage	1.00	2.00	4.00
Total	18.88	28.26	44.50

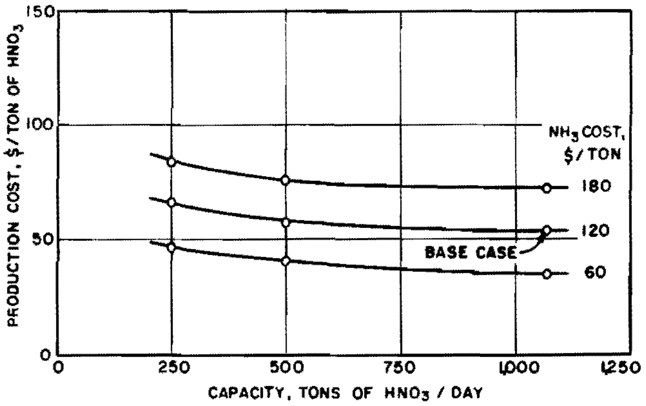


Figure 15. Effect of Plant Capacity and Ammonia Cost on Production Cost of Nitric Acid (High Pressure Process).

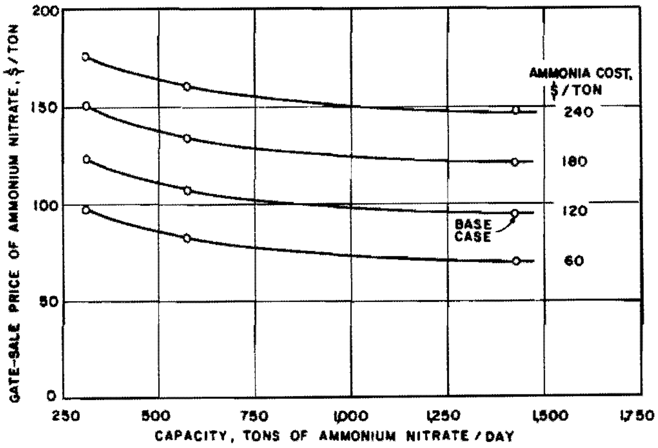


Figure 16. Effect of Plant Capacity and Ammonia Cost on Gate Sale Price of Bulk Ammonium Nitrate (34% N) for Nitric Acid-Ammonium Nitrate Complexes.

The 1,353-tpd complex would produce the same amount of nitrogen as a 1,000-tpd urea plant. The investment for a 1,000-tpd urea plant including storage is $32.5 million as compared with $44.5 million for an ammonium nitrate complex. Thus, ammonium nitrate facilities are more capital-intensive than urea facilities. However, as noted in chapter XI, ammonium nitrate can be produced from imported ammonia; whereas, urea cannot. Thus, countries that wish to minimize capital investment and/or take advantage of low-cost imported ammonia might well decide to produce ammonium nitrate. The AN investment curve in figure 17 cannot be safely extrapolated beyond about 1,600 tpd since the world's largest nitric acid plant has a capacity of 1,250 tpd of HNO_3 which would produce about 1,600 tpd of AN. For larger plants two nitric acid units may be required which would change the shape of the curve. The estimated cost of the nitric acid plants is for units with "extended absorption" that reduce the NO_x concentration to 200 ppm or less. The expense of this additional efficiency is not justifiable by economics, and its justification for pollution control is doubtful in view of the fact that nitric acid plants contribute no more than 1% of the NO_x discharged to the atmosphere. (Most of the NO_x comes from internal combustion engines, fuel-fired electric-generating plants, and natural sources.) Thus, in countries where pollution control standards are more flexible, a saving in nitric acid plant costs is possible provided that the NO_x concentration in the local ambient atmosphere is within acceptable limits (see chapter XXIII).

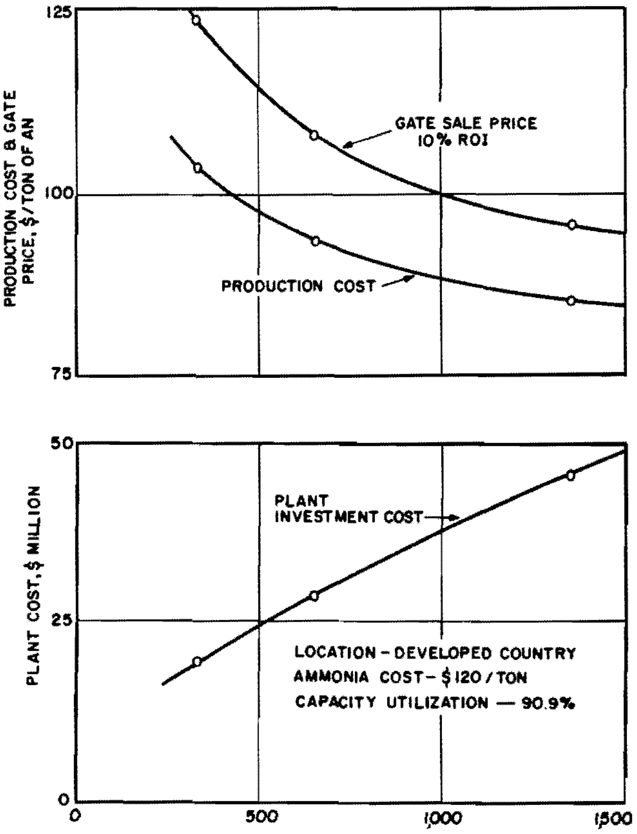


Figure 17. Estimated Plant Costs, Production Costs, and Gate Sale Prices of Ammonium Nitrate for Nitric Acid-Ammonium Nitrate Complexes.

Estimated production costs and gate sale prices for AN are shown in figure 17 for a developed country location assuming an ammonia cost of $120/ton. The cost is rather sensitive to scale, especially below 650 tpd. At 1,353 tpd the estimated gate sale price of bulk AN is $96; this corresponds to $130/ton of urea on an equivalent nitrogen basis. If bagging and transport costs were considered, the comparison would be less favorable to AN.

Phosphate Fertilizers

Sulfuric Acid

Estimated plant investment costs for sulfuric acid facilities are shown in figure 18 which is identical with figure 3 of chapter XII. These costs are for double-contact, double-absorption units in a developed country location. Estimated production costs were shown in tables 5 and 6 of chapter XII. However, these estimates did not use the standard assumptions listed in the present chapter; therefore, the production costs were recalculated for the purposes of figure 19. The differences were minor; for a base case of a 600-tpd plant operating at 90.9% capacity (300 times daily capacity) the difference was within a few cents per ton of the value given in table 5, chapter XII, because of offsetting adjustments. The recalculated production cost for the base case is tabulated below.

Production Cost, $/ton of H_2SO_4

Sulfur, 0.34 ton x $50	17.00
Catalyst and supplies	0.50
Electricity, 35 kWh x $0.027	0.95
Cooling water, 25.8 m^3 x $0.01	0.26
Boiler feedwater, 1.25 m^3 x $0.26	0.32
Labor-related costs, 0.16 man-hours x $17.60	2.81
Capital-related costs, 17.67%	9.81
Steam credit, 1.2 ton x $4.00	-4.80
Total production cost	26.85

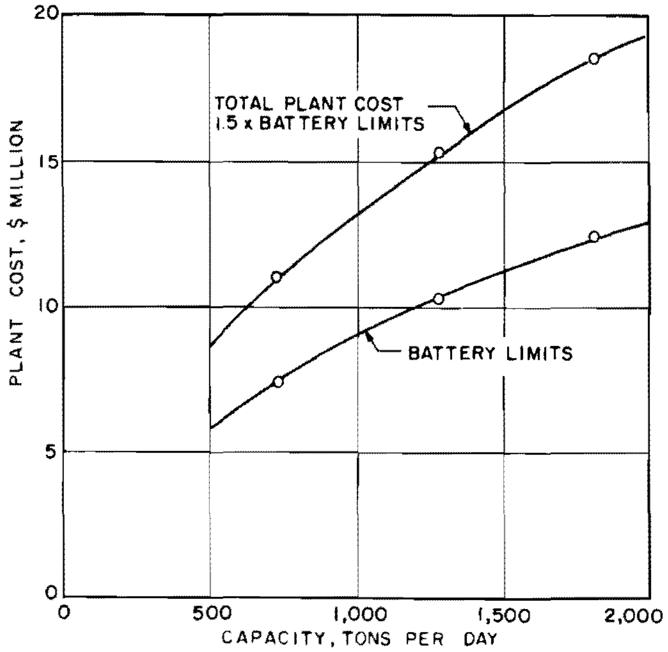


Figure 18. Capital Cost of Sulfur-Burning Sulfuric Acid Plants, Double Contact, U.S. or European Location.

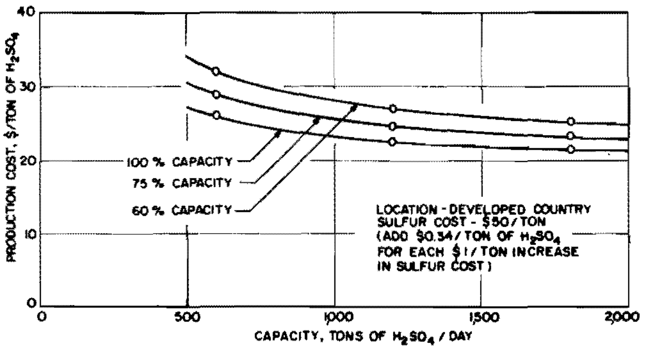


Figure 19. Estimated Production Cost of Sulfuric Acid as Affected by Plant Capacity and Capacity Utilization.

Phosphoric Acid

Estimated capital requirements are shown in figure 20, which is identical with figure 7, chapter XIII. The estimates are for a standard dihydrate-process plant. Facilities included and excluded were discussed in chapter XIII. Estimated operating costs, exclusive of raw materials costs, have been given in chapter XIII for a developing country location, and the costs for various combinations of phosphate rock and sulfuric acid were calculated. However, the estimates used somewhat different assumptions than the standard ones used in this chapter; thus, the production cost was recalculated for a developed country location with the following results for a base case:

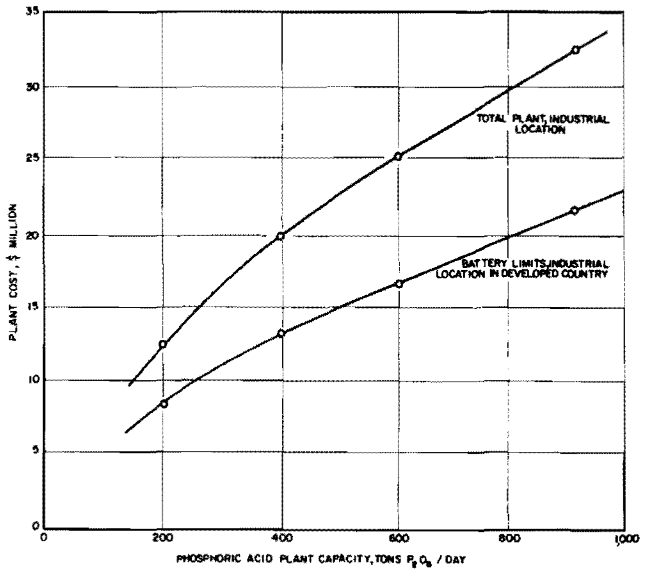


Figure 20. Estimated Cost of Wet-Process Phosphoric Acid Plants.

Estimated Production Cost of Phosphoric Acid (Base Case)
Plant capacity--400 tpd P_2O_5
(120,000 tpy = 90.9% capacity utilization)
Plant cost--$20 million, developed country location

		$/ton of P_2O_5
Phosphate rock, 33% P_2O_5	3.22 tons x $20	64.40
Sulfuric acid, 100% H_2SO_4	2.78 x $30	83.40
Chemicals and supplies[a]		1.00
Water[b]	150 m^3 x 0.1	1.50
Electricity[c]	150 kWh x 0.027	4.05
Steam[c]	1.9 ton x $4.00	7.60
Labor-related costs	0.36 man-hour x $17.60	6.34
Capital-related costs	17.67%	29.45
Subtotal		197.74
Adm. & misc. expense, 5% of subtotal		9.89
Production cost		207.63
10% ROI		16.67
Gate sale price		224.30

a. Includes antifoam chemicals.
b. Includes process water, recirculated cooling water, and recirculated pond water for scrubbing systems.
c. Steam usually is obtained from an onsite sulfuric acid plant, and part of the electricity may be generated by surplus steam or replaced by steam-turbine power.

Figure 21 shows the estimated operating cost for phosphoric acid production, not including raw materials, as affected by plant capacity and capacity utilization. The operating costs do not include a return on investment or administrative and miscellaneous costs. They are estimated for a developed country location. Figure 22 shows the effect of the cost of phosphate rock and sulfuric acid costs on production costs of phosphoric acid for a plant of 600 tpd of P_2O_5 capacity with an annual output of 180,000 tpy. For example, a production cost of $200/ton of P_2O_5 could be attained with phosphate rock at $20/ton and sulfuric acid at about $32/ton or with rock at $30/ton and acid at $21/ton. For comparison, the world mar-

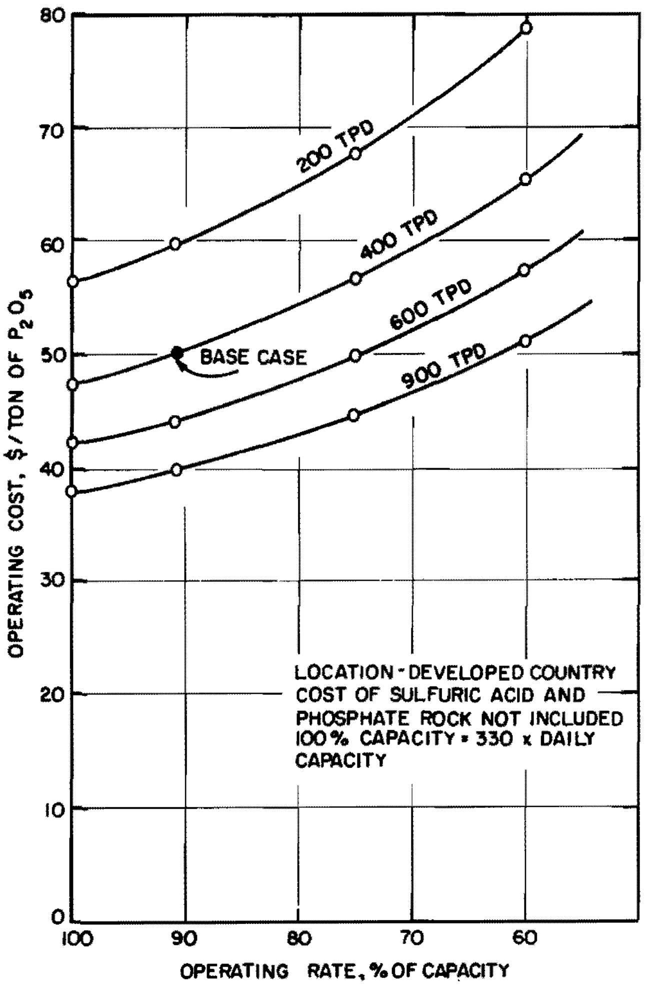


Figure 21. Operating Cost of Phosphoric Acid Plants as Affected by Capacity and Capacity Utilization.

ket price is about $220/ton (December 1978). However, additional costs would be involved in producing acid for shipment (clarification and shipping terminal costs).

TSP, DAP, and MAP

Figure 23 shows estimated turnkey plant costs (1.5 times battery limits costs) of TSP, DAP, and MAP production by slurry processes. As discussed in chapter XIV, lower cost processes are available such as the melt process for MAP or APP, the pipe reactor process for DAP, and the ex-den granulation process for TSP. However, these processes are relatively new and little commercial-scale experience is available. Also, they may lack versatility. For discussion of operating costs and process requirements of these processes, see chapter XIV.

Phosphate Complexes

Unlike urea-ammonia complexes, phosphate complexes seldom produce a single product. In an export-oriented complex, several products may be manufactured to supply various markets--phosphoric acid, nongranular MAP, granular MAP, DAP, and TSP, e.g., or some combination of these products. When intended for domestic markets, the products may be any of those mentioned above or, quite often, a series of compound fertilizers. In this chapter, two types of complexes are considered--sulfuric acid-phosphoric acid-TSP and sulfuric acid-phosphoric acid-DAP. With very minor changes, the latter complex could also produce granular MAP. The estimated investment cost

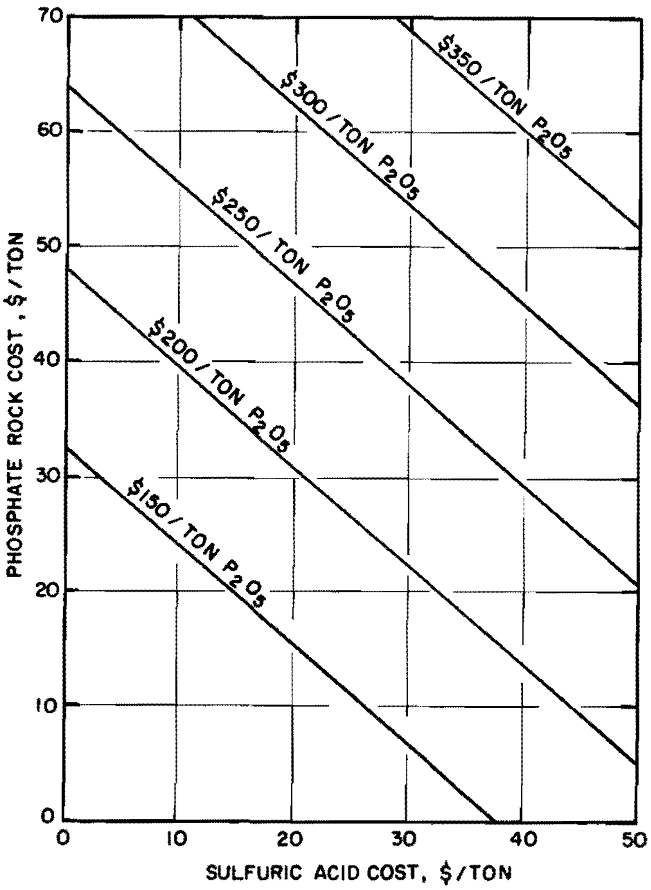


Figure 22. Production Cost of Phosphoric Acid for Various Combinations of Sulfuric Acid and Phosphate Rock Cost; Location—Developed Country; Rock Grade—33% P_2O_5; Plant Capacity—600 tpd; Operating Rate—180,000 tpy.

of the complexes is shown in the following tabulation and in figure 24.

	Cost, $ Million			
P_2O_5 in DAP, tpd	200	400	600	800
Sulfuric acid plant	9.6	14.2	18.5	22.7[a]
Phosphoric acid plant	12.6	20.0	25.4	29.7
DAP plant	7.1	10.9	13.6	17.4[b]
Product storage	1.1	2.3	3.4	4.5
Total DAP complex[c]	30.4	47.4	60.9	74.3
P_2O_5 in TSP, tpd	274	548	822	1,096
TSP plant	10.9	15.6	22.1[b]	25.0[b]
Product storage	1.6	3.1	4.7	6.1
Total TSP complex[d]	34.7	52.9	70.7	83.5

a. Two sulfuric acid units assumed.
b. Two granulation units assumed.
c. Does not include NH_3 terminal and NH_3 storage facilities.
d. Includes H_2SO_4 and H_3PO_4 production facilities listed above.

The estimated production cost of DAP or TSP in a phosphate complex has been calculated on the basis of data in preceding chapters and in the present chapter, using the estimated capital cost shown in figure 24. In this calculation, administrative and miscellaneous costs were added to the final product only (not to intermediate products). Also, steam was assumed to be in balance for the complex as a whole, and no charge or credit for steam was involved. The base case involved production of 400 tpd of P_2O_5 as phosphoric acid, with production of 870 tpd of DAP

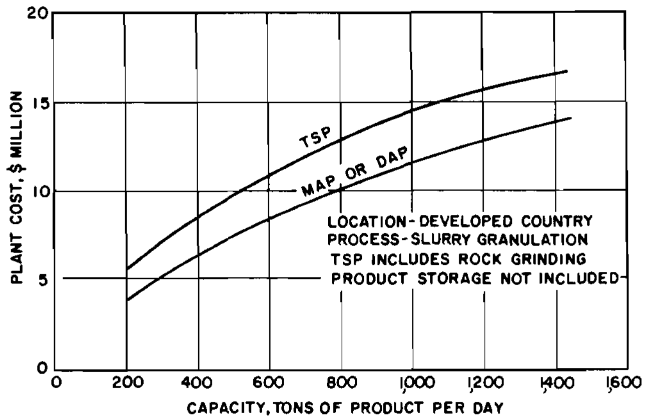


Figure 23. Estimated Cost of Plants for Producing TSP, MAP, or DAP.

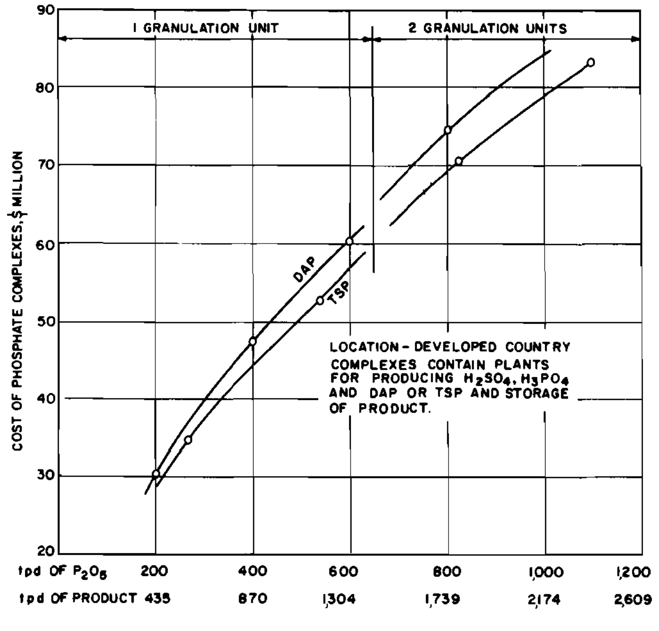


Figure 24. Estimated Cost of Phosphate Fertilizer Complexes.

or 1,191 tpd of TSP. Raw material requirements were adjusted to allow for 3% P_2O_5 loss in conversion of phosphoric acid to the final product. Calculations for the base case are summarized below:

Phosphate Complex, Base Case
(400 tpd of P_2O_5 as H_3PO_4)

Capital cost, DAP--$47.4 million; TSP--$52.4 million
Production rate, DAP--870 tpd, 261,000 tpy
Production rate, TSP--1,191 tpd, 357,300 tpy

	$/ton of Product	
	DAP (18-46-0)	TSP (0-46-0)
Sulfur @ $50/ton	22.39	16.35
Phosphate rock @ $20/ton	30.51	30.27
Ammonia @ $120/ton	26.88	-
Total raw materials	(79.78)	(46.62)
Utilities, fuel, supplies, etc.	7.22	6.54
Labor-related costs	10.20	7.97
Capital-related costs	32.09	26.16
Subtotal	129.29	87.29
Adm. & gen. expense, 5%	6.46	4.36
Production cost	135.75	91.65
ROI, 10%	18.16	14.67
Gate sale price (bulk)	153.91	106.32

In the base case above, labor- and capital-related costs are higher per ton of product for DAP because the calculations are based on the same amount of P_2O_5 input as phosphoric acid. The additional P_2O_5 input as phosphate rock in the case of TSP results in a larger scale of operation and higher output of P_2O_5. The increased scale of operation results in lower costs per ton of product for TSP relative to DAP.

An alternative method for comparison would be on the basis of the same production of product P_2O_5. In this case a smaller input of phosphoric acid would be required for TSP than for DAP, and unit costs for phosphoric acid would increase. Comparisons of this type were given in chapters XIV and XVII.

The production cost was calculated for plant capacities ranging from 200 to 800 tpd of P_2O_5 as phosphoric acid which would provide 200-800 tpd of P_2O_5 as DAP or 274-1,096 tpd of P_2O_5 as TSP. The results are shown in figure 25 in terms of production cost per ton of product and per ton of nutrient (N + P_2O_5). By coincidence, the production cost per ton of nutrient is about the same for TSP and DAP and is represented by a single line. However, this coincidence depends on the assumed cost of the raw materials, particularly sulfur and ammonia (about the same amount of phosphate rock is required for each product). The cost of the raw materials comprises about half of the production cost of both products in the base case estimate. A 50% increase in capital-related costs, which could occur in some developing countries, would add about $16/ton to the production cost of DAP or $13/ton for TSP. The production cost per ton of nutrient (N + P_2O_5) is not a satisfactory basis for comparison of the relative merits of DAP and TSP. Criteria for comparison of these and other products were discussed in chapters XIV and XVII.

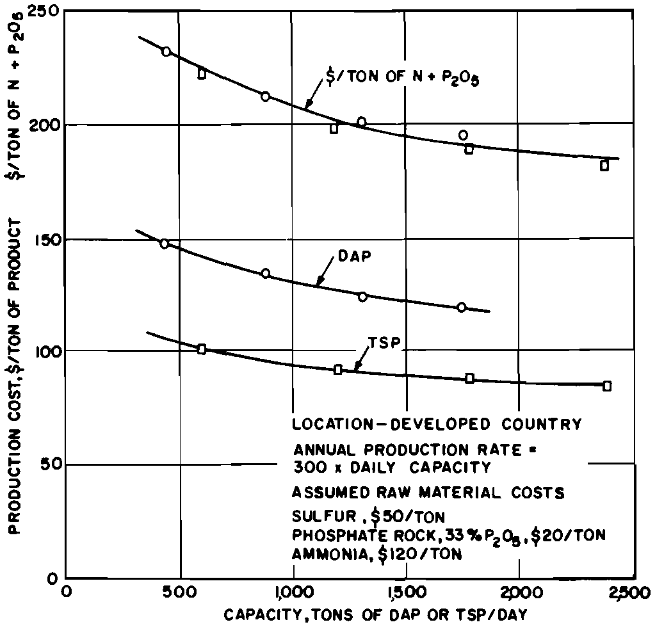


Figure 25. Estimated Production Cost of DAP or TSP Produced in a Phosphate Complex.

The effect of capacity utilization on production cost and gate sale price of TSP in a phosphate complex located in a developed country is shown in figure 26. The calculations were based on a capacity of 1,191 tpd of TSP corresponding to a phosphoric acid capacity of about 400 tpd of P_2O_5.

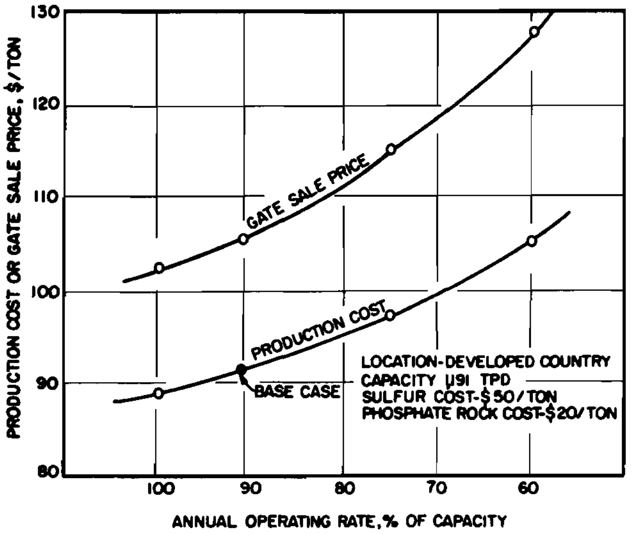


Figure 26. Effect of Capacity Utilization on Production Cost and Gate Sale Price of TSP (bulk, 46%, P_2O_5). Based on a Complex Containing Facilities for Production of Sulfuric Acid, Phosphoric Acid, and TSP (Slurry Granulation Process).

Other Fertilizer Products

The economics of production of other fertilizer products was discussed in previous chapters within limitations of available data and will not be repeated here.

XXVI Problems Facing the World Fertilizer Industry

A worldwide consultation meeting on the fertilizer industry was held by UNIDO in January 1977 to discuss ways and means of increasing fertilizer production in developing countries and to consider the problems facing the industry. The purpose of this chapter is to report some of the problems identified at this meeting and give some suggestions for dealing with them.

Need for More Fertilizer

It is a platitude to state that increased output from agriculture requires essentially addition of plant nutrients to the soil. It is like stating that human beings need food to survive and improve their health. Estimates show that the broad order of magnitude of increase in the use of all fertilizer nutrients (NPK) which can be expected in the period 1975-2000, compared with that achieved in the past 25 years, is as follows:

	Population (Billions)			Fertilizer Use, NPK Million Tons			Fertilizer Use, kg per Capita		
	1950	1975	2000	1950	1975	2000	1950	1975	2000
Developed countries	0.86	1.13	1.35	13	62	171	15	55	126
Developing countries	1.64	2.84	4.89	1	20	92	0.6	7	19
Total world[a]	2.50	3.97	6.24	14	82	263	-	-	-

a. See chapter II for further details of projections, including application rate, kg/ha.

This estimate suggests that consumption of fertilizers in developed countries by the year 2000 will be 2.8 times the 1975 level; the 1975 level was 4.8 times the 1950 level. In developing countries the consumption is estimated to increase to 4.6 times from 1975 to the year 2000. However, because of the estimated increase in population, the per capita consumption of fertilizer in developing countries (including China) is expected to be only 2.7 times the 1975 level by the year 2000. The application rate in kilograms per hectare in the year 2000 is expected to be 332 and 83 for developed and developing countries, respectively. The estimate is based on projected demand, not on requirements to provide the higher standard of nutrition that the increased population will need. Requirements based on population growth and nutritional needs may well be higher.

In 1975 the developing countries consumed about 30% of the N and 22% of the P_2O_5 supplied by the world fertilizer industry; however, they produced only two-thirds of this fertilizer themselves and contributed only 18% of world production of N and a lesser percentage of P_2O_5 fertilizers.

By the year 2000, the estimate suggests that the developing countries will consume about 92 million tons of fertilizer nutrients or about 35% of the world consumption. It was suggested that the developing countries should set a minimum goal of increasing fertilizer production sufficiently to supply their needs by the year 2000, or earlier, if possible. The report did not imply that each developing country should be self-sufficient in fertilizer production, only that developing countries as a group should set a goal of self-sufficiency.

From the above discussions, whether a forecast of a higher or lower figure is taken for world demand for NPK in the year 2000, the increased need to produce and use more fertilizer is evident.

Infrastructure Difficulties

The problems facing the world fertilizer industry, particularly in developing countries, were discussed in detail during UNIDO's First and Second Consultation Meetings on the fertilizer industry which were held in January 1977 and November 1978, respectively. The consensus reached is reflected in the following paragraphs (1).

> The Consultation Meeting recognized that the major programme of construction of fertilizer plants in developing countries that has already started would necessitate the building up of an adequate infrastructure. The Consultation Meeting considered various aspects of infrastructure planning. They included:
>
> 1. Transportation infrastructure (roads, railways, port facilities, railway rolling stock, and ships);
> 2. Utilities infrastructure (power supply, water supply, and a drainage and sewage system);
> 3. Raw materials infrastructure (critical raw material inputs, particularly feedstocks);
> 4. Marketing infrastructure (storage facilities and a distribution network that would make it possible for the product to reach the farms);
> 5. Infrastructure of agricultural extension services and modern agronomic practices;
> 6. Human infrastructure (entrepreneurial skills, managerial skills, and maintenance and operation skills);
> 7. Policy infrastructure (the broad framework of government planning, laws, and pricing and economic policies).
>
> The Consultation Meeting felt that the construction of fertilizer plants would be greatly facilitated if there were a composite infrastructure including the types described above. In locating fertilizer plants in developing countries, it would therefore be desirable to place them in areas where infrastructural facilities already existed.

When the specific location of plants within individual developing countries was being considered, local infrastructure should be taken into account.

Although the Consultation Meeting emphasized the need for a composite infrastructure, it appreciated that the creation of an infrastructure could not be related solely to fertilizer plants. The infrastructure would be part of overall internal planning and development and would be required to support a variety of industries within the regional and national plans.

The Meeting recognized that the absence of an infrastructure should not be allowed to inhibit decisions to set up plants. On the other hand, the Meeting felt that the setting up of plants would assist in the overall economic development of less developed areas and would stimulate the creation of an infrastructure.

Considering the costs involved in establishing an infrastructure and the need to produce fertilizers cheaply so that they would be within the reach of the farmer, the Consultation Meeting was of the view that it would not be correct to expect fertilizer projects to bear the total costs of infrastructure. There was a need to define and demarcate clearly those items of infrastructure that should fall within the responsibility of the State and public authority and that should consequently be financed from the public exchequer and items of infrastructure which were directly associated with fertilizer projects.

The Meeting recognized that the conditions and practices in different developing countries would not be identical and that the demarcation of the State's and project's areas of responsibility would therefore have to be adjusted to local conditions. It was generally felt, however, that the public authority should assume responsibility for the basic physical, transportation, and utilities infrastructures up to the site boundary. The projects should assume responsibility for the marketing infrastructure and the environmental infrastructure, including the disposal of effluents. There would be joint responsibility for the building up of the human infrastructure: the State would provide the basic facilities for training and development, and the projects would assume responsibility for the specialized skills required for fertilizer plants.

The Consultation Meeting felt that the demarcation must be so arranged as to reduce, as far as possible, capital costs in fertilizer projects and, consequently, total production costs.

The Consultation Meeting emphasized the need for a clearly defined policy infrastructure and suggested that developing countries should work out a scheme of laws, regulations, and economic and planning policies that would facilitate the growth of the fertilizer industry.

The Consultation Meeting recognized that the development of human skills was most important. It suggested that managers and workers should participate at all stages of project conception, planning, and implementation. The Consultation Meeting also suggested that measures should also be included for the health and safety of workers and the protection of the environment and that the relevant International Labor Organization (ILO) conventions should be duly observed.

The main recommendation was that efforts must be made to reduce infrastructure costs by apportioning them between fertilizer projects and state and public authorities. The advantages and cost reduction by building centrally located large fertilizer plants to supply satellite units and to add new capacities to existing projects rather than to start "grass-roots" plants in "green fields" are discussed later.

Delays in Constructing Fertilizer Projects and Bringing Them Into Production

During the last few years, much study, research, and development have been devoted to finding ways to reduce delays in construction and bringing into production at full capacity new fertilizer projects. Experience shows that the time lag from the date that finances are obtained and orders placed to the date production starts in a project involving a 1,000-tpd ammonia plant and 1,650-tpd urea plant is 2 years in a developed country; whereas, it is about 4 years in a developing country. The time lag between feasibility studies, issues and analyses of tenders, preparation of a bankable project submission, assessment of the economic and social returns to the time finances are obtained, and orders placed is 1-3 years. Thus, an average of 5-7 years elapses between the feasibility study and first starting of trial production. The experience in developing countries of many projects based on natural gas or naphtha is that, during the first year of operation, the production is only 60% of designed or "name-plate" capacity, 70% in the second year, and so on. Coal-based plants may have an even poorer record. It is very rare to see a project in developing countries which comes to 100% of the designed or "name-plate" capacity in the first year of production; whereas, in developed countries the projects often but not always attain 100% capacity in the first year. Various attempts and measures have been suggested to reduce the time lag in developing countries and thereby avoid the losses due to not only the blocking up of capital but also production losses which may entail loss of income from products to be exported or, in countries with large demand, drain on foreign exchange balances for importing fertilizers.

Other reasons claimed for the delays in developing countries are the delays in supply of local equipment; availability of trained manpower; and supply of electric power, water, and raw materials. Transportation bottlenecks and other infrastructure problems are serious in "grass-roots" or remote locations.

It is therefore logical to ask the question in countries where few fertilizer projects are already in existence whether the time lag in construction and erection can considerably be reduced if the existing units with infrastructure and trained personnel are allowed to expand or allowed to build additional parallel units. In any case, "grass-roots" plants are estimated to cost about 40% more than other plants, if expansion or parallel capacities are built in existing plant locations. However, the saving in construction time and cost by expansion of existing plants must be balanced against the increased cost of transporting the product over a wider market area.

Full Utilization of Existing Capacities

One of the most important problems facing fertilizer projects in developing countries is underutilization of existing capacities. It has been estimated that if the existing projects fully utilized their capacities the developing countries as a group would be self-sufficient in nitrogen fertilizers or nearly so.

There are various reasons why an ammonia plant and an associated urea plant using modern technology are unable to attain and sustain 100% of the designed or "name-plate" capacity. There are internal and external reasons.

The internal reasons are:

1. Problems arising from faults in plant design and inadequacies of equipment:

   One of the major precautions to be taken when setting up fertilizer plants would be to design them on the basis of a careful analysis of basic data. A wrongly conceived or faultily designed plant will experience problems of operation. The need to prepare feasibility studies and project reports so as to ensure that viable and efficient fertilizer plants are installed was emphasized. Studies and reports should be followed by the selection of reputable contractors, the adoption of proved technologies, and the careful drawing up of bid documents and proper contracts.

2. Problems caused by faulty maintenance:

   The Consultation Meeting noted that one of the keys to fuller utilization of capacity and higher operational efficiency was a regular system of preventive maintenance backed by trained manpower and a regular flow of spare parts. The Meeting was of the view that contractors and consulting engineers should assist buyers to draw up schedules of maintenance and should provide lists of critical spare parts that should be carried in stock. Because of difficulties in obtaining spare parts, developing countries should, with the assistance of contractors, ensure that their workshops were so equipped that spare parts could be manufactured locally wherever possible. The developing countries should also shorten the procedures for importing urgently required spare parts.

3. Problems caused by inadequately trained operation and maintenance personnel:

   The Consultation Meeting recognized that the development of skilled manpower was essential if fertilizer plants were to operate efficiently. The manpower would include plant management staff, plant operators, and maintenance staff. It would be necessary to train personnel well in advance of the commissioning of plants. There was also a need for a continuous process of training.

4. Inadequate supply and high prices of raw materials and spare parts.

The external reasons are:

1. Market constraints:

   The Meeting noted that capacity could be underutilized if no adequate arrangements were made for the local, regional, or international marketing of the product. The problem is of special significance in developing countries that were installing capacity mainly for export.

2. Inadequate infrastructure:

   The most important factors affecting high utilization of capacity in many countries are transport and storage bottlenecks, insufficient and fluctuating supply of electric power and, most importantly, supply of good quality water. It has been reported that the poor quality of demineralized water used for boiler feed and closed circuit cooling is reducing efficiencies of turbines and heat exchangers. It is a step in the right direction that many developing countries are providing captive power units with fertilizer projects to ensure a dependable supply of electric power.

3. Cyclical and inequitable prices of fertilizers:

   In developing countries with large internal demand, unless grain prices give a reasonable return to farmers using fertilizers and unless fertilizers reach the large number of subsistent-level farmers who now seldom use them or use inadequately or inefficiently, demand will not grow.

Contracting Procedures

The recent Technical Seminar on Contracting Methods and Insurance Schemes for Fertilizer and Chemical Process Industries, Lahore, Pakistan, November 25-29, 1977, (see Document No. ID/WG.259/26) highlighted contract procedures intended to ensure the successful construction and operation of fertilizer plants. Many countries that are planning construction of fertilizer plants do not fully know how to protect their interests. Although guarantees, penalties, bonuses, and liabilities for machinery breakdown during the first year of operation and arbitration procedures are well known to countries having long experience, it is necessary to identify the drawbacks, if any, and correct them at an early stage.

An important question being considered by the UNIDO and other UN agencies is how to compensate a large fertilizer project costing, e.g., $200 million, for consequential losses for whatever causes by insurance in which the buyer, the seller, the countries involved, and the financing institutions can take part. Commercial insurance companies will hesitate to enter the field and quote premiums unless the exact reason and responsibility for losses can be identified. The premiums will undoubtedly be high, and fixing cause and responsibility for consequential losses is difficult and time consuming.

Another approach, which has been suggested, is to create a fund supervised by an international agency to which all fertilizer projects being built in the world will pay a premium. The fund will then compensate any project which suffers consequential losses due to faults of any party. It is not an easy approach, but it is well worth considering. It is noted that while many developed countries cover the investments and loans they or contractors make to developing countries, the buyers in developing countries have no guarantee that the large sums they invest will produce goods and returns as foreseen. In this connection it was suggested that protection from consequential losses is also a responsibility and should be an aim of supplier countries and financial institutions which will ensure the productive use of their money and services.

Rising Capital and Raw Material Costs

Five to ten years ago, a 1,000-tpd ammonia plant and a 1,700-tpd urea plant could be installed in a developing country for about $90-$100 million. The present costs may range from $180 million to $330 million depending on the remoteness of the site and the extent of infrastructure development. Raw material costs have also increased sharply, especially that of imported ammonia feedstocks.

For those developing countries that have already built large fertilizer projects, one way to reduce total investments in new fertilizer production capacity is to build the capacities parallel to or adjoining existing facilities. These existing units already have trained manpower, infrastructure, marketing and storage experience, raw material availability, and above all trained and well-informed management. However, the cost of transporting and marketing the products must be considered. Expanding production at existing sites will involve greater marketing costs than dispersal of production sites in market areas. Thus, the choice is likely to depend on the transportation and distribution system (see chapter XXIV).

Financing

It has often been stated that a well-conceived, viable fertilizer project, either export oriented or internal market oriented, will have no difficulty in obtaining bilateral, multilateral, or international financing. This is well demonstrated by financing statements by The World Bank, Asian Development Bank, the German Kreditanstalt fur Wiederaufbau, and others.

A summary of projects financed by The World Bank and Industrial Development Association (IDA) in the years 1974, 1975, and 1976 shows that loans for fertilizer plants totaled $807 million, which was about 45% of total loans by these agencies for all industrial projects.

It is, therefore, safe to say that for "credit worthy countries" building large viable fertilizer projects financing is not a constraint. But this is not true in the case of so-called "non-credit worthy countries" or countries which are landlocked or island countries which do not have cheap raw materials, "know-how," or large internal demand. Many such countries want to build ammonia plants of capacities from 100 tpd to 300 tpd using fuel oil, coal, electric power, or other available raw materials. They find it difficult to locate finances at reasonable rates and also engineering and constructing firms willing to undertake and build such projects. Those firms that are willing to help seek high rates of return and the costs to such countries is disproportionally higher. These are the countries which need regional, interregional, and international assistance.

Cyclic Nature of World Fertilizer Prices

We are all aware of this phenomenon. Many experts are predicting that we are going through such a cycle right now. After the traumatic experiences of 1974 and 1975 when price of urea, f.o.b., went up as high as $300/ton and the supply position in the world deteriorated, both developed and developing countries wish that prices, as well as supply and demand, would remain at equitable levels.

For the continued improvement in effective demand and use of fertilizers in developing countries, it is necessary to have an advantageous ratio between the price of grains and fertilizers. There is no way to increase food grain prices in many developing countries since the purchasing power of the vast majority of the population is stagnant. Therefore, fertilizer prices must be maintained at a reasonable level. Further, yields must be improved and a larger number of farmers must be induced to use fertilizer and other inputs not only by credit, demonstrations, and availability at reasonable prices but also by reasonable price of agricultural products.

As is well known, United Nations Conference on Trade and Development (UNCTAD) and FAO are discussing buffer stocks not only for agricultural products but also for agricultural inputs such as fertilizers. Price equalization or stabilization commodity funds are also an outcome of the North South negotiations in Paris recently.

Both FAO and UNIDO have proposed long-term purchase option schemes to ensure an adequate supply of fertilizers to developing countries, especially those most seriously affected by fertilizer shortages. UNIDO's "option scheme" for fertilizer would work as follows. Every developed country or companies or organizations in such countries like Japan, United States, and Europe pledge a certain percentage of their production to the "option scheme." These amounts will represent the excess over the internal demand. Developing countries will then call on these quantities pledged to the "option scheme" at prices to be negotiated on a long-range basis but with mutual understanding for escalations. In such a scheme, the developed countries may be able to run their plants even up to 110% of their installed capacity while meeting their internal demand which may be equivalent to 80% capacity. Thus, they will be able to reduce production costs, and developing countries will have a source with reasonable prices to fall back upon. Even in the foreseeable future, many developing countries do not seem to be at a stage to avoid imports.

Technology and Know-How Transfer

This brings us logically to the questions of technology and know-how transfer. Technologies must be appropriate and the recipient should be able to use and improve the technology. The subject is attracting great attention in UNCTAD, UNIDO, UN Science and Technology Programme, IFDC, and many other organizations. Technology of fertilizer production is vital to many developing countries, and the terms and conditions of such transfer should be equitable and urgent. UNIDO is starting a technical information and data bank and will benefit by the experience of FAO, IFDC, and The World Bank.

An important aspect of this subject is the impact which developing countries that possess advanced technologies can have on other developing countries that are not as far advanced. Technology transfer among developing countries and economic cooperation between developing countries are, at present, basic programs of many UN agencies. A case in point is the production and use of catalysts. Countries like India and Mexico can help many other developing countries. "Know-how" in fabrication of fertilizer plant equipment and transfer of experience in evaluating and using different technologies are available in India, Pakistan, Iran, Mexico, and Brazil, to mention only a few countries.

Regional and Subregional Cooperation

Examples of such cooperation are evident in the ANDEAN Group, the ASEAN Group, etc. Noteworthy examples are the efforts of India to build or take part in building fertilizer projects in the Gulf area, in Sri Lanka, and in Bangladesh and the proposal of cooperation between the Philippines and Indonesia whereby the Philippines will concentrate on phosphates and Indonesia on nitrogen.

The Consultation Meeting on Fertilizer Industry organized by UNIDO stated the following (1):

Regional Cooperation

The Consultation Meeting recognized that the installation of fertilizer plants and the establishment of a marketing and distribution network would be easier in developing countries that had large fertilizer markets. In countries with smaller markets, it would be desirable to plan for regional cooperation and a combination of resources and skills. The opportunities for broader cooperation among all developing countries should also be pursued.

The Consultation Meeting reviewed the efforts that had already been made, including the regional cooperation arrangements of the Andean Group, the Latin American Association for the Development of the Fertilizer Industry (ADIFAL), the Latin American Economic System (SELA), the Senegal River Development Organization (OMVS), the Mano River Union, the Arab Federation of Chemical Fertilizer Producers, the Industrial Development Centre for Arab States (IDCAS), the ASEAN group of countries, and the region served by the Economic and Social Commission for Asia and the Pacific (ESCAP).

The Consultation Meeting expressed its support for those efforts. It recommended that they should be intensified and that:

1. High priority should be given in the programs of those regional groups to (a) the preparation of feasibility studies, (b) the setting up of fertilizer plants, and (c) the building up of a marketing and distribution network within each region;
2. UNIDO should extend technical and professional assistance to those regional cooperative efforts and should provide consultant services in response to requests and should follow up the suggestions made at the Consultation Meetings;
3. UNIDO should consider giving assistance to establish regional development centers for the fertilizer industry;
4. International technical and financial assistance from bilateral and other sources should also be made available for such regional group efforts.

In conclusion, it may be stated that, to increase output from agriculture to feed the world population, the most important input to agriculture, namely fertilizers, must be produced and delivered even to the poorest farmers at the lowest possible price. These farmers will need help to use fertilizers efficiently and increase yields. This will improve rural economy and hopefully raise the living conditions of those who are now left out of the development process.

Future Developments That May Reduce the Cost of Fertilizer Plants or Reduce the Quantity of Fertilizer Required

A tremendous amount of research and development is in progress in many countries which may result in lowering fertilizer plant construction costs, decreasing the time required for constructing plants, lowering the cost of fertilizer products, or decreasing the quantity of fertilizers needed. While some of these studies are not directly concerned with fertilizer production, they may have an impact on it. A brief mention of some of these developments follows.

New Methods for Gasification or Liquefaction of Coal

Many new processes are in various stages of research and development which aim to produce liquid or gaseous fuel from coal more efficiently or more economically than present processes. It seems likely that some of these studies will eventually result in lower cost ammonia feedstocks or more efficient processes for using coal as feedstock.

Other Fossil Fuels

Utilization of oil shale and tar sands is receiving much attention. Other studies are directed toward extracting methane that is trapped in tight sands, shale formations, or coal seams or dissolved in salt water in geopressurized aquifers (see chapter V).

Nuclear Energy

Several schemes have been proposed to utilize nuclear energy for production of nitrogen fertilizers. Improved means for producing nuclear energy might make these schemes attractive.

Energy from Ocean Currents

Methods for utilizing temperature differences in ocean currents to generate electricity have been proposed (2). One use of the electricity would be to produce electrolytic hydrogen for ammonia production.

Better Use of Organic Wastes

Wider or more efficient use of organic wastes could decrease the amount of chemical fertilizer required. Perhaps a more promising prospect is to generate methane for ammonia feedstock by anaerobic fermentation of organic wastes while utilizing the residue as a supplemental source of fertilizer nutrients. Also, pyrolysis of organic wastes is being studied to produce fuel gas suitable for ammonia feedstock.

Biological Fixation of Nitrogen

Much of the world's nitrogen supply already comes from biochemical fixation of nitrogen in the soil or in surface waters. Many studies are in progress for making better use of these microbiological processes. One approach involves development of new genetic varieties of plants that are capable of fixing atmospheric nitrogen through symbiotic processes.

Enzymatic or Catalytic Fixation of Nitrogen

Several studies are in progress for developing methods for fixing nitrogen by enzymatic or catalytic processes at near ambient temperature and pressure. Some encouraging results have been reported, but even the most optimistic forecasts predict that 10-20 years will be required to develop an economical process (3).

More Effective Use of Nitrogen Fertilizer

Probably more than half of the nitrogen fertilizer applied to crops is lost through various mechanisms. More efficient utilization of applied nitrogen is possible through improved techniques of timing and placement or by use of controlled-release nitrogen fertilizers. More efficient use of nitrogen would decrease the amount needed or increase yields. A better balance of nutrients would also contribute to a more efficient use of nitrogen as well as other nutrients.

Prefabrication of Fertilizer Plants or Modules

Several methods of prefabricating fertilizer plants or modules have been proposed, and some have been used to construct most of the plants in industrial facilities where it can be done faster, better, and cheaper than at remote locations. The plant or module is then transported to the site and assembled. While most of the previously mentioned areas of research and development are long-term possibilities, the general area of prefabrication of production facilities is currently finding extensive use in many fields, and its application to fertilizer plants appears feasible in the near future. Therefore, it seems appropriate to examine the feasibility of prefabricating fertilizer plants in more detail, especially those that are barge mounted, skid mounted, or placed on ocean platforms.

Modules and Skid-Mounted Plants--An obvious way to reduce onsite construction and assembly time is to build a plant in the form of prefabricated units or modules in the works of a fabricator in a developed country and transport them to the site overseas. However, this is not as easy as it first appears. Process plants are usually complex assemblies of piping and precision equipment, such as instruments, pumps, and other rotating machines. Attempts to ship subassemblies of this nature (especially as deck cargo on standard ocean-going vessels) and transport them overland frequently result in considerable damage, with consequent lost time and extra cost. Furthermore, transfer from ship to land transport is often hampered by lack of suitable gear. Therefore, adoption of prefabrication under these conditions is limited to relatively light loads of robust equipment.

However, by using specially constructed ships or barges and land vehicles that can accommodate large roll-on/roll-off skids, contractors have planned to move prefabricated modules weighing up to 1,000 tons. The modules may be constructed 2,000 km or more away and towed on 120 by 30 m barges to the site. A 10% saving in total project cost has been claimed compared with a comparable plant constructed on the site, despite the expenses for special barges and other equipment, such as huge "four-point" land crawlers that can haul 750-ton modules several kilometers inland and climb 6% grades. Examples of major plant units modularized and handled in this way include power plants, reformer furnaces, living quarters, cooling towers, and boilers. Perhaps the biggest example of modularization to date is a large, \$1.6 billion oil and gas processing complex being built at Prudhoe Bay on Alaska's North Slope (4). It is understood that about 75% of this project will be brought in as modules, some being nine stories high and coming from yards 16,000 km away. It should be mentioned that the principle of shipping prefabricated process modules is not new. Contractors were supplying small "packaged" ammonia plants of 50- to 100-tpd capacity as long as 20 years ago (see chapter VI). Packaged urea plants of matching capacity are also available. Such installations, consisting of about 17 skid-mounted assemblies weighing about 20-40 tons each, that are connected onsite, required less preparation and civil construction work and less space requirements.

Some of the advantages of such installations listed by the contractors are (5):

1. They serve the needs of remote agricultural areas having access to limited or small reserves of feedstock (natural gas or naphtha).
2. They serve locations where the infrastructure for erection of the plant, including equipment required, is not available and would have to be imported.
3. In case feedstocks are depleted, the plants can easily be transported to another site close to supply of available raw materials.
4. Such plants make it easier to obtain a lump sum bid on international competitive bidding.
5. They make it easier to obtain financing and insurance as well as on-schedule commissioning for the manufacturing plant.

Besides ammonia and urea skid-mounted nitrogen plants, contractors have constructed a number of skid-mounted granulation plants in South America for the manufacture of NPK fertilizers (6). The capacity of these plants ranges from about 5 to 20 tph, and they serve a regional agricultural center or small market logistically separated from larger agricultural producing areas or markets.

Platforms--For many years, prefabricated rigs built on platforms installed in shallow offshore waters have been used for exploration and production purposes in the oil, gas, and sulfur industries. As technology advanced, various operations such as gas/liquid separation, injection, and steam and power generation to meet rig needs have been added to result in large, self-contained processing/living units. Various methods of positioning and stabilizing such platforms have been developed. In shallow waters, it is often possible to mount the platform on piles or let it float within the confines of suitable anchored moorings. As exploration and production moved into deep and/or rougher waters (e.g., the North Sea), new techniques were developed. These include semisubmersible rigs, as well as jack-up ships, barges, and platforms which fix themselves firmly into the sea bed by adjustable "spuds" or legs. Other types include huge structures that are towed horizontally to a production area and then tipped and sunk. Such rigs can now operate in several hundred feet of rough water and may include provisions for crude storage, drilling-mud processing, oil and gas separation, power generation, and habitation for many operators.

Several organizations have proposed the use of such platforms in conjunction with ammonia, urea, methane, or LPG and production from offshore gas wells, where the cost of a long pipeline to the shore, plus the construction of a dock for handling export shipments, would be prohibitive. The products would be loaded directly into small- or medium-sized ships moored alongside the platform or into large "nurse" vessels which would store product, pending the arrival of a large bulk carrier. A recent multiclient study indicated offshore wells with a flow rate of 3.0 million m^3/day or less are likely candidates for jack-up platform processing. It appears that, for availabilities of 6.0 million m^3/day and greater, piping the gas ashore is a more economical alternative, although this will depend on the distance to shore. The advantages of mounting process plants on jack-up platforms are claimed to be much greater than transporting modules to distant onshore sites.

Barges and Boats--Currently, much interest is being devoted to the technology and economics of building large process plants (as well as hotels, hospitals, power plants, etc.) on barges or powerless boats. As in the case of modules and platforms, the principle of maximizing fabrication in the supplier's country and minimizing the onsite construction work applies. However, the use of barges and boats can be undertaken in several ways. For example, the plant can be built on a barge or into a boat hull which can be moored near an offshore gas well (or adjacent to a shoreline if gas or other feedstock from an onshore well can be piped aboard). Products such as ammonia, methanol, urea, LPG, and even LNG can be produced and transported ashore or to other countries via appropriate ships. A venture to produce ammonia and urea from natural gas in the Bontang area of Indonesia in this manner was started a year or two ago, but it has been abandoned for various reasons. This project was based on installing a 1,700-tpd urea plant in the hull of a former 30,000-ton ore carrier and supplying it with ammonia made from a plant built in a similar adjacent vessel. The conversion of the ships and installation of the process plants were being undertaken in some European yards, but the project was never completed.

Several organizations believe that the construction of specially designed barge-type vessels for accommodating process plants is much superior to converting orthodox ocean carriers and is ultimately less costly and more flexible. Some claim their barge-mounted ammonia/urea plant (1,700 tpd) will have a draft of 4-7 m when in service, and the soil-bearing load at any point is only 0.14 kg/cm^2. It can thus be positioned in deep or shallow water, in a swamp, or even on dry land without extensive foundation preparation and can also be readily moved to a new site.

Several shipbuilding companies in Belgium, Germany, Japan, Norway, Spain, and Sweden have associated themselves with engineering construction companies who have the process know-how in building large ammonia/urea plants in order to offer barge-mounted plants to developing countries (7). Their justification for barge-mounted ammonia/urea plants can be summarized as follows as the case may be:

1. To make use of offshore resources of feedstock;
2. To deliver "turnkey" erected plants saving approximately 2 years in delivery time;

3. To enable implementation of projects in areas where no infrastructure exists (saving of time);
4. To permit easier financing, i.e., short-term loans and softer terms;
5. To reduce the cost of constructing and lower the contingencies allowed for unknown liabilities when quoting a fixed price for the plant.

One design for a barge-mounted 1,000-tpd ammonia plant has provision for the following utilities included in the above estimates:

1. A 100-tph seawater desalination plant--the normal requirement of desalinated water is 46 tph.
2. An electric power supply consisting of 15-MW steam turbine-driven alternator for the plant that requires 10 MW for startup (included is a 2.5-MW diesel motor-driven alternator for emergency).
3. A 20,000-ton storage capacity for ammonia with the possibility of doubling the capacity for shipping purposes.

There are various sizes of barges for a typical 1,000-tpd ammonia plant with 20,000 tons of ammonia storage on board. One shipbuilder was able to accommodate the plant on a barge 74 m wide and 116 m long. In some cases, the electrical power plant or water desalination plant can be accommodated on a separate smaller barge. A typical size for such a barge having 1,800-ton displacement with two 25-MW units is 20 m wide and 65 m long (5).

A recent example of this type of construction is the 750-tpd bleached kraft pulp mill built on two barges to be towed to a location on the Jari River in the Brazilian hinterland (8). Others (of a smaller nature) include complete gas and water reinjection plants towed to remote places in the Middle East and elsewhere. It is understood that complete, barge-mounted LNG plants are currently in the design stage by several major engineering companies.

The use of barge-mounted plants for permanent onshore location is also under active consideration. It may be necessary to build a large project on several barge modules, e.g., one for each major process section, another for the power plant, etc. These would be towed from the fabricator's yard to the site which would have been prepared in advance. The site could be a shallow man-made lake close to a shoreline or river; the barges would be maneuvered into position; the lake would be isolated, pumped out, and backfilled. Another configuration, where access to an inland area is difficult and the sea is shallow, is to build a pier (or two piers) out to sea and float or sink the barges in appropriate positions. Other alternatives exist, depending on circumstances.

Certain project locations (in some Middle East areas, for instance) where skilled labor and adequate port facilities or deep water are lacking may justify detailed technical and cost studies regarding the use of prebuilt barge-mounted plants. One such example is a large 2,500-tpd methanol, 1,000-tpd ammonia/urea project intended to be built in the Middle East. Initial studies (1975-76) showed if conventional (site construction) methods were used the capital cost was likely to be at least $500 million, which was about 35% greater than the cost of a comparable plant built in a developed country. Preliminary investigations on the proposed alternative method of building the plant on six barges, towing these to their final location, and installing them in a backfilled lagoon indicated the probable cost would be no more than if the project were to be built onsite in a developed country (9). In addition, the plant (which would be thoroughly tested before leaving the builder's yard) could start production at least a year earlier, thereby making the project more profitable. While the plant was under construction, the lagoon and local facilities such as product storage, offices, and roads would simultaneously be built.

Summary of Major Advantages and Disadvantages--The advantages of modules are:

1. Construction can be undertaken under controlled conditions of quality, labor, and material cost.
2. Skilled shop labor rates and overheads are often lower than skilled field labor rates for identical work.
3. Work planning is usually easier under shop conditions, thereby helping to minimize labor costs.
4. Usually, modules can be thoroughly tested before shipment to site.
5. One fabricator can be made responsible for an entire plant or subsection.
6. Significant saving in plant construction time and cost is possible.
7. Lump-sum bidding on an entire plant or subsection can be undertaken with much greater confidence than in the case of field-erected units.
8. It is often possible to design for future plant disassembly and relocation, if foreseen.

The disadvantages of modules are as follows:

1. Special equipment such as roll-on/off barges, skids, cranes, and crawlers must be rented or purchased for large modules.
2. Current weight limitations are about 1,000 tons.

The advantages of platforms are:

1. They have advantages similar to those of modules, in addition to the following advantages.
2. Most types can be easily relocated if required.
3. Ample cooling water is usually available.
4. Treated effluents can be easily discharged.
5. They are useful where shore space is restricted.
6. They obviate the need for costly port and shiploading facilities.
7. They make it possible to take advantage of competitive worldwide shipbuilding and plant construction facilities to achieve minimum project time and cost.
8. Environmental and pollution control problems are simpler.
9. Ocean platforms are proven and accepted; therefore, requisite financing and insurance can usually be obtained.

The disadvantages of platforms are:

1. Operations may have to be curtailed during bad weather periods.
2. They require frequent supplies of food and marine stores to be brought in by boat or helicopter.
3. Labor rates and crew overheads are usually higher than for land-based operations.
4. Cost of corrosion protection may be significantly higher than for a land-based plant.

The advantages and disadvantages of floating barges are similar to those of platforms. However, they may be more sensitive to adverse weather conditions than platforms.

The advantages of grounded barges are:

1. They are similar to those of modules and platforms, especially regarding opportunities to save project time and cost compared to a site-built plant.

2. Usually less foundation work is required than is necessary with a site-built plant.
3. They can be designed and positioned to permit future relocation.
4. They are not affected by rough sea conditions.

The disadvantages are as follows:

1. They may require appreciable dredging for constructing a canal between the sea and an inland site.
2. It may be necessary to build the plant on several barges to make towing and siting easier.

Conclusion

It is evident that building process plants and other facilities by modular, platform, and barge techniques is proven technology, with a good potential in many developing countries, especially those with hydrocarbons and other materials located near a sea or a large river.

It is worth noting that contractors experienced in these techniques emphasize the importance of designing *from the beginning* and integrating a modularized, *platformed*, or *barge-mounted* plant. Attempts to mount large process units designed for orthodox land construction on any available platform, ship's hull, or barge are likely to prove very costly.

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