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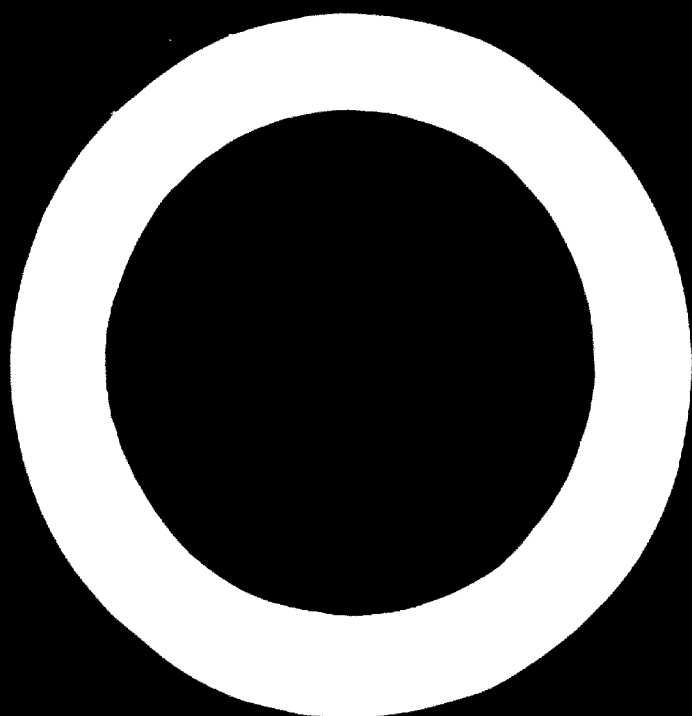


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Photograph No. 2



UNITED NATIONS



The photograph on the cover shows two kilns used for the production of sulphur dioxide from gypsum.

By courtesy of Marchon Products Ltd. Whitehaven, United Kingdom

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
VIENNA

Fertilizer Industry Series

Monograph No. 3

**THE REDUCTION OF SULPHUR
NEEDS IN FERTILIZER
MANUFACTURE**



UNITED NATIONS
New York, 1969

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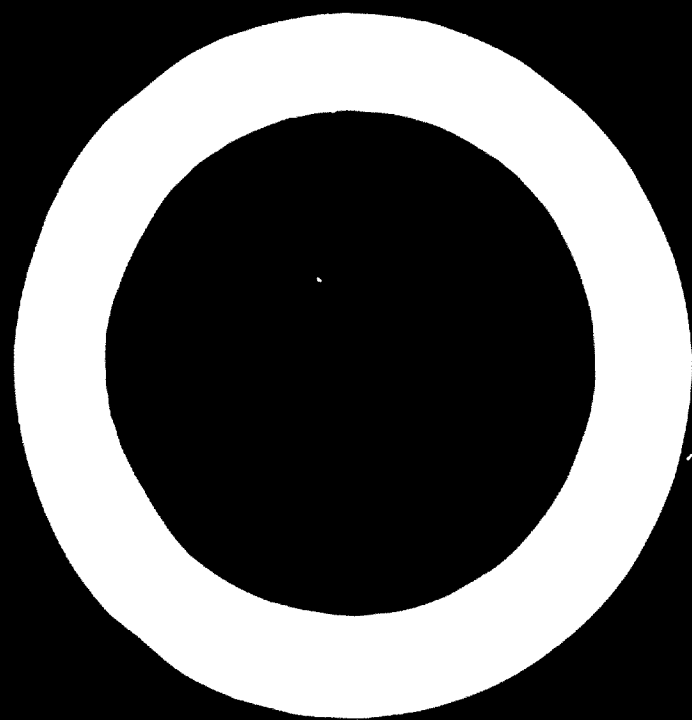
Foreword

This is the third of a series of monographs in the Fertilizer Industry Series to be published by the United Nations Industrial Development Organization. It will be followed immediately by other studies in the series on: the ammonium chloride and soda-ash dual manufacturing process in Japan and the new process for the production of phosphatic fertilizers using hydrochloric acid.

The increasingly acute shortage of food that has resulted from rapid population growth on the one hand, and from rising living standards on the other, confronts the world with the pressing problem of how to increase agricultural production quickly and efficiently. To this end, the expansion of the fertilizer industry and the rational use of fertilizers, particularly in the developing countries, must be encouraged by every possible means.

It is the purpose of this series of monographs to assist the developing countries by providing them with the most recent technical and economic information in this field and advice on the steps that must be taken to establish a fertilizer industry.

The present paper was prepared by Christopher J. Pratt of Mobil Chemical Company, New York, serving as consultant to UNIDO. The views and opinions are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.



Contents

Foreword	
1. Patterns of world sulphur supply and demand	1
2. Patterns of world fertilizer supply and demand	13
3. Sulphur-consuming fertilizer processes	18
4. Sulphur-saving fertilizer processes	30
5. Summary and conclusions	57
References	60

EXPLANATORY NOTES

Reference to tons is to metric tons unless otherwise stated.

Reference to dollars(\$) is to United States dollars unless otherwise indicated.

One mill equals \$0.001.

The following abbreviations have been used:

cal	=	calorie
f.o.b.	=	free on board
kcal	=	kilocalorie
kWh	=	kilowatt hour

1.

Patterns of world sulphur supply and demand

Sources - general

Sulphur is found in numerous forms in many parts of the world; deposits of sulphur in the elemental form, however, amount to only about 0.06 per cent of the earth's crust. Sulphur exists in combination with heavy metals, such as iron, lead, copper, zinc and mercury, as well as with lighter metals, such as sodium, calcium and magnesium. Coal, oil and gas deposits in many areas of the world also contain appreciable percentages of sulphur, sometimes in sufficient quantities to justify recovery (Kohl and Riesenfeld, 1960, pp. 240—281),¹ but more often not, under normal circumstances. At the same time, serious corrosion and air pollution frequently arise from the use of fossil fuels containing sulphur. These factors present a continuing challenge, since the benefits to industry and mankind resulting from the use of sulphur-free fuels are incalculable, and the recovered sulphur would considerably supplement world supplies.

The search for further deposits of elemental sulphur continues throughout the world, both on land and off shore, but no new discoveries of significance have been announced to date. Hence, an alternative approach to reducing the amount of elemental sulphur required in the manufacture of fertilizers is to turn to minerals and fuels containing combined sulphur. This also provides as a by-product

¹ All references are listed at the end of this monograph.

metals and other profitable materials. It is, therefore, particularly important for developing nations to examine thoroughly their known resources of sulphur-containing minerals or fuels and to search for new deposits that could be of commercial or strategic value.

Sulphur is also recovered in elemental form or as a gaseous oxide (SO_2) or sulphide (H_2S) from various chemical processes and gas-purifying operations. Compared with natural sources, total quantities so obtained, however, are relatively small.

Elemental sulphur

Quantities of elemental sulphur sufficiently great to be of commercial importance are found in relatively few areas of the world, such as southern parts of the United States, Mexico, central and southern parts of the Union of Soviet Socialist Republics and Sicily. Smaller deposits exist in various volcanic regions but are often in local pockets usually too small to justify an economic return on the capital investment necessary. (A reserve of five million tons would normally be the minimum size of deposit justifying commercial exploitation. However, specific national needs and a mounting world shortage of sulphur could make smaller reserves attractive.)

Thus, most countries lack commercial sulphur supplies. This imbalance has led to considerable world trade in sulphur as can be seen in tables 1 and 2 below.

Table 1. Production and consumption of elemental sulphur, 1967
(Thousand tons)

Country or area	Production	Consumption ^a
Western Europe	2,078	3,700
USSR and Eastern Europe	2,145	2,145 est.
Canada and United States	10,691	9,025
Mexico and Latin America	2,088	700
China (mainland)	150 est.	150 est.
Japan and rest of Asia	351	950
Africa and the Middle East	19	525
Australasia	21	725
	17,543	17,920

^a Balance from stockpiles.

The excess of consumption over production during 1964—1967 was met by the use of material that had been stockpiled. Because of geographical, political, economic and commercial factors, actual

world trade in sulphur and other commodities is usually much larger than the difference between the production and consumption figures would indicate. For example, large countries such as the United States and Canada are both exporters and importers of sulphur and other materials, to each other and with other countries. An indication of the principal patterns of world trade in elemental sulphur for the latest period available (1967) is given in table 2 below.

Table 2. Principal patterns of world trade in elemental sulphur, 1967
(Thousand tons)

Importing countries or areas	Exporting countries					
	USA	Mexico	Canada	France	USSR Eastern Europe	Others
Western Europe						
Belgium	186	—	—	58	—	—
Federal Republic of Germany	250	—	—	104	—	—
France	5	220	—	—	4	—
Netherlands	196	—	—	67	—	—
Sweden	48	—	—	70	8	8
United Kingdom	150	300	11	270	1	1
Others	205	—	38	237	47	6
Total	1,040	520	49	806	60	15
USSR	—	—	45	—	—	—
Eastern Europe	5	—	54	30	250	20
Total	5	—	99	30	250	20
Central America	25	—	—	—	80	—
South America	275	—	10	15	33	—
Africa	71	73	60	100	22	—
Australasia	280	180	285	8	—	—
North America						
Canada	115	—	—	—	—	—
United States	—	725	760	—	—	—
Grand total	1,811	1,498	1,263	959	445	35

Production methods

Frasch process

The majority of United States and Mexican elemental sulphur is produced by the Frasch process (Shreve 1956, pp. 363—393), which in 1967 yielded some 8.2 million long tons. In this process, wells are

drilled into the sulphur-bearing limestone cap rocks of salt domes found in the Mexican Gulf area, and the sulphur is melted and displaced by superheated water.

Sour-gas stripping

Elemental sulphur is also recovered on an appreciable scale from sour natural gas and petroleum refinery operations. In one popular method the hydrogen sulphide present is extracted by a solvent, such as ethanolamine, and subsequently converted to sulphur by oxidation, as in the well-known Claus process:



During 1967 some five million tons of elemental sulphur were recovered from sour natural gas in western Canada, the United States and France. Appreciable additional supplies will become available from treatment of the sour natural gases of the Middle East during the next 2 or 3 years. It has been reported that in Iran projects are well advanced for recovering up to one million tons of sulphur per year from sour gases by 1970. An additional quantity of 15,000 tons will be recovered from crude oil containing sulphur produced from off-shore wells near Kharg Island in the Persian Gulf (Verghese).

Native sulphur in mineral form

In some volcanic regions of the world, such as southern Italy, Sicily, Japan and also parts of Poland, the Soviet Union and Central and South America, elemental sulphur deposits of commercial significance exist and can be mined by conventional stripping or underground means. These deposits are frequently contaminated with clay, sand and other minerals. Sulphur is recovered by direct heat or by extracting the finely-ground ore with steam and hot water. Flotation is another method employed.

Such methods are relatively simple to operate and can be applied to small local deposits in developing areas, provided mining methods and costs are not prohibitive and that the reserves are sufficient to justify the capital expenditure.

Pyrites

In most countries sulphur is predominantly used to produce sulphuric acid, which in turn is largely consumed by the fertilizer and other heavy industries. This need for sulphuric acid can also

be partly met, under certain circumstances, by recovering the sulphur in the gases evolved when roasting pyrites, marcasite (iron sulphide, FeS_2) and pyrrhotite (FeS). Deposits of pyrites are found in many industrial countries (e.g. Australia, the Federal Republic of Germany, Japan and the United States). After roasting, the iron content in the residual cinder can be transformed into blast-furnace feed for local use. The roaster gas is washed, purified and converted to sulphuric acid. Deposits of pyrites also exist in regions devoid of large industries, in which case the ores can be shipped to the consuming areas. Occasionally, as in Morocco, an iron ore (pyrrhotite) is found near phosphate deposits, and this permits the local production of sulphuric acid, and hence concentrated phosphate fertilizers suitable for sale in both domestic and export markets. Table 3 below gives the figures for the world production of pyrites in 1967.

Table 3. World production of pyrites in 1967 ^a
(Million tons of sulphur equivalent) ^b

Country or area	Production
North America	0.80
South America	0.01
Asia	1.47 ^c
Africa	0.36
Australia	0.13
Western Europe	3.55
USSR	2.16
Eastern Europe and other	1.89
	Total 10.37

^a Consumption is similar to production.

^b Average S content: 44 to 45 per cent.

^c Japan: about 1.35 million tons.

As in the case of elemental sulphur, a considerable amount of international trading is undertaken in pyrites that is not evident from the patterns of production and consumption. Some of the principal movements for 1967 are indicated in table 4 below.

Production methods

Sulphur is usually recovered from pyrites in the form of sulphur dioxide (SO_2), which is subsequently converted to sulphuric acid, as is described later. In one long-established method, the pyrites ore is roasted with air in vertical furnaces, which are composed of several stacked hearths fitted with mechanical rakes. The ore is fed in at the top and emerges from the bottom hearth as a spent oxide, or

Table 4. Principal patterns of world trade in pyrites in 1967
(Thousand tons)

Importing countries	Exporting countries					
	Spain	Portugal	Cyprus	USSR Eastern Europe	Norway	Others
Belgium	27	189	25	—	small	small
Federal Republic of Germany	480	40	233	200	390	40
France	126	8	135	—	—	43
Italy	—	—	325	760	—	133
Netherlands	—	9	85	—	11	small
United Kingdom	19	—	99	86	8	39
Others	112	4	—	—	73	small
Total	764	250	902	1,046	482	260

cinder. The SO_2 evolved is scrubbed to remove dust and other impurities prior to conversion to sulphuric acid.

In recent years the use of fluidized-bed calciners coupled with controlled roasting, waste-heat recovery and power generation has led to highly efficient methods of producing sulphuric acid from pyrites. Such techniques (Shreve, 1956, pp. 363—393; Anon., 1964) can also produce an iron oxide suitable for the manufacture of iron and steel. The economies resulting from the use of these methods help them to compete increasingly with sulphuric acid processes based on elemental sulphur.

Other sources of sulphur

Metallurgical

Substantial quantities of sulphuric acid are also produced from the smelter gases evolved during the treatment of ores containing copper, zinc, lead and other metals. Some of these ores yield a lean gas containing marginal amounts of sulphur the recovery of which is not economic. However, the recovery of such amounts of sulphur dioxide may eventually become justified because of local pollution regulations limiting the permissible amount of sulphur dioxide emission and rising prices of sulphuric acid. Indeed, an appreciable number of large non-ferrous smelters throughout the world have become large fertilizer producers as well, because of their ability to produce low-cost sulphuric acid from their waste gases.

Chemical

Another mineral source of sulphur for making sulphuric acid is calcium sulphate, in the form of gypsum or anhydrite. Reduction with coal plus a little silica, is sometimes carried out in rotary kilns to yield a cement clinker and a gas rich in sulphur dioxide. The gas is scrubbed and used to make sulphuric acid in conventional contact plants. In Great Britain, Western Europe and Turkey nearly one million tons of gypsum and anhydrite are being used for this purpose, and additional plants are being built, largely to offset rising sulphur costs, which bring with them an increased need for foreign exchange.

Sulphur, both in elemental form and as sulphur dioxide or hydrogen sulphide, is recovered from various chemical processes and purification systems of gas-works. A variety of solvent extraction and wet and dry oxidizing methods are also available (Kohl and Riesenfeld, 1960, pp. 240–281). An indication of world sulphur production (largely as sulphuric acid) from miscellaneous sources is shown in table 5 below.

Table 5. Production of sulphur from miscellaneous sources in 1967^a
(Thousand tons of sulphur equivalent)

Country or area	Production
Western Europe	
Belgium	180
Federal Republic of Germany	250
Finland	170
France	140
Italy	215
United Kingdom	485
USSR and Eastern Europe	2,000 (estimated)
North America	
Canada	290
United States	1,100
Central and South America	95
Asia	
Australasia	135
Japan	840
Africa	160
	Total 6,060

^a Consumption is similar to production. Frasch, brimstone ores, natural gas and pyrites are excluded.

Fossil fuels

The present major source of elemental sulphur from fossil fuels is natural gas, which in areas such as western Canada, southern France and Iran, can contain up to 25 per cent or more sulphur, chiefly as hydrogen sulphide. The present tonnage of sulphur recovered from the French Lacq fields, for example, amounts to about 1.6 million tons annually. Recovery is undertaken by several methods, often based on solvent extraction and or oxidation (Anon. 1965 f. and 1966; Kohl and Riesenfeld, 1960, pp. 240—281; Priestley, 1964). Figures for world production of elemental sulphur from natural gas are included in table 1, figures for sulphur recovered from coal-gas and coke-oven gas purification processes are included in table 5.

Many petroleum crude oils contain from 1 to 2 per cent sulphur, but desulphurization is normally undertaken on selected refinery products in the lighter ranges. Hence, if economic methods could be found, desulphurization of crude oils would considerably increase world sulphur supplies.

By-product sulphuric acid and sulphates

Some processes, such as caprolactam manufacture and the pickling of steel and other metals, yield appreciable quantities of spent sulphuric acid that must be recovered because of waste-disposal restrictions or for economic reasons. Some caprolactam plants yield several hundred tons per day of ammonium sulphate (five tons ammonium sulphate per ton of caprolactam) as a by-product, and this is often recovered and sold for the manufacture of fertilizer. Most acid recovered from pickle-liquor concentrators is recycled to the process after separating the iron sulphate salts, thereby reducing sulphur requirements.

Calcium sulphate, either as natural gypsum or anhydrite, is used by some fertilizer producers to make ammonium sulphate by a reaction with ammonium carbonate.

World production and consumption

Based on the preceding tables, table 6 below gives the approximate pattern of world production and consumption of sulphur.

Excluding countries with centrally planned economies, sulphur consumption in 1964 increased by about 9 per cent from the preceding year. For 1965 there was a further increase of some 10 per cent. In view of the industrial and agricultural activity taking place generally, similar increases on a global scale are probable. Past growth rates, however, have fluctuated considerably; the approximate

Table 6. World production and consumption of sulphur,
1967
(Million tons of S or S equivalent)^a

Country or area	Production	Consumption
Western Europe	7.30	9.5
Eastern Europe	2.00	7.5 est.
USSR	4.60	
Canada	3.00	1.3
United States	9.90	9.3
Mexico	1.92	0.3
Central and South America . .	0.26	0.6
Japan	2.56	3.5
Rest of Asia	1.39	
Africa and the Middle East . .	0.54	1.0
Australasia	0.29	1.0
	Total 33.76	34.0 approx.

^a All types.

annual growth rates in world sulphur consumption were 8 per cent from 1953 to 1955, 2 per cent from 1956 to 1961 and 7 per cent from 1962 to 1967.

In 1956 and 1957, consumption of sulphur actually declined, and it is believed by some authorities that the future rates of consumption will rise as the fertilizer and other industries progressively expand. The weighted average annual growth rate, based on the figures from 1953 to 1967, is 5.5 per cent.

Past and present movements in the annual consumption of sulphur have been due to the great expansion in the fertilizer industry, especially in the manufacture of phosphate fertilizer. It has been estimated that global fertilizer needs will climb from about 30 million tons of primary nutrients in 1964 to at least 90 million tons in 1980; this corresponds to an annual growth rate of slightly more than 7 per cent. Most of the other sulphur-consuming industries in the world are expected to expand, on an average, by about 5 per cent annually.

Fertilizer producers in a number of industrial countries were responsible for using some 40 per cent of all forms of sulphur produced until the present wave of expansion, which is now believed to have raised the figure to approximately 50 per cent. In some developing countries fertilizer needs may initially account for 75 to 85 per cent of sulphur requirements; but as other industries are established, this percentage can be expected to fall gradually until it approximates to that of the industrialized countries (about 50 per cent).

Therefore, annual growth rates of world sulphur consumption should be about the same in the immediate future as those for the fertilizer industry (slightly more than 7 per cent) and for general industrial expansion (some 5 per cent). This gives an average figure of 6 per cent per annum, compared with the weighted average of 5.5 per cent for preceding years.

Total sulphur consumption may be subdivided into consumption of elemental sulphur and sulphur derived from pyrites and other sources in approximately equal proportions. With regard to the expansion of the fertilizer industry, especially in the developing areas, elemental sulphur is a much easier material to process than pyrites or sulphur from other sources, hence the rate of growth of consumption of elemental sulphur can be expected to be greater than that of sulphur from other sources, provided supplies are not restricted. Some economists believe a 7 per cent average annual growth is likely during the next fifteen years.

Figure 1 below shows the projected world sulphur consumption to 1980 based on an average annual increase of 6 per cent. Estimated elemental sulphur requirements increasing at a 7 per cent annual average are also indicated, as well as pyrites-sulphur consumption. These projections assume no restriction on the availability of any form of sulphur. The total tonnages from 1964 to 1980 amount to about 800 million tons for sulphur in all forms, and 410 million tons for elemental sulphur.

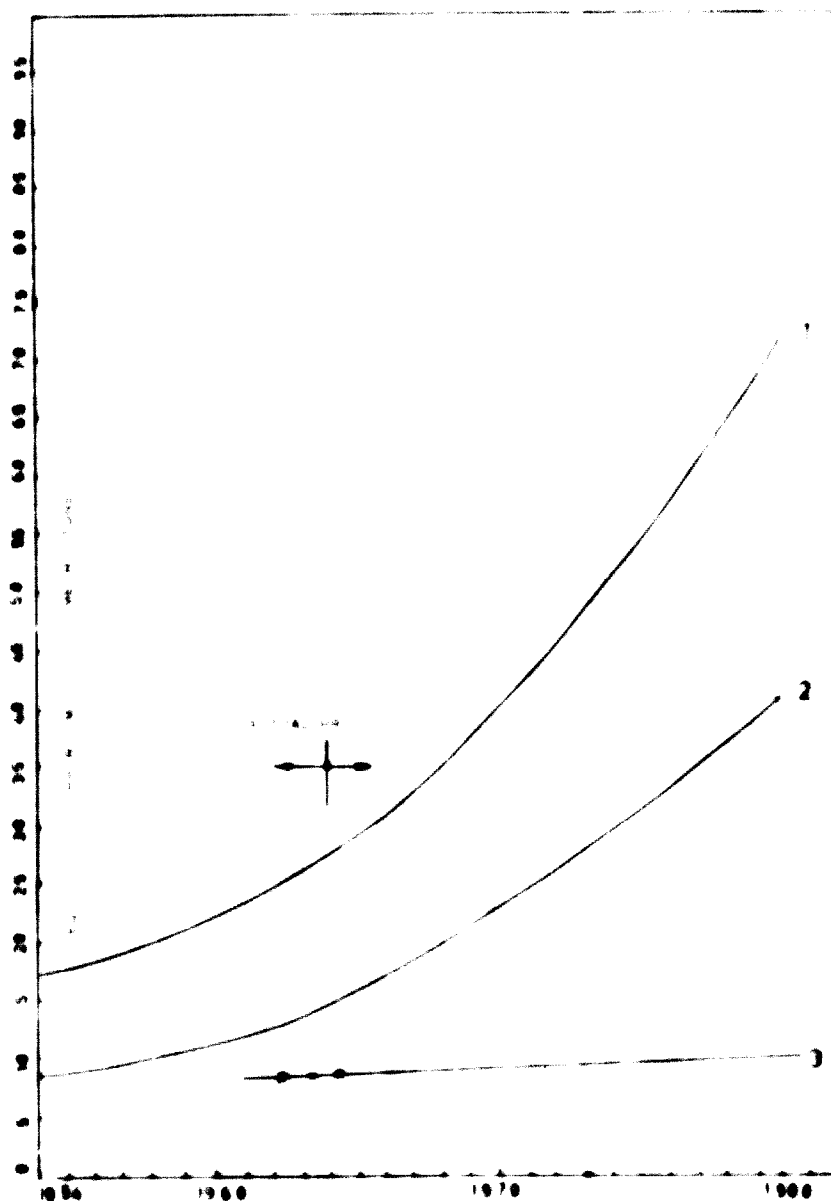
However, current estimated main reserves of elemental sulphur (excluding sour gas sources) have been estimated to be approximately:

	<i>Million tons</i>
Mexico	110
Poland	100
USA	90
USSR	70
Italy	30
Total	400

Principal sulphur producers are usually reluctant to disclose their deposits. It is hoped that considerably greater sulphur deposits will be found in the next decade; otherwise supplies will be exhausted by about 1980. Because of this fear the Mexican Government in 1965 restricted sulphur exports to quantities proportional to newly found deposits.

Should supplies become greatly restricted, alternative sources (e.g. pyrites, calcium sulphate and other sulphur-containing minerals) would, no doubt, be expanded or developed. Sulphur recovery

Figure 1. Projected increase in world sulphur consumption*
 (1) all forms, (2) native, (3) purities



* Basis of projection (1) Past and present patterns of consumption, (2) Unrestricted availability of supplies.

from natural gas, oil and solid fossil fuels could be undertaken to a greater extent than at present. A potential new source are the Athabasca tar sands in Canada, believed to contain at least 1,000 million tons of sulphur, which would become a co-product with the various petroleum products now planned. It is understood, however, that large-scale production will not begin for several years.

Similarly, lack of sulphur supplies at reasonable prices would stimulate the development and use of alternative industrial processes requiring little or no sulphur. Typical examples already in commercial operation include the hydrochloric process for titanium dioxide, the use of hydrochloric acid for metal pickling and various nitrophosphate fertilizer processes.

As might be expected, the current excess of elemental sulphur consumption over production has led, in the absence of long-term contracts to large price increases, from about \$20 per long ton f.o.b. some years ago to about \$40 in 1969. Prices have been mounting steadily, and this would justify operating many hitherto unprofitable or marginal mines and using various alternative sources of sulphur.

This brief review of the patterns of sulphur supply and demand emphasizes the concern of the United Nations to anticipate and overcome possible handicaps to the fertilizer and other sulphur-consuming industries, especially in developing countries that are short of sulphur.

2.

Patterns of world fertilizer supply and demand

A review of the patterns of world fertilizer supply and demand in terms of principal products and those that consume sulphur during their manufacture permits the potential sulphur shortage as

Table 7. Fertilizer production in 1966/1967
(Million tons of primary plant nutrients)

Country or area	N	P ₂ O ₅	K ₂ O	Total
Western Europe	6.88	4.90	4.64	16.42
Eastern Europe	1.88	1.46	2.00	5.34
USSR	3.10	1.71	2.65	7.46
Canada and United States	5.97	5.14	4.81	15.92
Latin America	0.55	0.22	0.02	0.79
Japan	1.80	0.66	—	2.46
India	0.31	0.16	—	0.47
China (mainland)	0.80	0.36	n. a. ^a (approx.)	1.50
North Korea	0.10	n. a.	n. a. (approx.)	0.20
Rest of Asia ^b	0.38	0.10	0.30	0.78
Africa	0.24	0.54	—	0.78
Australasia	0.04	1.26	—	1.30
Total	22.05	16.51	14.42	53.42

Source: Food and Agriculture Organization of the United Nations, *Production Yearbook and trade magazines*.

^a Not available.

^b Excluding North Viet-Nam

it affects the fertilizer industry to be seen in perspective. Tables 7 and 8 show approximate production and consumption figures in terms of primary plant nutrients for 1966/67.

Table 8. Approximate fertilizer consumption in 1966/1967
(Million tons of primary plant nutrients)

Country or area	N	P ₂ O ₅	K ₂ O	Total
Western Europe	4.95	4.46	3.94	13.35
Eastern Europe	2.09	1.52	1.87	5.48
USSR	2.66	1.66	1.90	6.22
Canada and United States	5.74	4.30	3.45	13.49
Latin America	0.92	0.54	0.35	1.81
Japan	0.85	0.63	0.64	2.12
India	0.83	0.27	0.13	1.23
China (mainland)	1.75	n. a. ^a	n. a. (approx.)	2.75
North Korea	0.20	n. a.	n. a. (approx.)	0.40
Rest of Asia ^b	1.12	0.44	0.29	1.85
Africa	0.57	0.40	0.20	1.17
Australasia	0.10	1.29	0.18	1.57
Total	21.78	15.51	12.97	51.64

Source: Food and Agriculture Organization of the United Nations, *Production Yearbook and trade magazines*.

^a Not available.

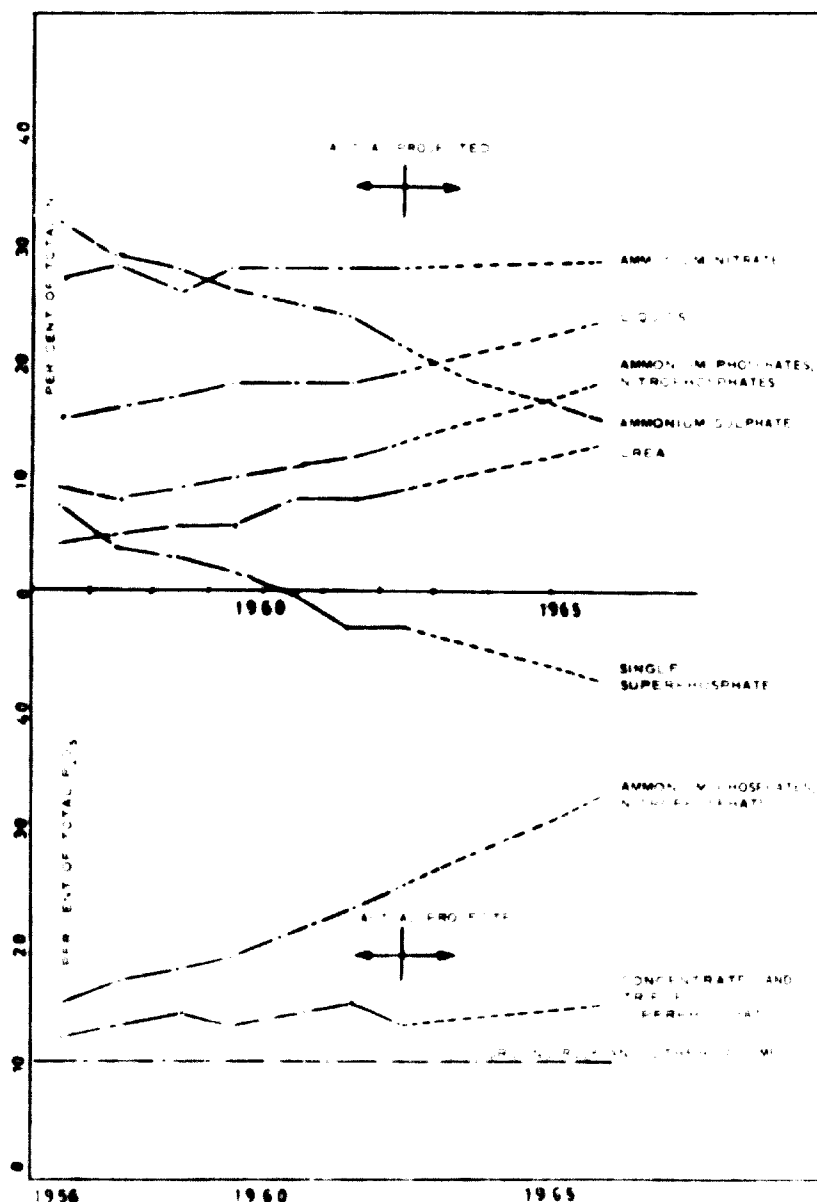
^b Excluding North Viet-Nam.

Figure 2 below indicates the relative percentages of the principal types of fertilizers used, together with past and projected trends. Of particular significance are the falling percentages for ammonium sulphate and single superphosphate, compared with the rising percentages for urea, liquid nitrogen solutions, ammonium phosphates and nitrophosphates.

However, these trends in percentages of fertilizer use do not necessarily indicate corresponding changes in actual tonnage produced, since they are also part of the total fertilizer production figure. For example, world production of ammonium sulphate has remained at a fairly constant level of about 3 million tons annually, whereas world nitrogen production has been increasing at a rate of nearly 10 per cent per year, and much of this increase is due to the growing popularity of the newer fertilizers such as urea, ammonium phosphates, and liquid nitrogen solutions.

Table 9 below shows the relative amounts of sulphur required for the manufacture of each of the principal fertilizers.

Figure 2. Component percentages of principal types of world nitrogen and phosphate fertilizers



(K₂O fertilizer types are 96% potassium chloride (KCl); the balance is composed of nitrate, sulphate and mixed salts.)

Table 9. Relative sulphur requirements in fertilizer manufacture

A. Nitrogen fertilizers		
Type	Formula	Theoretical content of S in lb per lb of final product
Ammonium chloride	NH ₄ Cl	0
Ammonium nitrate	NH ₄ NO ₃	0
Ammonium sulphate	(NH ₄) ₂ SO ₄	0.24*
Calcium nitrate	Ca(NO ₃) ₂	0
Potassium nitrate	KNO ₃	0
Sodium nitrate	NaNO ₃	0
Urea (solid)	CO(NH ₂) ₂	0
Nitrogen solutions	Various	Usually nil

B. Phosphate fertilizers

<i>Product</i>	<i>Formula</i>	<i>Approx. content of S in lb per lb of final product</i>
Ground phosphate rock Defluorinated	$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$	0
phosphate rock	$\text{Ca}_{10}(\text{PO}_4)_6$	0
Thermal phosphates	$\text{CaO}_n \cdot \text{P}_2\text{O}_{5m} \cdot \text{CaF}_2$	0
Sulphuric acid . . .	H_2SO_4	0.33 (100% H_2SO_4)
Single superphosphate	$3\text{CA}(\text{H}_2\text{PO}_4) \cdot 7\text{CaSO}_4 +$ impurities	0.13 (18% P_2O_5)
Phosphoric acid (furnace)	H_3PO_4	0 (100% P_2O_5)
Phosphoric acid (wet-process) . . .	$\text{H}_3\text{PO}_4 +$ impurities	0.93 (100% P_2O_5)
Triple superphosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 +$ impurities	0.31 (47% P_2O_5)
Monoammonium phosphate	$(\text{NH}_4)\text{H}_2\text{PO}_4$	0.45 (48% P_2O_5) (in practice)
Diammonium phosphate	$(\text{NH}_4)_2\text{HPO}_4$	0.43 (46% P_2O_5)
Nitrophosphates . . .	CaHPO_4 a. NH_4NO_3 b. CaSO_4 c	0 to 0.2 (10 to 22% P_2O_5)
Basic slag	$4\text{CaO} \cdot \text{P}_2\text{O}_5$	0

C. Potassium fertilizers

<i>Product</i>	<i>Formula</i>	<i>Approx. content of S in lb per lb of final product</i>
Potassium chloride . .	KCl	0
Potassium nitrate	KNO_3	0
Potassium sulphate . .	K_2SO_4 (synthetic)	0.19
Potassium metaphosphate . . .	$(\text{KPO}_3)_n$ (synthetic)	0.56

* If made by direct neutralization of sulphuric acid by ammonia.

The principal sulphur-consuming fertilizers, therefore, are: ammonium sulphate, single superphosphate, wet-process phosphoric acid, triple superphosphate, ammonium phosphates, and potassium sulphate (synthetic). Nitrogen fertilizers, with the exception of ammonium sulphate, are not considered further, as they do not consume sulphur in manufacture. The principal potassium fertilizer is potassium chloride (KCl), and potassium sulphate is available in mineral form as an alternative to the synthetically produced salt. Potassium metaphosphate is an interesting high-analysis binary fertilizer but is only available in limited quantities, owing to the

KCl disposal problem and its high cost. Mixtures of potash and triple superphosphates are normally used to supply the requisite P_2O_5 and K_2O .

Thus, the principal ways in which savings in sulphur can be made are:

- (a) Substitution of other nitrogen salts for ammonium sulphate;
- (b) Substitution of "non-chemical" phosphates for chemically produced materials;
- (c) Use of furnace-type phosphoric acid in place of wet-process acid, when costs permit;
- (d) Greater use of nitrophosphate processes;
- (e) Improved conversion efficiencies, especially in phosphate fertilizer production;
- (f) Recovery of sulphur lost as waste gypsum from wet-process phosphoric acid plants;
- (g) Use of mineral potassium sulphate instead of the synthetic salt;
- (h) Use of pyrites, calcium sulphate and other minerals containing sulphur, when circumstances permit.

3.

Sulphur-consuming fertilizer processes

Reasons for using sulphur in fertilizer manufacture

The principal reasons for using sulphur in the fertilizer industry are (a) to make a solid nitrogen product in the form of ammonium sulphate; (b) to make soluble the phosphate present in phosphate rock and (c) to produce a chloride-free potassium salt, such as potassium sulphate. An important secondary benefit can be the provision of a sulphur-containing radical in the fertilizer produced. Sulphur is an essential element in plant life, and during the last decade the use of high-analysis fertilizers containing little or no sulphur has created problems of sulphur deficiency.

Sulphur, however, is not normally used in its elemental form for fertilizer, as it is a relatively inert material, although some is used in a finely divided or colloidal state as a pesticide. Instead, it is first converted into sulphuric acid, which is then used to react with the corresponding nitrogen, phosphate or potassium-containing material. A brief description of sulphuric acid production follows.

Sulphuric acid production

Large quantities of sulphuric acid are made throughout the world, from both elemental sulphur and other sources. Table 10

below gives the figures for world production of sulphuric acid in 1966 and 1967

Table 10 World production of sulphuric acid 1966-1967*

	1966	1967
Western Europe	20.36	21.29
North America	27.26	27.15
Latin America	1.82	1.95
Japan and rest of Asia	7.50	8.03
Africa	2.11	2.29
Australasia	2.44	2.46

* Data for Eastern Europe and the USSR are not available.

Table 11 below gives the production figures for sulphuric acid by country; it shows that the production rate is growing by about 9 per cent annually.

Table 11. Production of sulphuric acid by country
(Million tons of 100% H_2SO_4)

Country	1965	1966	Growth rate %
Australia	1.64	1.80	9.8
Belgium	1.49	1.36	-8.6
Canada	1.96	2.31	18.0
Federal Republic of Germany	3.75	3.83	2.0
France	2.92	3.07	5.0
Italy	2.98	3.37	13.0
Japan	5.66	6.03	6.5
Spain	1.62	1.71	5.5
United Kingdom	3.36	3.17	-5.6
United States	22.54	25.83	14.0
Total	47.92	52.48	9.6

World sulphuric acid production in terms of the main sources of raw materials is shown in table 12 below.

Early processes for making sulphuric acid were based on the roasting of sulphur to produce sulphur dioxide (SO_2), which was then catalytically converted to sulphur trioxide (SO_3) by nitrogen oxide gases. The sulphur trioxide was absorbed in water and sulphuric acid to yield additional sulphuric acid, and the nitrogen oxides were returned to the process. A brown "oil of vitriol" containing some 70

Table 12. World sulphuric acid production in 1967 by raw-material source ^a

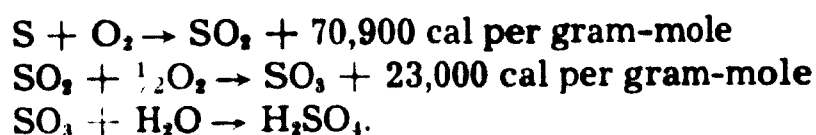
Source	Million tons of 100% H ₂ SO ₄
Brimstone	34
Pyrites	17
Other forms	12
	63

^a Excluding Eastern Europe, the USSR and China (mainland).

Most countries convert 80 to 85 per cent of their elemental sulphur consumption to sulphuric acid. Virtually all sulphur in pyrites and other non-elemental forms is also converted to acid.

per cent of H₂SO₄ was produced (Shreve, 1956, p. 367). The use of large lead chambers in this method gave it the name of the lead-chamber process. It has largely been replaced by the contact process.

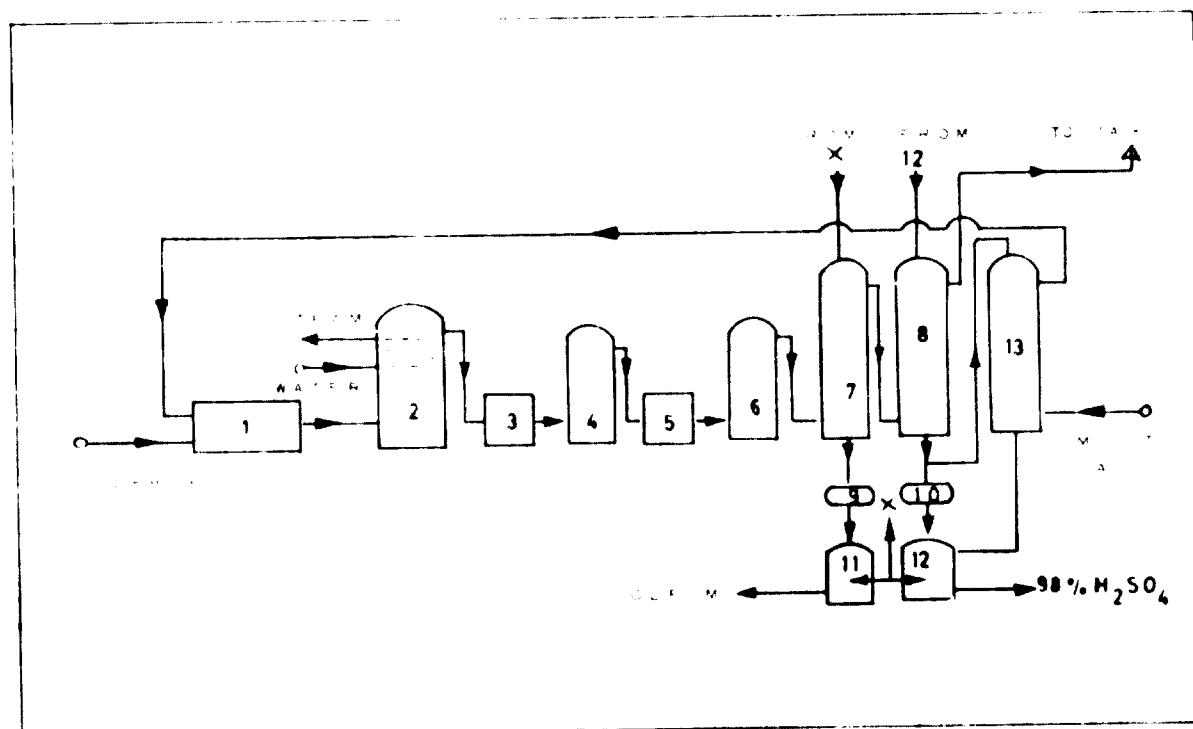
In the sulphur-type contact process (Shreve, 1956, p. 367), elemental sulphur is melted and injected into a specially designed combustion chamber, where it is burned with dried air to sulphur dioxide. The sulphur dioxide is converted to sulphur trioxide by passing it over beds of solid catalyst, such as vanadium pentoxide and/or other materials. The sulphur trioxide is absorbed in strong sulphuric acid to produce highly concentrated sulphuric acid (up to 100% H₂SO₄ or even greater) in the form of a heavy, colourless liquid. The principal reactions are:



The exothermic heat produced in this process is recovered in waste-heat boilers and is normally used to provide most or all of the power needs of the plant, as well as surplus low-pressure steam for other process purposes. Figure 3 below shows a simplified flow diagram of a typical sulphuric acid plant using the contact process.

Present-day sulphuric acid processes are highly efficient with respect to total sulphur conversion and power consumption. Some plant suppliers claim sulphur conversion efficiencies to be in the range of 98 to 98.5 per cent, expressed on the basis of the acid produced. The opportunity to reduce substantially the amount of sulphur needed for sulphuric acid production is thus limited to inefficiently operated or obsolete units.

Figure 3. Contact-type sulphuric acid plant



(1) sulphur burner, (2) waste heat boiler, (3) No. 1 converter, (4) No. 1 cooler, (5) No. 2 converter, (6) No. 2 cooler, (7) oleum tower, (8) 98% acid tower, (9) and (10) acid coolers, (11) oleum tank, (12) 98% acid tank, (13) drying tower.

Nitrogen fertilizers (ammonium sulphate)

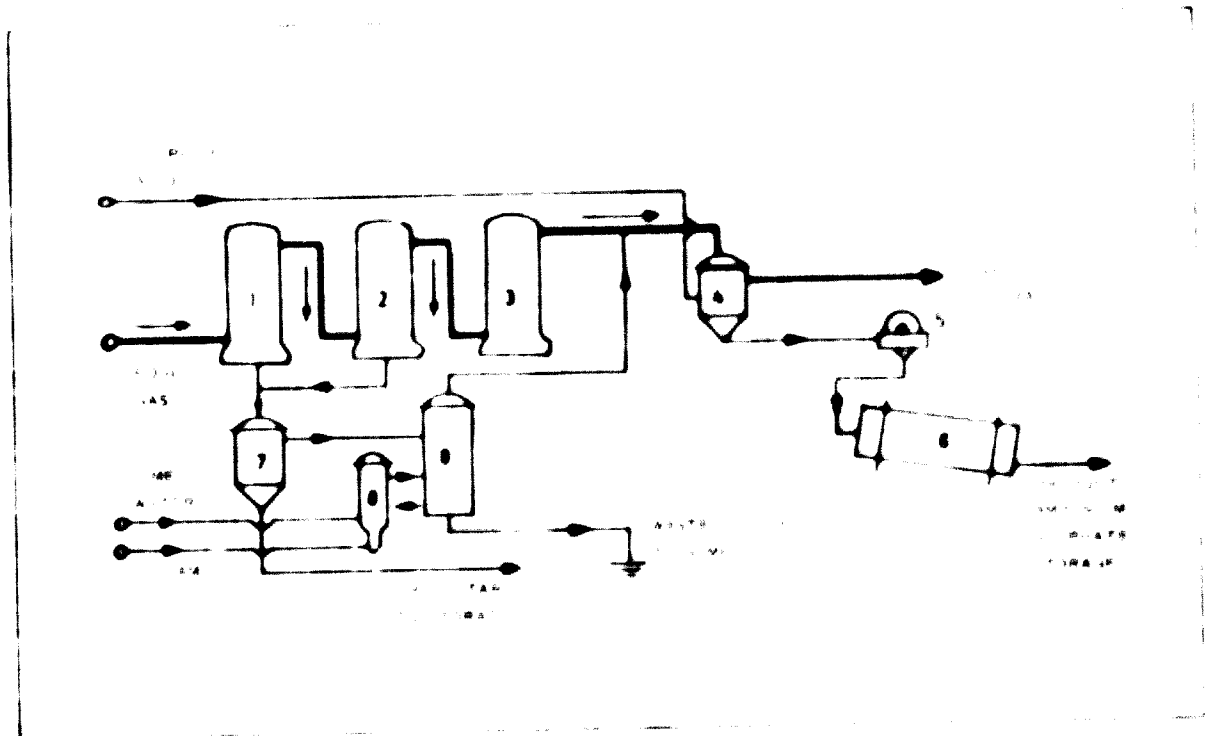
Ammonium sulphate was the earliest major synthetic chemical fertilizer, and large quantities of it are still produced throughout the world by various processes, the choice of which depends on technical and economic considerations (Pratt and Noyes, 1965).

Ammonium sulphate was first made on a large scale as a by-product from the manufacture of town gas and coke-oven gas. Many bituminous coals used for such purposes contain about 1 to 2 per cent of nitrogen, and some 15 per cent of this can be recovered in the form of 5 to 6 pounds of ammonia per ton of coal used. Several methods can be used for separating the ammonia from the gas and other materials evolved, ranging from direct washing with sulphuric acid to indirect methods involving the use of lime and steam distillation to purify the ammonia prior to neutralization. The ammonium sulphate crystals subsequently produced are separated, washed and dried, prior to bagging and shipping. Figure 4 below shows a typical flow diagram for the semi-direct process.

After the First World War, the increasing availability of synthetic ammonia led to the development of direct neutralization pro-

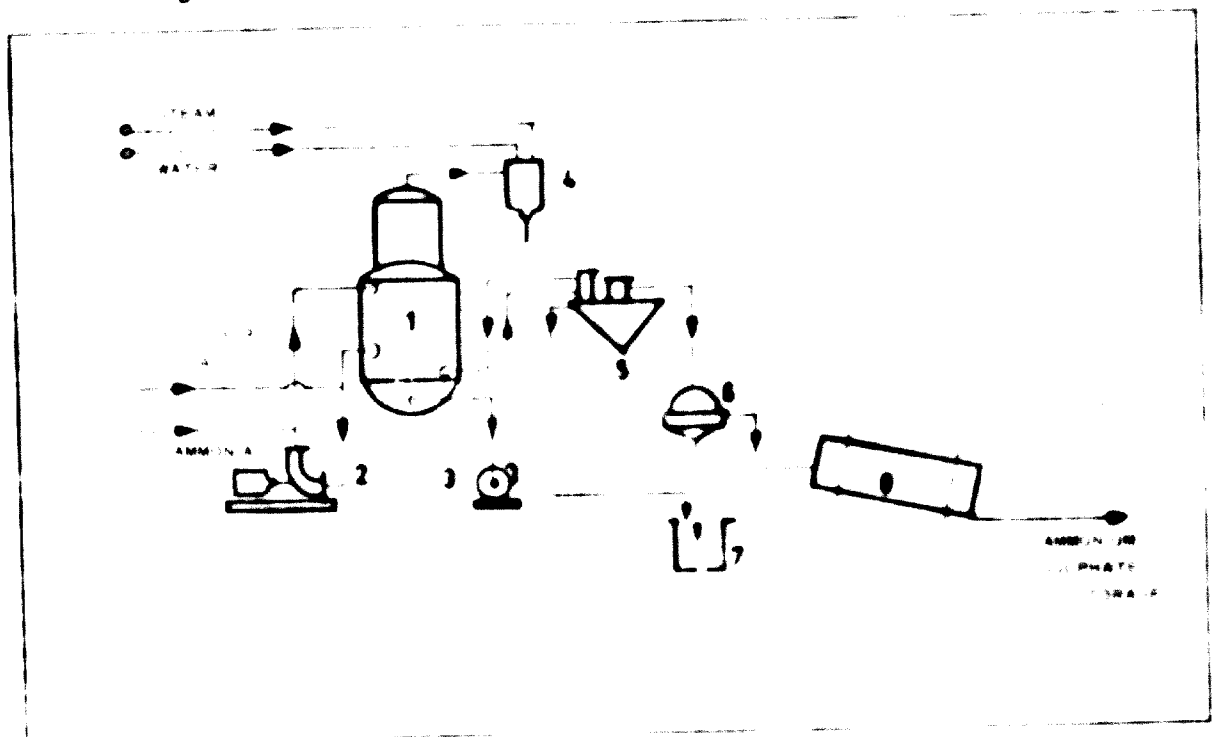
cesses. These also used vacuum evaporation and crystallization to reduce operating costs and to yield a uniform, superior product. Figure 5 below shows a simple flow diagram of this process.

Figure 4 Semi-direct process for ammonium sulphate production



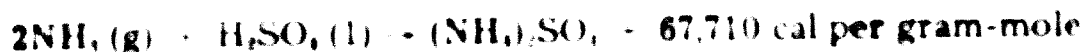
- (1) gas cooler, (2) tar precipitator, (3) gas reheater, (4) saturator-crystallizer, (5) centrifuge, (6) rotary drier, (7) tar separator, (8) ammonia still.

Figure 5. Ammonium sulphate vacuum-crystallizer unit



- (1) saturator-crystallizer, (2) recirculation pump, (3) slurry pump, (4) vacuum unit, (5) separator, (6) centrifuge, (7) liquor tank, (8) drier.

The basic reaction is



One ton of dry ammonium sulphate made by these methods requires about 0.74 ton of 100 per cent sulphuric acid and 0.25 ton of corresponding elemental sulphur (Ammonium sulphate can also be produced by methods not involving the initial use of sulphur and sulphuric acid.)

Potassium fertilizers

Although potassium chloride (KCl), or potash, is by far the dominant potassium fertilizer, some crops, such as tobacco, are extremely sensitive to chlorides, and potassium nitrate or potassium sulphate is used instead. Potassium sulphate can be produced from minerals such as burkeite, polyhalite and arcanite. It can also be made by the reaction of potassium chloride with sulphuric acid (Sauchelli, 1964, p. 392) to yield potassium sulphate and hydrochloric acid gas, according to the over-all reaction



Theoretically, one ton of dry potassium sulphate would require 0.57 ton of 100 per cent sulphuric acid, corresponding to 0.19 ton of elemental sulphur.

Combinations of ammonium sulphate, ammonium nitrate and potassium sulphate, perhaps in conjunction with other salts, are also produced either as mixtures or as double salts. Their sulphur requirements, if based on the use of sulphuric acid, can be determined stoichiometrically.

Phosphate fertilizers

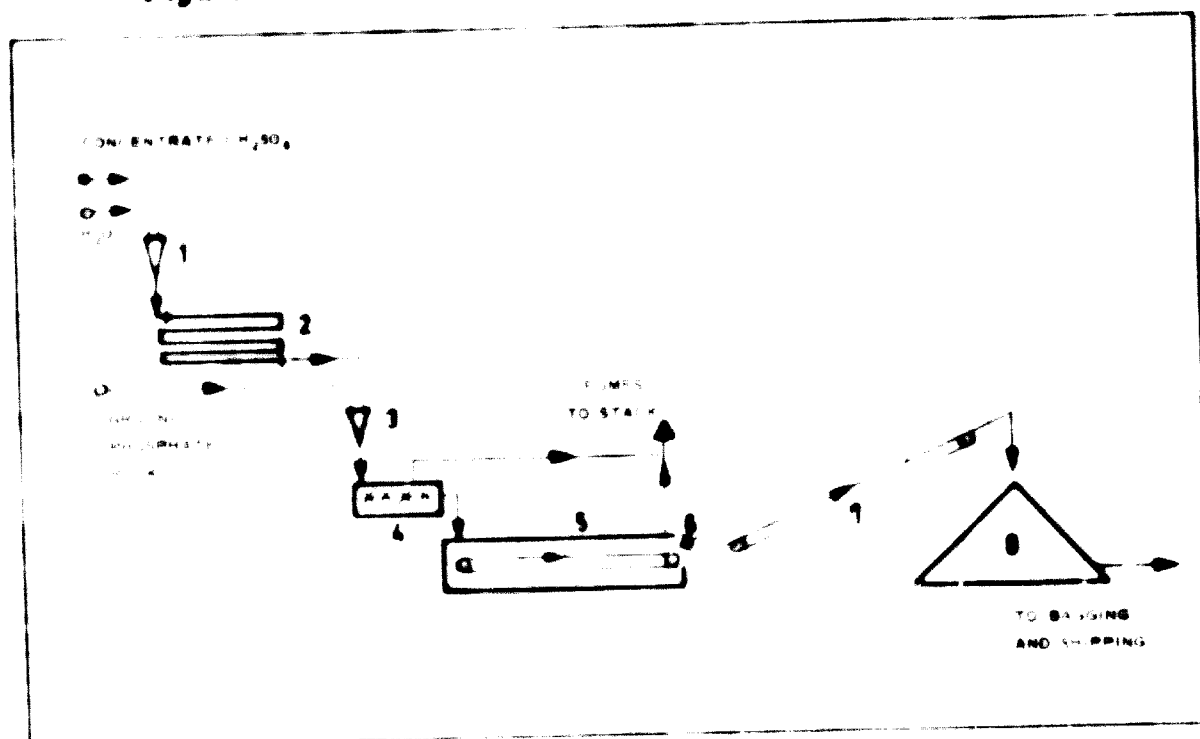
By far the greatest consumers of sulphur (as sulphuric acid) in the fertilizer industry are the phosphate manufacturers. Phosphate rock is virtually insoluble in most soils, unless the rock is finely ground and a favourable soil acidity exists. Therefore, a mineral acid is used to make the rock soluble prior to conversion to a fertilizer. For reasons of availability, suitability and economy, sulphuric acid has been the universal choice until comparatively recently, when an earlier shortage of sulphur in Europe led to the commercial development of alternative methods using limited quantities of sulphuric acid or even none at all.

Single superphosphates

About 1840, the German chemist Justus von Liebig recommended treating bones and other phosphoric substances with acid to improve supplies of phosphates. In England in 1842, John Lawes obtained a patent whereby phosphatic minerals, such as local coprolites, were mixed with sulphuric acid to make chemical manures. This was the beginning of the world-wide superphosphate industry, which by 1862 was producing 200,000 tons annually and today produces about 30 million tons a year.

Early manufacturing methods were based on mixing phosphate minerals with sulphuric acid by hand and allowing the slurry to set in a chamber or den. After a suitable curing period, the solid mass was dug out by hand. Modern processes employ the same principle, except that semi-continuous or continuous methods of acidulation and mechanical methods of handling are used in the interests of economy and product uniformity. (US Department of Agriculture, 1964; Sauchelli, 1963). The continuous den is a popular method and is normally used for outputs of between 10 and 50 tons per hour. Figure 6 below shows a simplified flow diagram.

Figure 6. Continuous-den single superphosphate plant



(1) acid diluter, (2) acid cooler, (3) acidulator, (4) mixer, (5) continuous den, (6) cutter, (7) storage conveyor, (8) curing and storage pile.

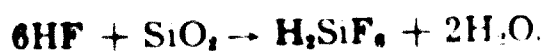
Besides calcium phosphate, phosphate rocks frequently contain calcium carbonate, calcium fluoride, iron and aluminium compounds, and clays and organic materials. These impurities must be reduced to suitable limits before the manufacture of fertilizer can begin in

order to ensure products of acceptable quality and to minimize sulphuric acid consumption and other processing requirements. Hence, phosphate rocks are often washed and up-graded by flotation or other means before use (Sauchelli, 1964). Significant amounts of calcium carbonate and/or organic material in the rock should be removed by chemical treatment or roasting to make processing easier.

The reactions between sulphuric acid and phosphate rock are complex, but under the usual operating conditions employed in single superphosphate manufacture, they can be empirically summarized as:



The HF evolved reacts with the silica present in most rocks as follows:

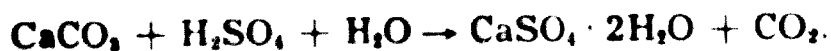


Iron and similar impurities, such as aluminium, in the rock react in the following general way:



These phosphates are largely insoluble in water; this shows the importance of using very pure rock in order to maintain high phosphate returns on a water-soluble basis.

Calcium carbonate in the rock reacts wastefully with sulphuric acid and generates carbon dioxide, which may also cause processing trouble, i.e.



Thus, the use of high-grade phosphate rock with a low impurity content and high reactivity is necessary when producing high-quality, single superphosphates. Choice of the proper acid-to-rock ratio is also important. Insufficient acid will leave part of the P_2O_5 in the rock in a form insoluble in water, while excess acid is wasteful and will also weaken fibre or paper bags after packing, unless "sweetened" by a suitable alkali-containing material.

Typical requirements of raw materials in pounds per ton of single superphosphate produced are:

Rock	1,190
Sulphuric acid (100%)	700
Dilution water	300
Total	2,190

Water vapour and gases containing fluorine are evolved during and after manufacture. The cured product usually contains 6 to 10 per cent moisture.

Single superphosphates are essentially mixtures of monocalcium phosphate, gypsum and various impurities, plus moisture. As a result, chemical analyses differ according to the rocks used and the process employed. Water-soluble P_2O_5 is usually between 16 and 20 per cent; a typical analysis for a cured product might be:

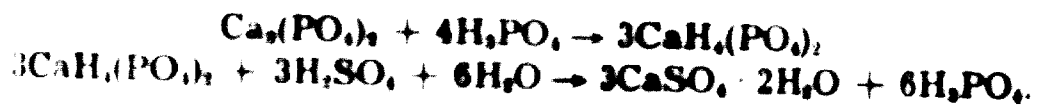
	<i>weight per cent</i>
Total P_2O_5	20.0
Citrate-insoluble P_2O_5	1.0
Available P_2O_5	19.0
Water-soluble P_2O_5	17.5
CaC	29.0
Sulphates as SO_3	31.0
Fluorine	2.0
Free moisture	2.0
Free acid	1.0

Concentrated superphosphates

The presence of gypsum in single superphosphate results in a low-analysis phosphate fertilizer. By making a product free from gypsum it is possible to raise the P_2O_5 content from about 20 per cent to nearly 50 per cent. This is done by making phosphoric acid and then reacting this with phosphate rock to produce concentrated or triple superphosphate (TSP)

Phosphoric acid

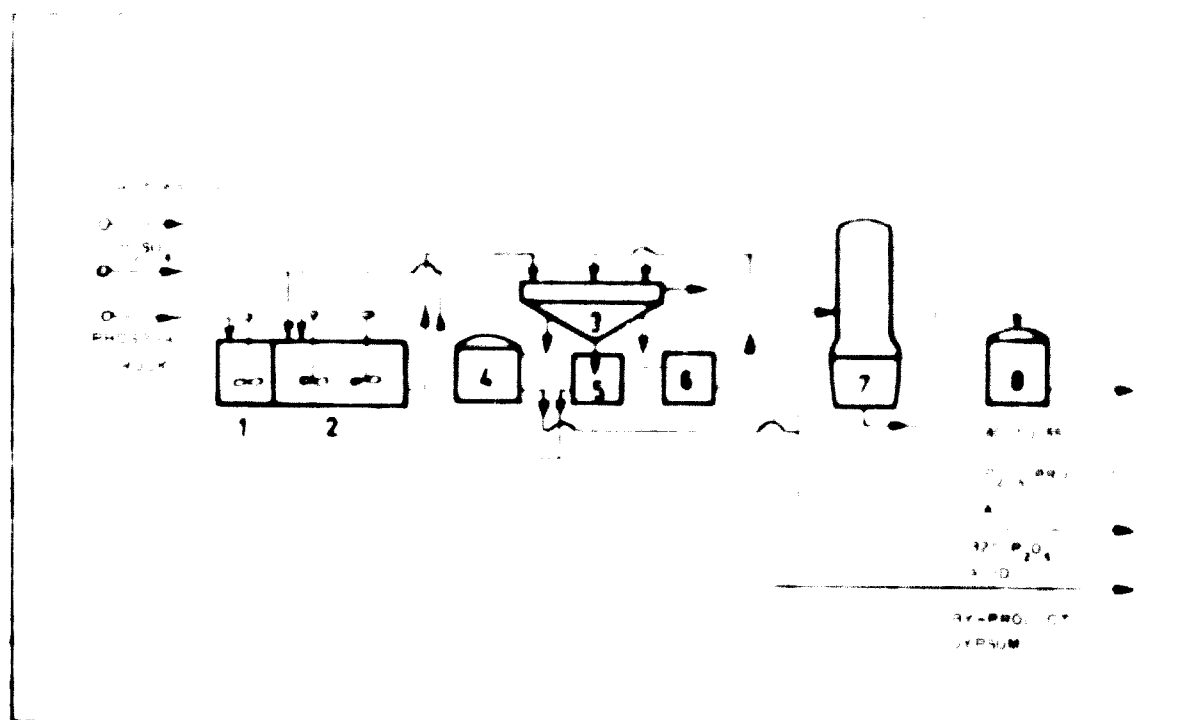
Beneficiated, ground phosphate rock normally containing 31 to 33 per cent P_2O_5 is reacted with a mixture of concentrated sulphuric acid (usually 90 to 98 per cent H_2SO_4) and recycled phosphoric acid to form additional phosphoric acid and gypsum, as shown empirically in the following equation:



Impurities in the rock consume sulphuric acid wastefully in accordance with the reactions shown earlier in connexion with single superphosphates

The gypsum is removed by filtration, and the phosphoric acid is evaporated to a maximum concentration of 54 per cent P_2O_5 , according to requirements. The gypsum, corresponding to most of the sulphuric acid used in the process, is usually discarded in a nearby waste pile or flushed to a local river or sea. Figure 7 below shows a basic flow diagram of a wet-process phosphoric acid plant.

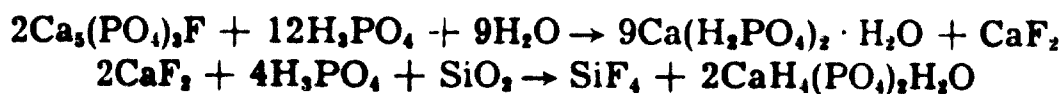
Figure 7. Wet-process phosphoric acid plant



(1) reaction section, (2) digestion section, (3) continuous filter, (4) 32% P₂O₅ acid tank, (5) recycle acid tank, (6) wash acid tank, (7) evaporator, (8) product acid tank.

Concentrated phosphates

Concentrated superphosphates are produced in a manner similar to single superphosphates, but concentrated phosphoric acid is used in place of sulphuric acid:



Impurities such as calcium carbonate, fluorides, iron and aluminium compounds in the secondary rock also consume phosphoric acid, and in turn lead to a waste of sulphuric acid. Therefore, use of a finely-ground, high-quality phosphate rock is of the utmost importance.

Various processes for manufacturing concentrated superphosphate exist. (Sauchelli, 1964, Ch. 8; Van Wazer, 1961, Vol. 2, p. 1,084). In one case the rock and acid are combined in a continuous mechanical mixer and allowed to cure partially on a slatted belt in a den before being disintegrated and conveyed to a storage pile for a further curing period of several weeks. In other cases a non-mechanical mixer and curing/conveyor rubber belt are used. Material retrieved from the storage pile can be used in run-of-pile form, or it can be screened and/or granulated to a specific size. In another process, phosphate rock is slurried with phosphoric acid of about 45 per cent P₂O₅ concentration, combined with the solid recycled granu-

lar product dried and screened to give a fully cured, granular, concentrated triple superphosphate

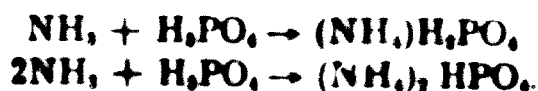
A concentrated superphosphate of the triple type may have the following analysis

	weight percent
Total P_2O_5	48
Citrate-insoluble P_2O_5	2
Available P_2O_5	46
Water-soluble P_2O_5	44
CaO	21
Sulphates	2
Fluorine	2
Free moisture	3
Free acid	4

In some cases concentrated superphosphates are produced with P_2O_5 concentrations in the range of 35 to 45 per cent by using mixed sulphuric and phosphoric acids. The addition of ammonia to single and concentrated superphosphates will yield products containing low percentages of nitrogen. Mixture with nitrogen salts and/or potash salts will permit a wide range of N-P and N-P-K or P-K fertilizers to be made

Ammonium phosphates

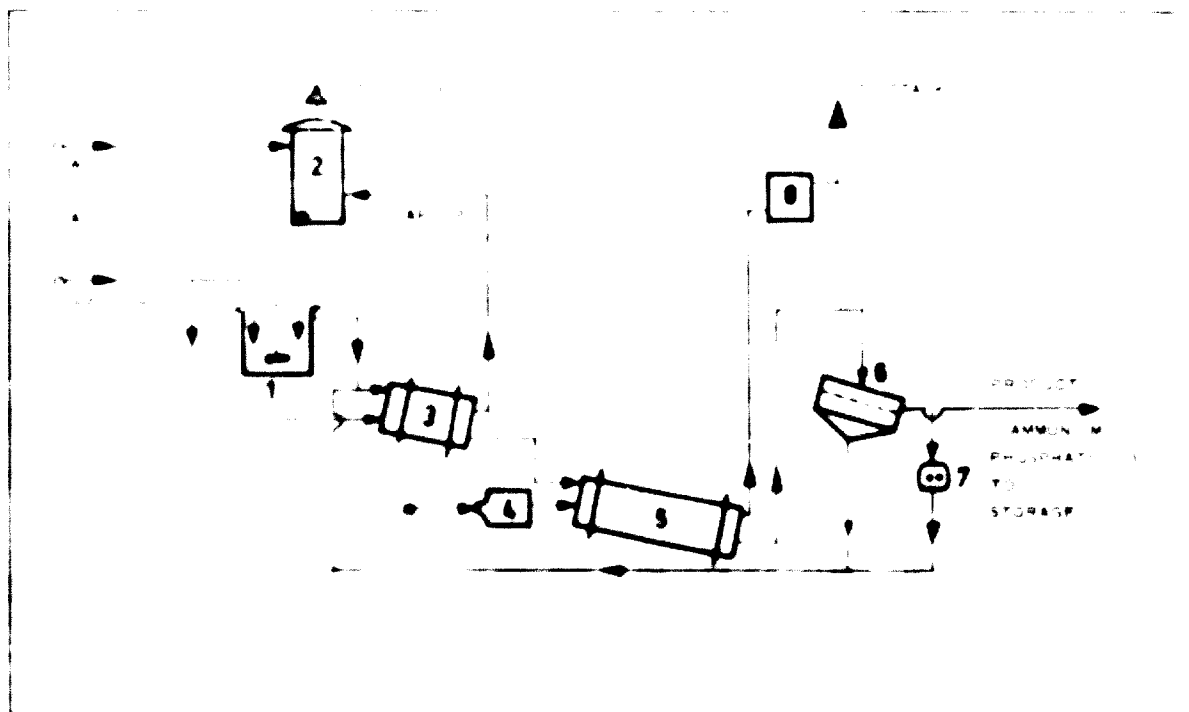
Ammonium phosphates, one of the fastest growing groups of fertilizers, are made by reacting ammonia with phosphoric acid. Usually, wet-process acid is employed, although electric-furnace phosphoric acid is sometimes used instead of sulphuric acid to recover ammonia from coke-oven gas, thereby producing ammonium phosphate instead of ammonium sulphate. According to the ratio of ammonia/phosphoric acid selected, either the monoammonium or the diammonium salt can be produced, or various combinations of these, such as



Ammonium phosphates derived from electric-furnace acid are usually crystallized from the reaction liquor, dried and bagged. When made with wet-process phosphoric acid, the reaction slurry is normally produced in granular form in a conventional recycling system as shown in figure 8 below.

Using ammonium phosphate slurry as a base, a wide range of water-soluble, granulated binary and ternary N-P and N-P-K fertilizers can be made by adding nitrogen salts, such as ammonium nitrate or urea, and potash to the circuit. The system shown in figure 8 can

Figure 8. Diammonium phosphate plant of the type used by the US Tennessee Valley Authority (TVA).



(1) pre-neutralizer, (2) reaction scrubber, (3) TVA granulator, (4) furnace, (5) rotary drier, (6) screens, (7) crusher, (8) dust scrubber.

also be used to produce granulated triple superphosphate by adding ground phosphate rock instead of ammonia.

Polyphosphate fertilizers

In recent years a more highly concentrated form of phosphoric acid containing 68 to 76 per cent P_2O_5 has become available commercially. Known as superphosphoric acid, this product can be made either by electric-furnace or wet-process methods (Peterson et al., 1963) and is used to make high-analysis liquid and solid fertilizers, principally by ammoniating the super-acid.

The derivatives, known as polyphosphates, possess several desirable properties in addition to high analysis (Pratt and Noyes, 1965, p. 74). Limited commercial quantities are made from furnace acid, which, unlike the products of wet-process origin, avoids the use of sulphur.

4.

Sulphur-saving fertilizer processes

Under normal conditions, any fertilizer process designed to reduce or eliminate the use of sulphur must also meet the following requirements:

- (a) The product must be agronomically successful, commercially acceptable and sell at a competitive price with established materials of equivalent nutrient value.
- (b) The raw materials, plant, utilities and other manufacturing needs must be readily available at the site.

However, a sulphur shortage and/or extremely high sulphur prices could turn a normally uncompetitive process or product into a competitive one. A sulphur famine would modify all prerequisites, with the exception of agronomic suitability, and even in this regard, some compromise might have to be accepted.

With these considerations in mind, the various processes and products either commercially available or partly developed can be studied as possible alternatives offering economies in the use of sulphur.

Nitrogen fertilizers (ammonium sulphate)

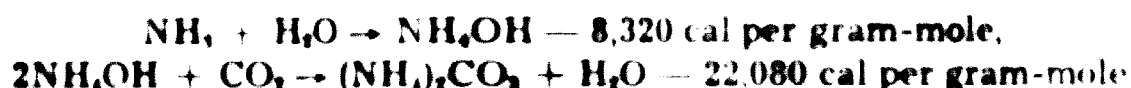
The principal nitrogen fertilizer containing sulphur is ammonium sulphate, for which several methods of production are

available (Pratt and Noyes, 1965, p. 74; United Nations Industrial Development Organization, 1967). Where plentiful supplies of low-cost sulphuric acid exist, direct neutralization processes incorporating simultaneous evaporation and crystallization are normally used as they are able to make crystals of excellent quality for minimum operating costs.

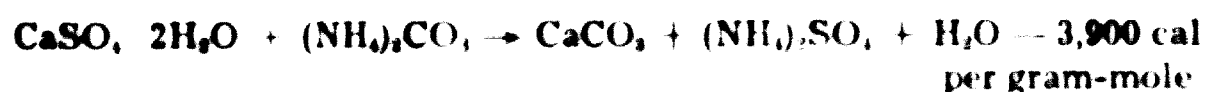
In some countries lacking sources of sulphur, such as Austria, Great Britain and India, large tonnages of ammonium sulphate are made from native gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4). In some cases by-product gypsum from wet-process phosphoric acid plants is used. Methods based on the use of waste gases containing sulphur are also available or have been proposed (Pratt and Noyes, 1965, p. 74). These processes will now be briefly described.

Ammonium sulphate from calcium sulphate

This method, sometimes called the Merseburg process, is based on the reaction between ammonium carbonate and calcium sulphate, which yields ammonium sulphate and calcium carbonate. Ammonium carbonate is first made from ammonia and carbon dioxide.



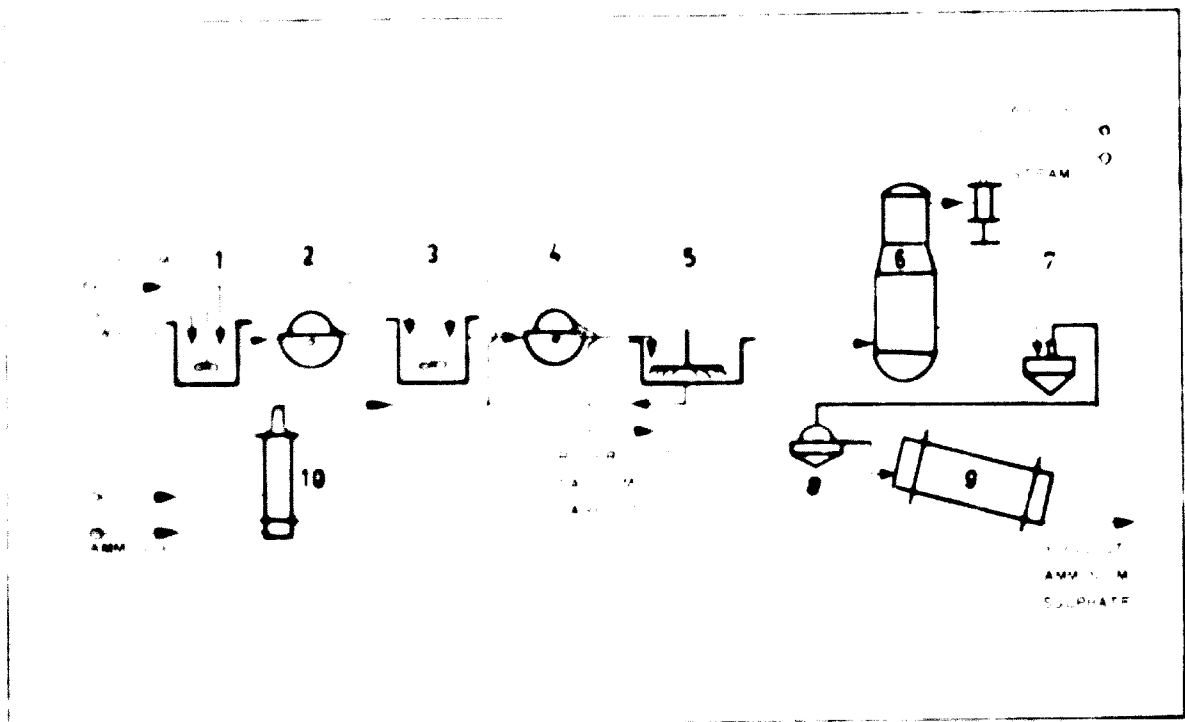
Ammonium sulphate is then produced according to the following reaction:



The ammonium carbonate solution is made by absorbing anhydrous ammonia in water and carbonating either at atmospheric pressure or higher to produce a liquor containing about 170 grams of NH_3 and 225 grams of CO_2 per litre. In some plants jet mixers are used as an alternative to large absorbing and carbonating towers. Heat from the reaction is removed by inter-coolers and used to vaporize the ammonia feed.

The natural gypsum or anhydrite raw material is normally ground to a fineness of about 90 per cent through 100 mesh and reacted for some 4 to 6 hours in wooden or mild steel tanks. The calcium carbonate is removed by filtration, and the sulphate liquor containing about 500 to 520 grams $(\text{NH}_4)_2\text{SO}_4$ per litre is concentrated in multiple-effect evaporator crystallizers. The ammonium sulphate crystals produced are centrifuged and dried at 120° to 130° C and are comparable in quality to sulphate produced by direct neutralization, provided, of course, the process is properly operated. Figure 9 below shows a basic flow diagram of the method.

Figure 9. Gypsum process for ammonium sulphate production



(1) gypsum wash tank, (2) gypsum filter, (3) reaction tank(s), (4) carbonate filter, (5) clarifier, (6) vacuum evaporators, (7) crystal separator, (8) centrifuge, (9) rotary drier, (10) ammonium carbonate unit.

To furnish the required ammonia and carbon dioxide, an ammonia plant must either be built or should be located nearby. An alternative might be to transport refrigerated ammonia to the site and to generate the carbon dioxide by burning the by-product calcium carbonate in a shaft furnace or rotary kiln. The calcium carbonate and any quicklime made from it should find a market as an agricultural dressing and as a raw material for the manufacture of cement.

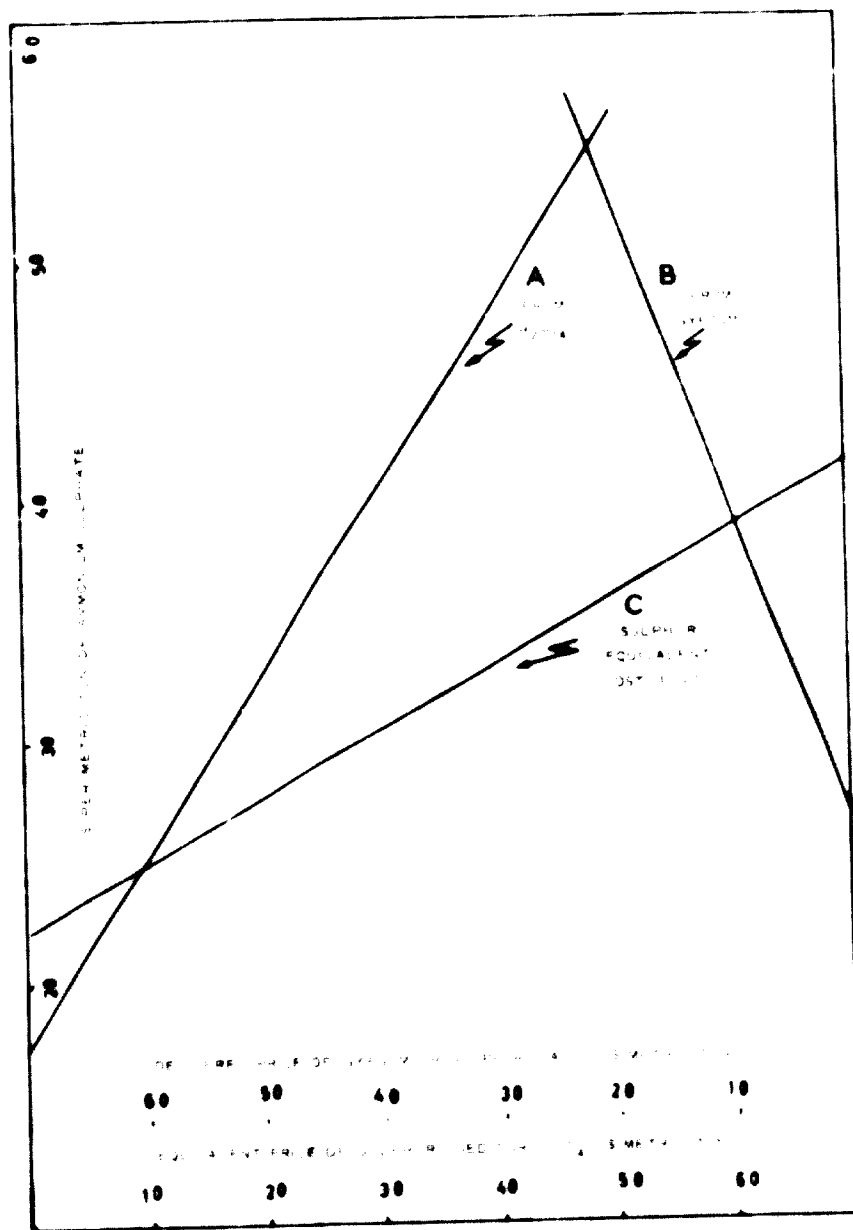
An important item of cost is the delivered price of the calcium sulphate, and for this reason, anhydrite (CaSO_4) is preferable to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). A little more than one ton of anhydrite is required to make one ton of ammonium sulphate, but anhydrite contains only about 25 per cent of sulphur. Thus, by weight about four times as much anhydrite as sulphur is needed.

Both gypsum and anhydrite are low-price materials (about \$2 to \$4 per ton ex-mine in some parts of the world); however, transport can increase ex-mine prices considerably. If possible, therefore, the plant should be built, as in England, near a large source of calcium sulphate to be competitive with processes based on the use of sulphuric acid made from pyrites or sulphur. One large ammonium sulphate plant in India uses gypsum transported by rail from mines nearly 1,000 miles away; nevertheless, the savings in foreign ex-

change are said to justify the relatively high delivered cost of the raw material.

It is difficult to make cost comparisons between ammonium sulphates produced from sulphur and from calcium sulphate without

Figure 10. Relative production costs for the manufacture of ammonium sulphate using various sulphur sources



Basis: 300 metric tons per day; \$40 per ton of NH_3 . Capital costs for A — \$2.0 million, for B — \$3.5 million.

knowing the details of each specific case and the delivered costs of raw materials. Accordingly, in figure 10 above comparative costs are given in terms of elemental sulphur and gypsum at various costs, including delivery, based on an output of 300 tons of ammonium sulphate per day.

Capital costs for the direct neutralization plant and the gypsum-based plant are assumed to be \$2 and \$3.5 million respectively. The

higher cost of the latter is due to the need for handling larger quantities of materials as well as the need for an ammonium carbonate unit and a reaction filtration section. Labour and other production costs are also corresponding v higher. The direct neutralization plant, however, needs a supply of sulphuric acid, preferably from a captive source, amounting to about 240 tons per day, which in terms of a battery limits unit would bring the total investment to a figure as high as the cost of a gypsum ammonium sulphate plant.

In figure 10, ammonia has been assumed to be available at a delivered cost of \$40 per ton and carbon dioxide to be obtainable cost-free, both from a captive ammonia unit situated nearby. It would be possible to use anhydrous ammonia purchased in bulk elsewhere, provided a separate source of carbon dioxide were available. This could be supplied by calcining the by-product calcium carbonate and making up the difference by burning additional limestone, or perhaps by using local flue gases. In the cost calculations, no credits have been allowed for the possible sale of by-product calcium carbonate, or for waste steam from the sulphuric-acid neutralization units.

Figure 10 demonstrates that anhydrite or gypsum at a reasonably low delivered cost is a competitive source of sulphur for the manufacture of ammonium sulphate when delivered elemental sulphur costs are about \$40 per ton.

Many established concentrated phosphate fertilizer plants have a large accumulation of by-product gypsum at hand. Although sometimes the gypsum may be flushed away to a local river or the sea, it is possible to use it for manufacturing ammonium sulphate, provided suitable treatment is undertaken beforehand. One leading Indian fertilizer company has used by-product gypsum in this way for some time and has recently offered to license the technology of the process to others (George and Gropinath, 1964).

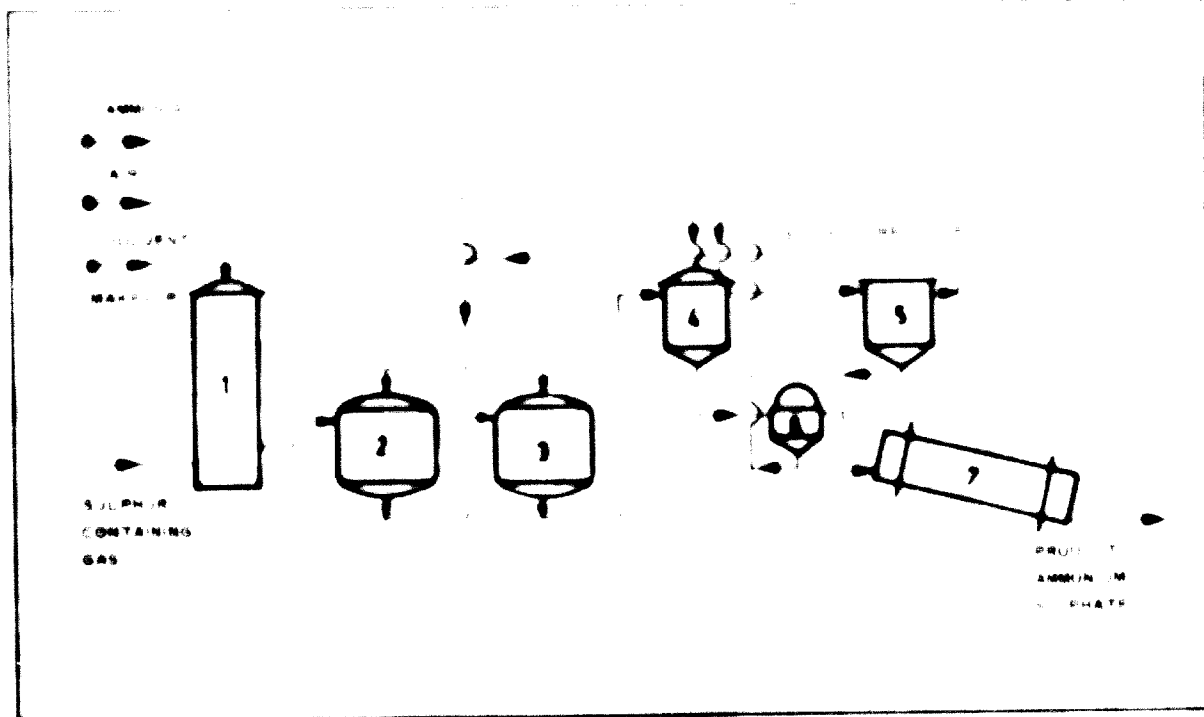
Ammonium sulphate from lean off-gases

A more recently developed method for producing ammonium sulphate offers possibilities of recovering sulphur from lean stack gases containing marginal amounts of sulphur dioxide. Known as the Piritas Españolas process (Anon. 1960), it is based on the absorption of sulphurous gas by a basic organic solvent, such as xylidine or monoethanolamine, in a packed absorption column to form a basic sulphite. The solvent then passes to oxidation reactors, where it is blown with air and cooled.

After complete oxidation, the liquor is sent to a saturator, where it is reacted with ammonia, which frees the organic base and produces a saturated ammonium solution. The base is recycled and the ammonium sulphate crystallized, centrifuged and dried.

Exothermic heat from the absorption and reaction units is used to provide most of the necessary evaporation and drying. Figure 11 below shows a simplified flow diagram of this process.

Figure 11 Pyritas Española's process for ammonium sulphate production



(1) absorber, (2) primary reactor, (3) secondary reactor, (4) saturator-crystallizer, (5) separation tank, (6) centrifuge, (7) rotary drier.

Potassium fertilizers

As an alternative to producing potassium sulphate from potash (KCl) and sulphuric acid by the Mannheim process, or from potash and sulphur by the Hargreaves process, potassium sulphate can be recovered from natural minerals by several methods and thus the need for elemental sulphur is eliminated (British Patent No. 902,363). Although these processes are highly specialized, they might possibly be made available from sources in the United States and in Europe, under licence, to developing countries possessing suitable mineral reserves and in need of appreciable quantities of potassium sulphate for special agronomic purposes.

Phosphate fertilizers

Because of the need to render soluble the phosphate component in phosphate rock, this group of fertilizers offers the greatest potential field for effecting savings in sulphur. As previously shown,

sulphuric acid is the principal material used for this purpose; hence, any method which reduces or eliminates the need for sulphuric acid should be carefully studied.

The main component of most phosphate rocks is the mineral apatite, which can be empirically expressed as $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$. The extreme insolubility of apatites in water has preserved their existence and widespread distribution throughout many geological periods, but when they are used as fertilizers, some method of rendering the phosphate component available to plant life must be used. It is generally understood that the insolubility is due to the chelating effect of the CaF_2 molecules in the crystal lattice, since removal of part or all of the F_2 imparts varying degrees of solubility in water and soils.

For convenience, the various methods for saving sulphur that are available or proposed will be grouped into physical and chemical processes according to their character.

Physical processes

Grinding

Although phosphate rocks are regarded as being generally insoluble in water and dilute acids, deposits found in different parts of the world do vary in this respect. For example, primary igneous rocks that have not been subjected to extreme weathering, such as the apatites found in the northern region of the Soviet Union and in South Africa, are virtually insoluble in water and soil acids and may also exhibit the low reactivity rates of strong acids. Other phosphate rocks may have been exposed to lengthy periods of weathering and may perhaps have been partly dissolved by sea-water and redeposited elsewhere. In such cases, solubility and reactivity might be relatively greater than for the true apatites, especially in acid soils.

By grinding the more soluble rocks to a small size, the amount of phosphate available can be greatly increased. Large tonnages of ground rocks from North Africa, Christmas Island and Florida have been used directly on acid soils in various parts of the world for many years. Although very fine grinding could be expected to increase proportionately the amount of phosphate available, limits are imposed by the cost of grinding and increased difficulty in handling and application. Phosphate rock ground to sizes in the 200-mesh range and below fluidizes readily, but it can also cause severe dust problems and excessive losses. Hence, rock in the 100-to-200-mesh range is often preferred for direct application to soil.

However, large low-cost granulation processes offer a new potential for ground phosphate rock, either alone or in conjunction with other fertilizer materials, such as ammonium sulphate and urea, or ammonium nitrate (British Patent No. 902,363) and potash.

In granulated form, a much finer particle can be tolerated, with correspondingly better availability to plants and negligible problems of dust and loss. As an alternative to granulation by rotary methods, trials have shown that compacting (Allis-Chalmers Co., Milwaukee, USA) also offers possibilities for producing mixtures of finely ground phosphate rock and other fertilizer materials in agglomerated form. The only binder needed when granulating and compacting such mixtures is 1 or 2 per cent of water. (In compacting, even subsequent drying is not required.) Properly made granules and compacted agglomerates of appropriate size (about 3 to 5 mm in diameter) exhibit good storage, handling and application properties yet readily disintegrate in the soil.

Granulated and compacted mixtures of this nature, incorporating finely or very finely ground phosphate rock of the more soluble and active type, are considered possible alternatives to phosphates made soluble by chemical means, especially in times of sulphur shortage. This is particularly important for developing countries because capital requirements are relatively small, the techniques are simple, and a wide range of raw materials and product formulations is possible. Of course, specific soil conditions and crop responses need to be checked before recommendations can be made.

Decomposition by heating

Defluorinated rock. Much work has been undertaken in the United States and in the Soviet Union on the decomposition of phosphate rock by heating (Sauchelli, 1964, p. 345; Waggaman, 1952, p. 376). One difficulty is that the temperature needed for defluorination is usually near the fusion point of the rock (approximately 1,500° C). Another is that reversion to unavailable tricalcium phosphate may occur by annealing, unless the defluorinated product is quickly cooled and ground. Hence, close temperature control in the rotary kilns used in this method is essential.

In practice, silica is usually added to the rock, which is fed into the cool end of the kiln, while water is injected into the hot, discharge end. The fluorine, water vapour and silica react at the high temperature to form HF and SiF₄ and escape from the kiln. The product contains mostly citrate-soluble P₂O₅ (principally alpha-tricalcium phosphate) and under 0.1 per cent fluorine. The principal end-use of this type of defluorinated rock is for animal feed and not for fertilizers. For developing countries, a more suitable alternative involving a lower capital investment might be the production of dicalcium phosphate by chemical means.

Fused tricalcium phosphate Extensive studies were undertaken some time ago in the United States on the production of

alpha-tricalcium phosphate from fused phosphate rock in a shaft furnace (Anon., 1963 e). Although the product proved to be suitable for some crops on acid soils, it did not produce good results on alkaline or calcareous soils. As far as is known, no large-scale process of this type is in operation at present.

Fused alkali-phosphate products. The addition of alkali salts to phosphate usually lowers the calcining temperature required for defluorination purposes, and several operating processes are based on this principle. In the Federal Republic of Germany, Rhenania phosphate is made by calcining phosphate rock, sodium carbonate and silica. Rochling phosphate is a similar product made from phosphate rock and a soda slag. In both products much of the total P_2O_5 is citrate-soluble, and little fluorine is removed.

Numerous other processes based on the fusion of phosphate rock with various salts have been developed or proposed. In one of these, a mixture of phosphate rock, magnesia and silica is fused in an electric-arc furnace to produce calcium magnesium phosphate, which has proved to be successful on acid soils (Van Wazer, 1961, Vol. 2, p. 1,093). The use of sodium sulphate and gypsum has also been studied (Sauchelli, 1964, p. 351), but no large-scale processes of this nature are yet known. One proposed method of potential interest is based on the low-temperature fusion of phosphate rock with ammonium phosphate and the addition of ammonium carbonate to produce more ammonium phosphate and calcium carbonate (Barnes).

In another thermal process in commercial operation in the United States, (Sauchelli, 1964, p. 354) elemental phosphorus is burned with air and phosphate rock to yield calcium metaphosphate $Ca(PO_3)_2$, containing about 64 per cent P_2O_5 , mostly in a citrate-soluble form, and approximately 0.2 per cent fluorine.

The foregoing thermal processes in general require high capital investment and appreciable quantities of fuel and energy. The products are mostly citrate-soluble and not especially suited to alkaline or calcareous soils. Although these processes do not use sulphur, they cannot be recommended as a first choice for a country wishing to reduce the sulphur requirements of its fertilizer industry.

The possible availability of phosphate-containing slags from iron and steel plants should also be borne in mind, since these give good results on pasture and non-alkaline soils, when finely ground.

Electric-furnace method. A major thermal process for treating phosphate rock is based on reduction with carbon, plus silica, to produce phosphorus, which can be empirically shown as:



Some silica also reacts with the fluorine present in the rock, while metallic impurities, such as iron compounds, are reduced and form ferrophosphorus, a material of commercial value.

In practice, electric-arc furnaces are generally employed (Van Wazer, 1961, Vol. 2, p. 1149), although the use of a shaft or blast furnace is also possible (Waggaman, 1952, p. 144), as well as rotary horizontal kilns. The phosphorus vapour evolved from the furnace is usually condensed to elemental phosphorus (P_4), which is used for numerous industrial purposes. In the United States and in Europe, much of the elemental phosphorus produced is burned with air to produce P_2O_5 , which is then absorbed in water to form high-purity phosphoric acid (H_3PO_4) (Van Wazer, 1961, Vol. 2, Ch. 18). Most of this is used in the detergent, food and chemical industries, and very little for fertilizer production because of the relatively high cost compared with wet-process acid.

However, furnace-grade phosphoric acid is occasionally used for fertilizer manufacture, especially from captive sources when in surplus supply and/or during peak fertilizer demand periods. It is also increasingly used to produce high-grade diammonium phosphate fertilizer from coke-oven gas (instead of ammonium sulphate by scrubbing with sulphuric acid), since the diammonium phosphate commands a higher price and a better margin of profit.

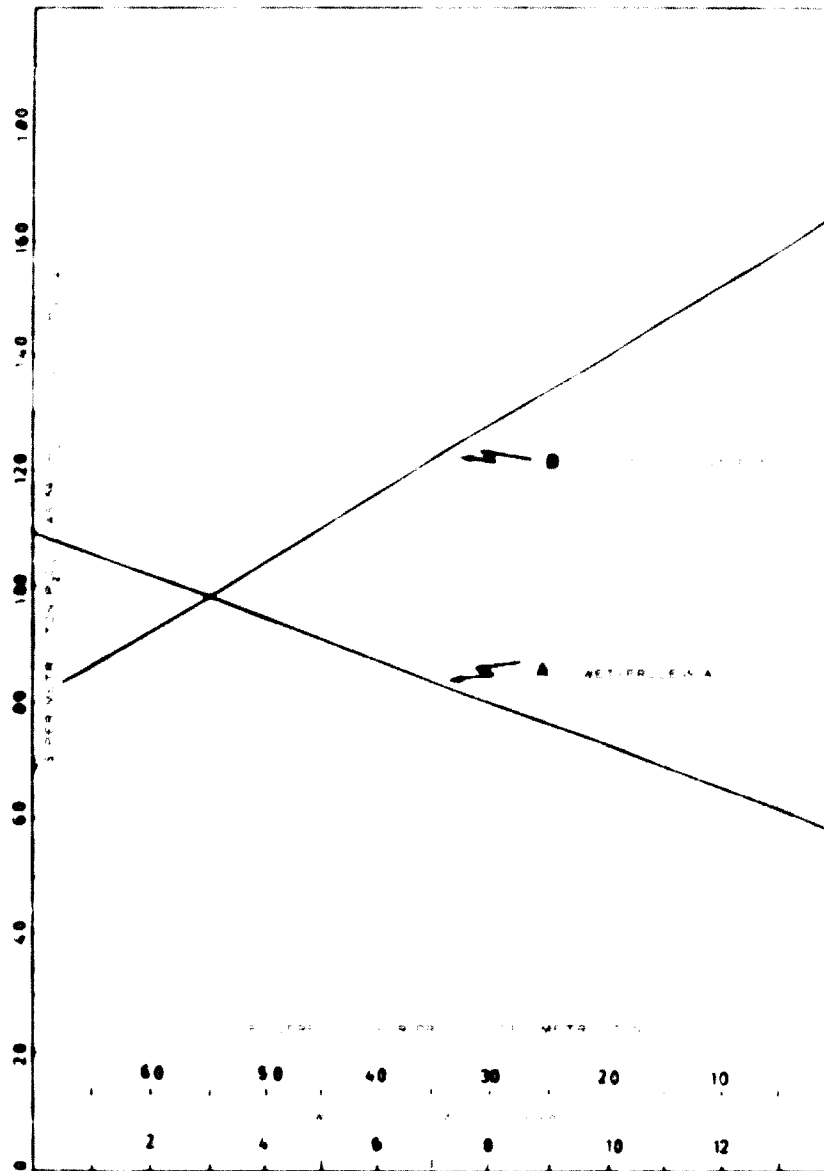
A sulphur shortage and correspondingly high sulphur prices, nevertheless, could make electric-furnace acid much more attractive for the production of fertilizers, especially in areas where low-cost power is available. In figure 12 below the costs of wet-process phosphoric acid and electric-furnace phosphoric acid are compared on the basis of 54 per cent P_2O_5 (75 per cent H_3PO_4) in each case. The effects of sulphur prices and power costs on the production costs of wet-process acid and electric-furnace acid are shown respectively. Other unit cost items are the same except the delivered phosphate rock costs. These figures are based on an output of 220 tons of P_2O_5 per day. Fixed investments for the sulphuric and phosphoric acid plants are taken as \$6.6 million and for the phosphorus furnace and furnace acid plant, \$7.3 million, including all off-site factories (Bixby et al., 1964). Phosphate rock costs for the furnace and the wet-process unit have been assumed to be \$6.9 and \$8.5 per ton respectively. A credit of \$5 per ton of P_2O_5 has been given for slag and ferrophosphorus sales in the case of the furnace acid and a cost of \$1 per ton of P_2O_5 has been included in the wet-process acid cost for gypsum disposal.

It should be noted that these costs are average ones and are intended to show the relative effects of sulphur prices and power charges, rather than specific acid costs for each process. However, approximate acid costs for higher delivered costs for rock can easily be calculated by including the corresponding cost of the transport of rock. Specific cost estimates can be worked out on the basis of actual local data in conjunction with published information (Bixby

et al., 1964; Van Wazer, 1961, Vol. 2, Ch. 18) and experienced plant contractors.

A delivered price for sulphur in the region of \$50 per ton causes the corresponding wet-process phosphoric acid cost to

Figure 12. Typical cost relation between electric-furnace and wet-process phosphoric acids



Basis: 220 metric tons P_2O_5 produced per day, rock for A 75 BPL at \$8.5/metric ton, rock for B 70 BPL at \$6.9/metric ton, power for A \$0.007 per kWh, other unit costs identical. A includes \$1 per ton of P_2O_5 for gypsum disposal; B includes \$5 per ton P_2O_5 credit for slag and ferrophosphorus. (Compare also with figure 14 b.)

approach the cost of furnace-grade phosphoric acid, if produced from low-cost power in the range of 3 to 5 mills per kWh. Of course, for power in the 10-mill range and over, the cost of electric-furnace acid becomes prohibitive, except in the case of sulphur famine or if there is no other means of making water-soluble fertilizers. Never-

theless, the production of phosphorus and corresponding phosphoric acid should be carefully studied as an alternative to wet-process acid for fertilizer production in cases of sulphur shortage, especially for developing areas.

Several additional factors must also be considered. First, in some developing areas, large hydroelectric projects or substantial natural gas supplies at low cost enable power to be supplied at low rates, yet there may not be sufficient local demand to yield an economic return. A medium or large phosphorus producer could be a welcome customer, as he would require a continuous, heavy load and could himself obtain power on a long contract at attractive rates, probably in the range of 3 to 5 mills per kWh. Second, electric-furnace acid can produce higher fertilizer grades than wet-process acid of corresponding P_2O_5 concentration because of the virtual absence of impurities (for example, 21-53-0 compared with 18-46-0 for diammonium phosphate). The higher-grade material commands a better price and can be expected to give better agronomic results. Third, phosphorus and furnace-grade phosphoric acid can be put to many uses in a developing area and thus attract new industries, which in turn mean a saving in foreign exchange. Typical end-uses for phosphorus include military needs, insecticides, and pyrotechnics, while high-purity phosphoric acid is a raw material for detergents, beverage, and numerous inorganic and organic chemicals.

Other methods. Phosphorus can also be produced by reducing phosphate rock in furnaces of the cupola or shaft type using coke or other suitable fuel, but these methods have been largely superseded by the electric-furnace process. Reduction in a rotary kiln, followed by the injection of oxygen or air to produce high-strength phosphoric acid is another promising method. A further possibility is the use of direct heating and reduction by means of reformed natural gas, or refinery gas in fluidized-bed furnaces on the lines developed for iron-ore treatment (Anon., 1965 b). In this way reformed gas might be used to manufacture ammonia and also phosphate fertilizers (via phosphorus) without the necessity for sulphur or low-cost power. Such a project might be well suited to the long-range programmes of those countries with access to phosphate rock and ample supplies of natural gas or refinery gas.

Chemical processes

Sulphur-saving chemical methods for phosphate fertilizer production are principally those which (a) reduce or eliminate the use of elemental sulphur in producing sulphuric acid and (b) those which reduce or eliminate the need for sulphuric acid as the principal reagent for dissolving phosphate rock.

Processes based on sulphuric acid

Sulphuric acid from pyrites, smelter gases and anhydrite. As indicated earlier, high tonnages of sulphuric acid are produced in many countries from pyrites (FeS_2) and pyrrhotite (FeS approximately), which contain about 45 to 48 per cent and 30 to 32 per cent of sulphur, respectively. Waste gases from sulphide-ore smelters are also used to produce sulphuric acid, where local markets exist. In a few cases anhydrite or gypsum is the primary raw material. These non-elemental sources of sulphur offer possibilities for greatly expanded use, should native sulphur become scarce or prohibitive in price.

To obtain the required sulphur dioxide, the iron sulphide ore is crushed and roasted, usually in a vertical multiple-hearth furnace fitted with rakes (Anon., 1965 d), or in a fluidized-bed calciner (Guccione, 1965). Dust and other impurities such as chlorine, fluorine and arsenic are removed from the gas by various types of scrubbers and washing towers, and the sulphur dioxide is converted to sulphuric acid in conventional plants, generally of the contact type.

The iron-oxide calcine can be sold for the manufacture of iron and steel when suitable markets are available; this helps to reduce the over-all sulphuric acid cost. Some of the exothermic heat can also be recovered by generating steam in waste-heat tubes and boilers built into the calcining unit.

The use of pyrites necessitates considerable additional equipment, such as facilities for storage, handling and crushing, a large calciner and a train of gas scrubbers and purifiers. In some cases equipment for processing the calcine (e.g. for leaching, briquetting and shipping) may also have to be installed. As a result, the investment cost for a pyrites-acid plant may be from 50 to 100 per cent higher than a sulphur-based plant having the same H_2SO_4 capacity. Labour and other operating costs are also correspondingly greater. Thus, to ensure a competitive operation, the price of the pyrites used must be lower per unit of sulphur than the price of native sulphur. Of course, in times of a sulphur shortage the price of pyrites can be expected to rise and so lead to higher costs for sulphuric acid.

When operations are carried on using smelter gas, considerable washing and purifying equipment is usually needed, since many ores contain arsenic and other impurities, which are active catalyst poisons. Thus, the capital cost of a sulphuric acid plant using smelter gas may be at least 50 per cent greater than an equivalent plant using sulphur; operating costs, too, will be increased.

For a captive operation, however, the equivalent sulphur costs are virtually nil, since the sulphur dioxide would otherwise escape up the stack and pollute the surrounding area. Indeed, in some cases local air pollution has been so bad that smelter operators have been

compelled either to install extensive gas-washing equipment and large, costly stacks or to recover the offending sulphur dioxide as sulphuric acid. In such instances the sulphuric acid can be regarded as a valuable by-product from a waste-gas cleaning operation. Yet minimum practical and economic limits exist for sulphur dioxide recovery from stack and smelter fumes. SO_2 contents in the range of 4 to 10 per cent usually justify conversion, but lean gases containing up to about 4 per cent SO_2 may possess only a nuisance value, except in cases of restricted sulphur supplies.

Nevertheless, practical methods of removing sulphur from waste and exhaust gases containing even less than 1 per cent SO_2 have been developed based on scrubbing with lime, sulphite salts, organic solvents and other materials (Hori *et al.*, 1963; Pratt and Noyes, 1965, pp. 106, 109). In some cases, such as scrubbing the stack gases from large power stations and various industrial plants, the volume of liquid effluents and the corresponding sulphur content, would reduce air pollution but create problems of liquid waste disposal. This reduction in air pollution, in addition to the value of the sulphur that has been removed, may justify sulphur recovery in some form. Hence, every possibility of sulphur recovery of this nature must be carefully studied.

Hematitic calcines (Fe_2O_3) from pyrites roasters have not always been readily saleable on world markets, owing to problems of handling, impurities, and sometimes a relatively low Fe content. In a new process recently installed on a large scale in Italy (Guccione, 1965), pyrites ore is first roasted in a fluidized-bed calciner to produce sufficient SO_2 for 2,200 tons per day of 100 per cent H_2SO_4 , 570,000 kWh of power from waste-heat steam and 1,500 tons per day of hematitic calcines. The calcines are reduced with the aid of fuel oil in a second fluidized-bed reactor system to produce magnetite (Fe_3O_4), which is magnetically and hydraulically concentrated, made into pellets and sold as high-grade iron-oxide pellets containing about 67 per cent Fe.

In another process of recent origin, pyrites ore containing minor amounts of other metals is flash-roasted in a specially designed furnace to yield pyrrhotite and a mixture of sulphur, arsenic and other metallic vapours, which are selectively condensed and recovered. Steam is generated in a waste-heat boiler from the heat given up by the furnace gases. The pyrrhotite is roasted to produce sulphur dioxide and hence sulphuric acid, and the calcine is made into pellets for use as blast-furnace feed.

The process is unusual in that it can operate on contaminated pyrites ore and, at the same time, recover valuable non-ferrous metals and elemental sulphur. For example, one installation under construction (Anon., 1964, 1965 a and 1965 e) is expected to produce

annually about \$3.5 million worth of elemental sulphur (113,000 tons), plus over \$15 million worth of iron ore pellets, sulphuric acid and other products, on a total investment of \$28 million. Based on plant fixed capital, this figure represents an annual return of 66 per cent.

Techniques recently developed for producing sulphur and sulphur-dioxide from various minerals by controlled roasting should also prove helpful in treating, for example, magnesium sulphate (to yield MgO and SO₂), and perhaps sodium sulphate and calcium sulphate.

Sulphuric acid from anhydrite and gypsum. In Great Britain and in Europe several plants using calcium sulphate as the source of sulphur for the manufacture of sulphuric acid have been built. Local anhydrite is used in preference to gypsum, in view of reduced transport costs and savings in fuel. The anhydrite is mixed with coke or coal and sand, plus a little clay or shale and roasted in a rotary kiln. The calcium sulphate is reduced to lime, which combines with the rest of the charge to form cement clinker. The SO₂ is scrubbed and used to produce sulphuric acid, while the clinker is ground and sold for cement manufacture. The reduction reaction can be empirically expressed as:



Capital investment for such plants is high, perhaps four or five times the cost of a sulphuric acid plant using elemental sulphur. However, if a continuous sale of the clinker at a reasonable profit can be assured (perhaps by a long-term contract to the cement industry), the plant can be considered to be a two-product installation. Therefore, capital investment, as well as a proportionate share of the operating costs and the cost of raw materials, should be borne by the cement clinker product, especially as about a ton of cement is produced per ton of 100 per cent sulphuric acid.

In Great Britain and in Europe the process received a great impetus during a sulphur shortage in the early 1950s, particularly as coal and anhydrite were available in ample quantities under the plant sites. The likelihood of another sulphur shortage has already led to the ordering of additional plants of this type. The ability to produce cement clinker and sulphuric acid should offer interesting possibilities to developing countries faced with a large construction programme. As previously mentioned, this process might be particularly suitable to the more recently developed controlled-roasting methods, using fluidized-bed or other techniques to reduce capital and operating costs.

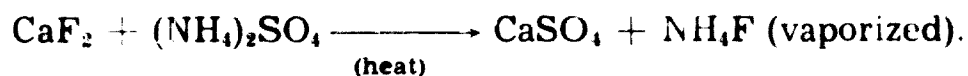
Wet-process phosphoric acid plants generate about 4.5 times as much gypsum as the P₂O₅ they produce. This by-product material

is rarely used, except in areas with limited supplies of sulphur and calcium sulphate, such as parts of India and Japan. In other regions of the world millions of tons annually are flushed to seas or rivers or allowed to accumulate in lagoons and storage piles. Although this seems wasteful, since most of the sulphur purchased to make concentrated phosphates is discarded, the re-use of by-product gypsum, or the recovery of its sulphur component, is not always economic. First, natural gypsum, either domestic or imported, may be relatively cheap and of high purity. Second, no local markets for by-product gypsum may exist; and third, the impurities, such as residual P_2O_5 , fluorine compounds and free moisture, may be technically impossible or economically prohibitive to remove. This applies to a greater extent to the manufacture of sulphuric acid than it does to ammonium sulphate, for which satisfactory purification techniques have been available for some time (George and Gopinath, 1963).

In Japan methods have been developed for producing phosphoric acid and gypsum of a high purity based on the initial formation of hemihydrate instead of gypsum, as in other wet-process plants. Such pure gypsums give excellent results when used for board and cement manufacture (Nippon Kokan; Pratt, 1964), and if the fluorine content can be reduced to appropriate limits, there seem to be good prospects also of using such by-product gypsums for the manufacture of sulphuric acid. In effect, this would result in a closed-cycle sulphuric-acid operation and lead to very considerable savings in elemental sulphur.

A prolonged sulphur shortage and high sulphur prices, together with continuing advances in the appropriate technology, might well provide the fertilizer industry in developing countries with the necessary stimulus to adopt some form of closed-cycle sulphuric-acid system. For countries with limited supplies of high-cost sulphur obtained from abroad and restricted foreign exchange, this method would be particularly advantageous.

Various processing methods introducing the production of ammonium sulphate have also been proposed or investigated for the purposes of purification and solubilization. For example, an excessive fluorine content in the gypsum might be reduced to satisfactory limits by reacting with ammonium sulphate as follows:



The P_2O_5 can be reduced to about 0.1 per cent (total) by using the latest hemohydrate processes and purification techniques. Hence, the re-use of by-product gypsum for sulphuric acid production should present excellent possibilities when special economic or other circumstances justify it.

Spent sulphuric acid recovery In the United States alone, some 2 million tons of spent sulphuric acid are recovered annually for captive re-use or sale. Principal sources in this category are the iron and steel industry, petroleum refiners, vegetable oil and soap factories, titanium-dioxide producers, nitration processes and some miscellaneous chemical and pigment operations. Several processes are available for pickle liquor treatment (Anon., 1965 c), some based on separation of the ferrous sulphate by concentration and others on the use of organic solvents.

Sludge acids from petroleum refineries are usually treated by burning in specially designed furnaces to yield SO_2 (and CO_2); the SO_2 is converted to sulphuric acid in conventional contact plants. A method of producing granular ammonium sulphate directly from sludge acid has also been reported (Wilson, 1962).

More stringent legislation against water pollution is focusing attention on the treatment and re-use of spent acid. Rising sulphur prices may transform some waste-disposal operations into recovery units for sulphuric acid or ammonium sulphate, which, if not profit-making, might be at least financially self-supporting.

Cost comparisons of various sulphuric acid processes. In figure 13 below, estimated manufacturing costs of sulphuric acid produced from elemental sulphur (A), pyrites (B), and anhydrite (C) are compared. They are intended to show the relative manufacturing costs of each process rather than real costs, which can only be calculated when specific factors are known. The relative manufacturing costs for producing sulphuric acid from these sources (A, B, and C of figure 13) are listed below.

(A) *Elemental sulphur*

Sulphur	\$ per ton \times 0.345
Other costs	\$7.16
Installed cost	\$2.7/m ³
Depreciation	10 per cent
Interest on total capital	6 per cent

(B) *Pyrites*

Capital and operating costs — 75 per cent additional to those for A. (No credits for cinder.)

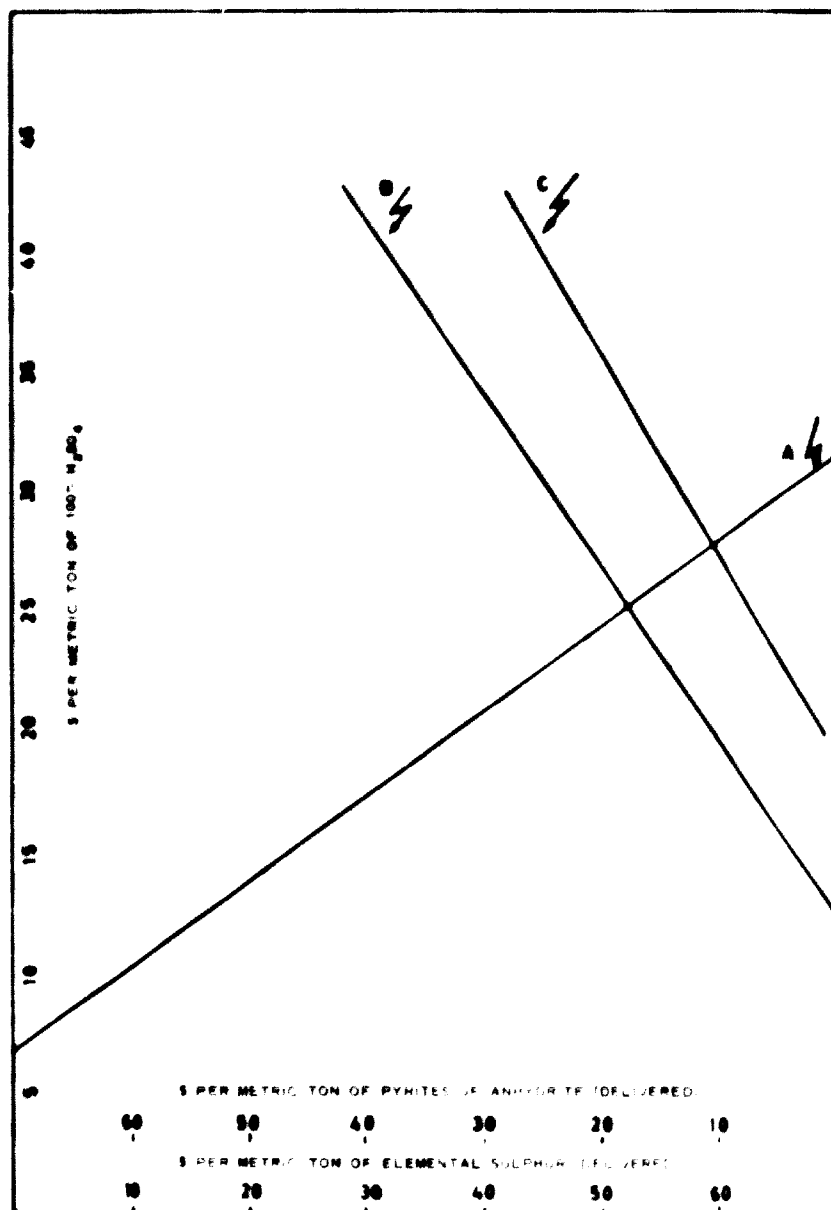
(C) *Anhydrite*

50 per cent of anhydrite and capital cost and fuel of \$4 per ton of acid allocated to cement; other costs taken as 100 per cent additional to those for A.

For comparative purposes, a daily capacity of 300 tons of 100 per cent H_2SO_4 has been assumed in each case. Total installed cost (plus \$100,000 for working capital) has been taken as \$2.7 million for a

plant based on elemental sulphur, and all other costs have been assessed at \$7.37 per ton of 100 per cent H₂SO₄. This includes a 10 per cent annual depreciation charge and 6 per cent capital interest charge.

Figure 13. Sulphuric acid manufacturing costs for alternative raw materials



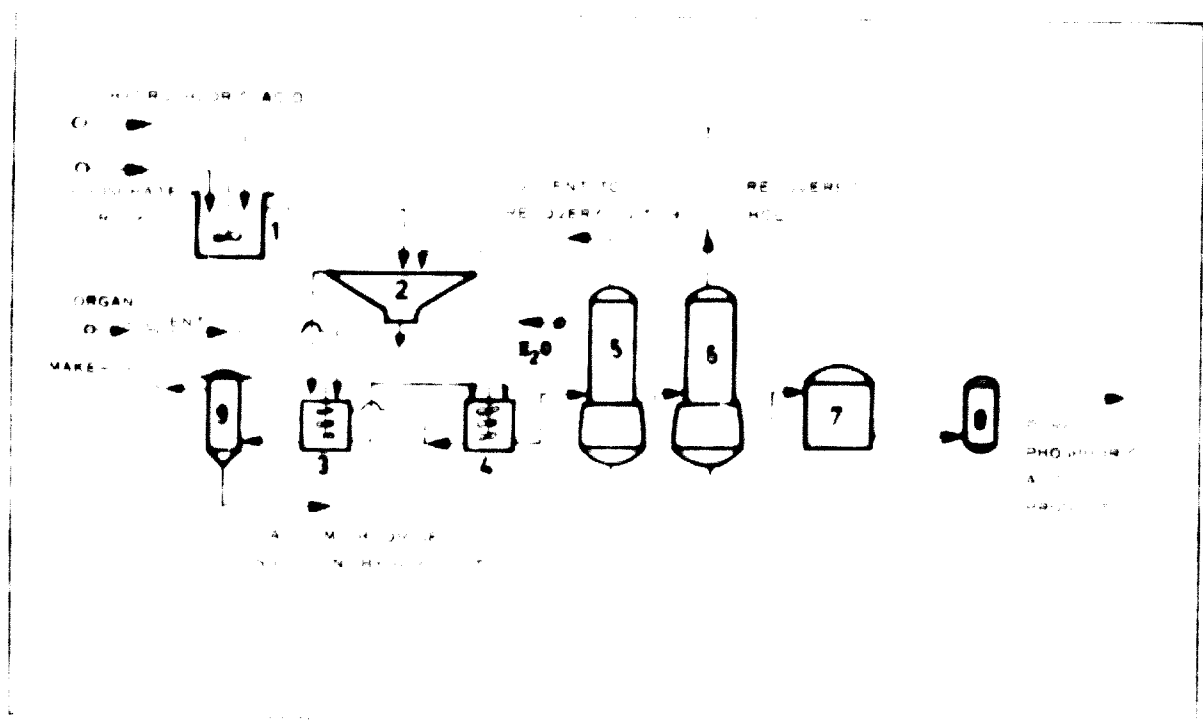
Basis — 300 metric tons per day of 100 per cent H₂SO₄.

For the pyrites plant, capital and operating costs have been taken as being 1.75 times the corresponding costs of the elemental sulphur plant. For the anhydrite plant, a total capital cost of \$13 million has been assumed, 45 per cent being allocated to sulphuric acid production and 55 per cent to cement manufacture, i.e. \$5.8 for the H₂SO₄ operation. Sulphuric acid operating costs have been taken as twice those of the elemental sulphur plant. Anhydrite costs

and fuel costs of \$4 per ton are apportioned equally between the H_2SO_4 and the cement produced, since about one ton of cement is made per ton of sulphuric acid.

From figure 13 above it can be seen that on the basis of the assumed costs and allocations, elemental sulphur at about \$40 per ton, including delivery, and pyrites at \$12 per ton, including delivery, would produce one ton of 100 per cent H_2SO_4 for approximately \$21. This would correspond to an anhydrite cost of about \$2.5 per ton. Hence, it can be seen that in cases where delivered sulphur prices are high, pyrites and anhydrite can both become competitive with elemental sulphur, especially when the mines are located near the plant.

Figure 14 a. Phosphoric acid process using the IMI process



(1) digesters, (2) clarifier, (3) solvent extractor, (4) water extractor, (5) and (6) evaporators, (7) acid storage tank, (8) ion-exchange unit, (9) solvent recovery unit.

Processes based on hydrochloric acid

Several processes using hydrochloric acid as an acidulant have been developed. The principal problem is to separate the calcium chloride and phosphoric acid produced, in a method developed by Israel Mining Industries (IMI), *n*-butanol is used for this purpose. The extracted phosphoric acid is transferred to an aqueous solution

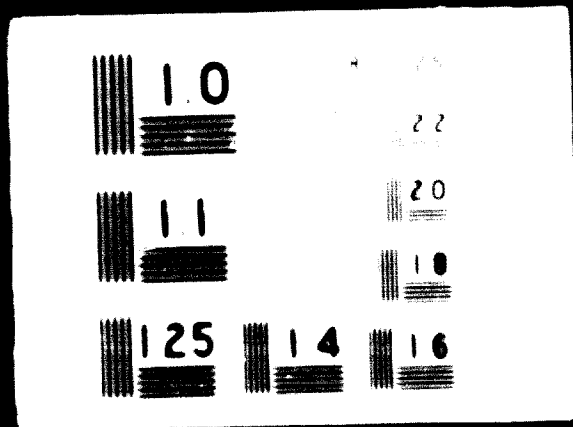


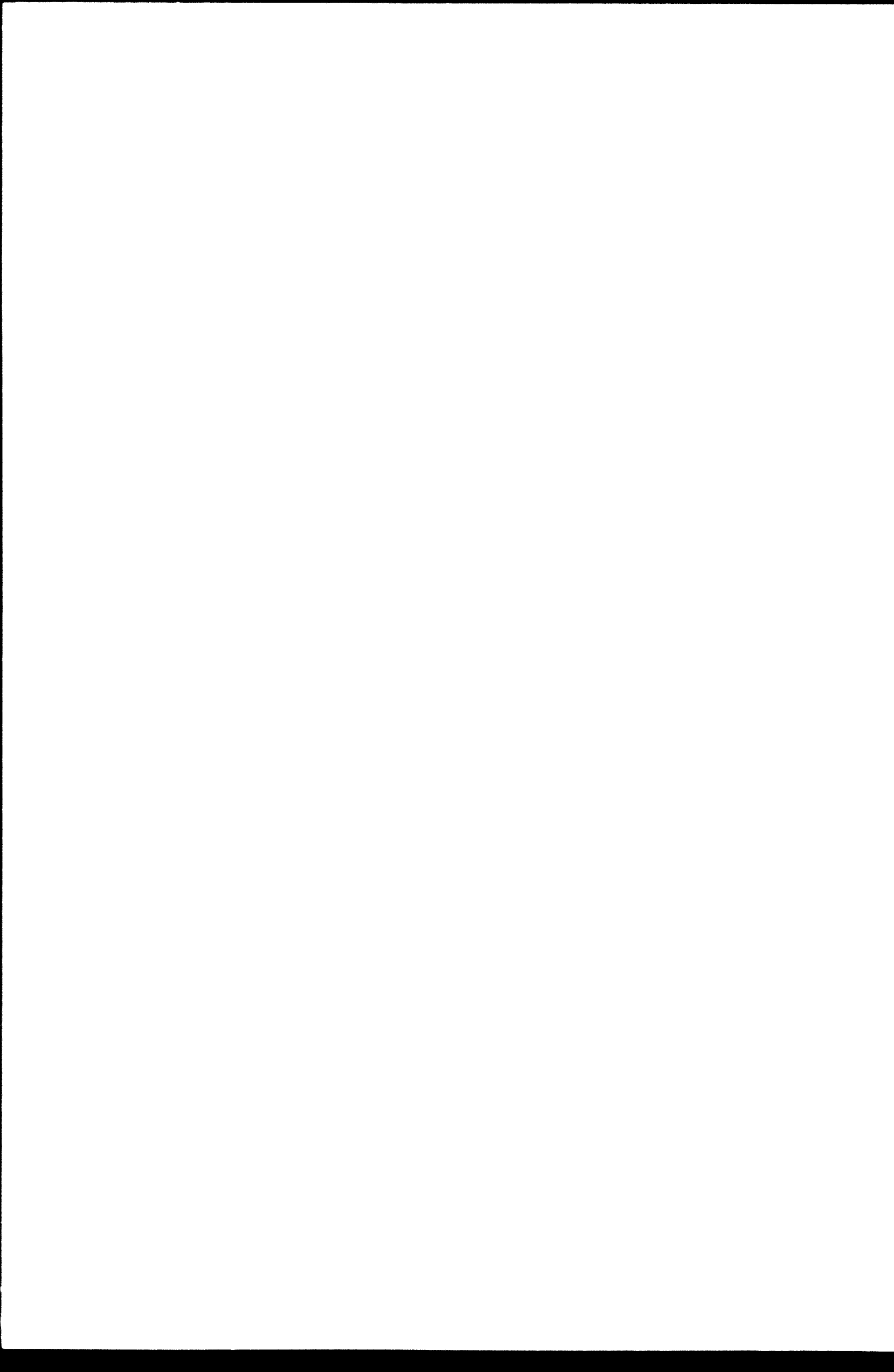
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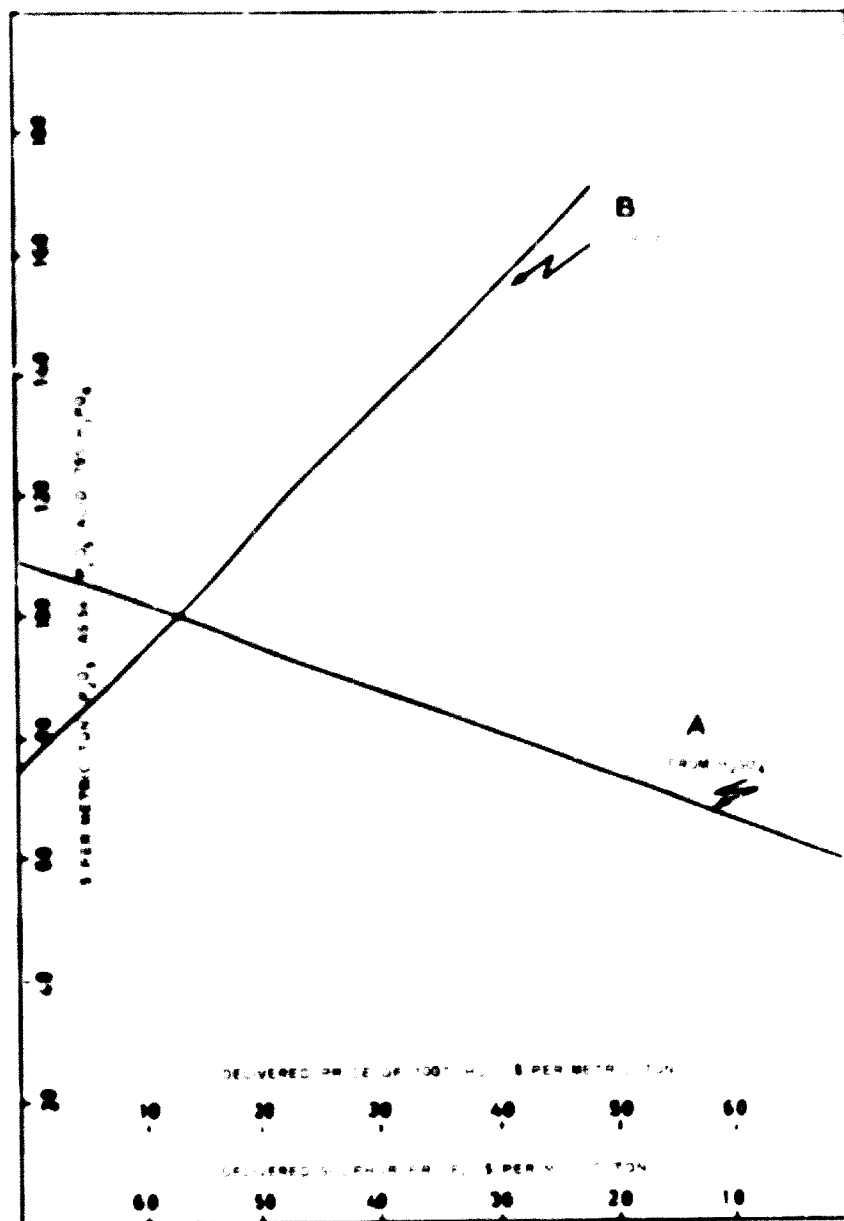




in a liquid-liquid contactor and evaporated to yield a very pure product containing about 58 per cent P_2O_5 . The solvent is recycled and the calcium chloride can be sold (figure 14 a).

Supplies of hydrochloric acid on a large scale are relatively limited in most parts of the world; consequently, HCl processes for phosphoric acid production have not been widely adopted. By-product acid is sometimes available from other processes and may even create disposal problems. In such cases, the production of phosphoric acid may be ideal. Figure 14 b indicates typical production costs in terms of costs of raw material.

Figure 14 b: Typical cost relation between phosphoric acid made from sulphuric acid and hydrochloric acid (IMI process)



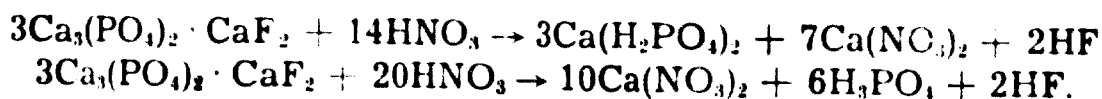
Basis for B 100 metric tons P_2O_5 produced per day, rock: \$13.2 per metric ton, capital cost: \$2.75 million (acid said to be of furnace-grade purity; compare also with figure 12). Basis for A 220 metric tons of P_2O_5 produced per day, rock: 75 BPL at \$8.5 per metric ton.

Processes based on nitric acid

A sulphur shortage in the early 1950s spurred in Europe the development of phosphate fertilizer processes in which the main acidulant is nitric acid. Numerous plants in this category have been built, and the total production of nitrophosphates now amounts to several million tons annually. These processes, however, have not been widely adopted elsewhere, partly because of the renewed availability of sulphur at a reasonable cost but also because of the limited P_2O_5 water-solubility of nitrophosphate fertilizers.

An acute sulphur shortage and related high sulphur prices could be relieved to a considerable extent by the greater use of nitrophosphate processes, if a compromise could be reached regarding the necessity for total water-solubility maintained by some agronomists. Furthermore, the increasing availability of low-cost ammonia (and derived nitric acid) permits nitrophosphate fertilizers to be produced at favourable price levels, a particularly important consideration for developing countries.

The principal empirical reactions between phosphate rock and nitric acid can be shown as



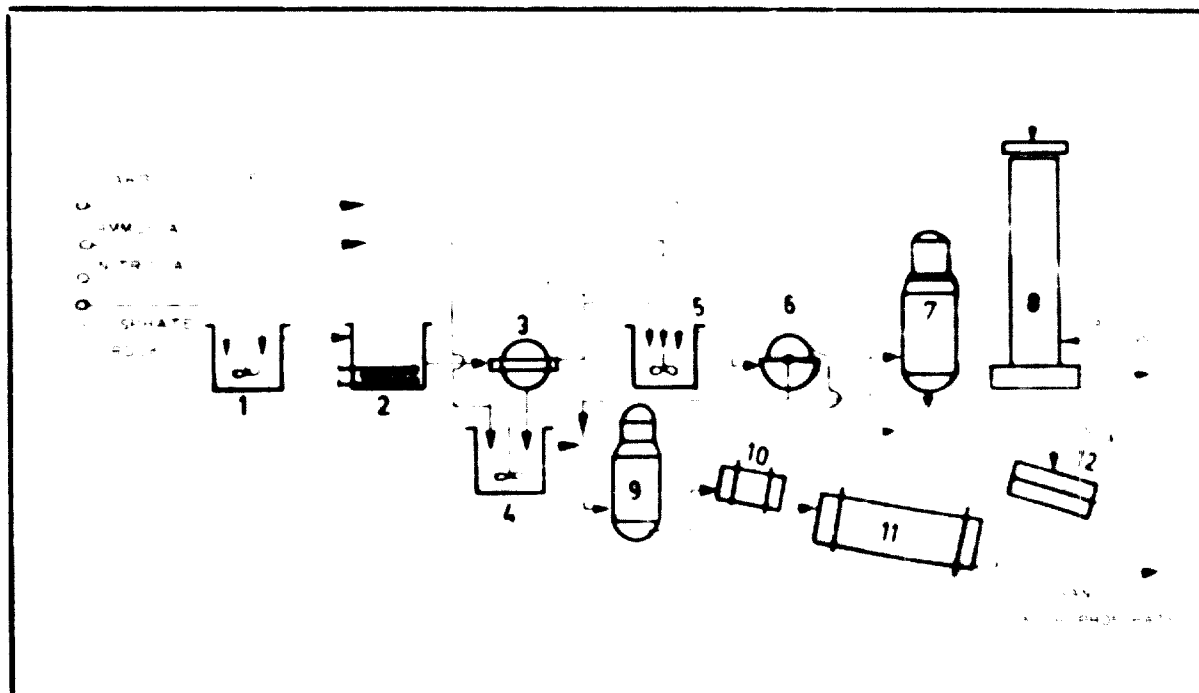
The presence of calcium nitrate, however, makes the reaction product extremely hygroscopic and also induces instability in the mono-calcium phosphate. Accordingly, the calcium nitrate must be removed or converted to less hygroscopic salts. This has led to the development of four main types of nitrophosphate processes:

- (a) Separation and removal of some calcium nitrate (Uhde-Odda process);
- (b) Conversion of calcium nitrate to calcium sulphate by the use of sulphuric acid or sulphate salts;
- (c) Conversion of calcium nitrate to calcium carbonate by carbon dioxide;
- (d) Conversion of calcium nitrate to dicalcium phosphate, using phosphoric acid.

In conventional versions of process (a), the separated calcium nitrate is crystallized or prilled. In a modified method (the Uhde-Odda process), the calcium nitrate is reacted with ammonia and carbon dioxide to produce calcium carbonate, which is removed by filtration, and ammonium nitrate, which can be recycled to the process or used separately.

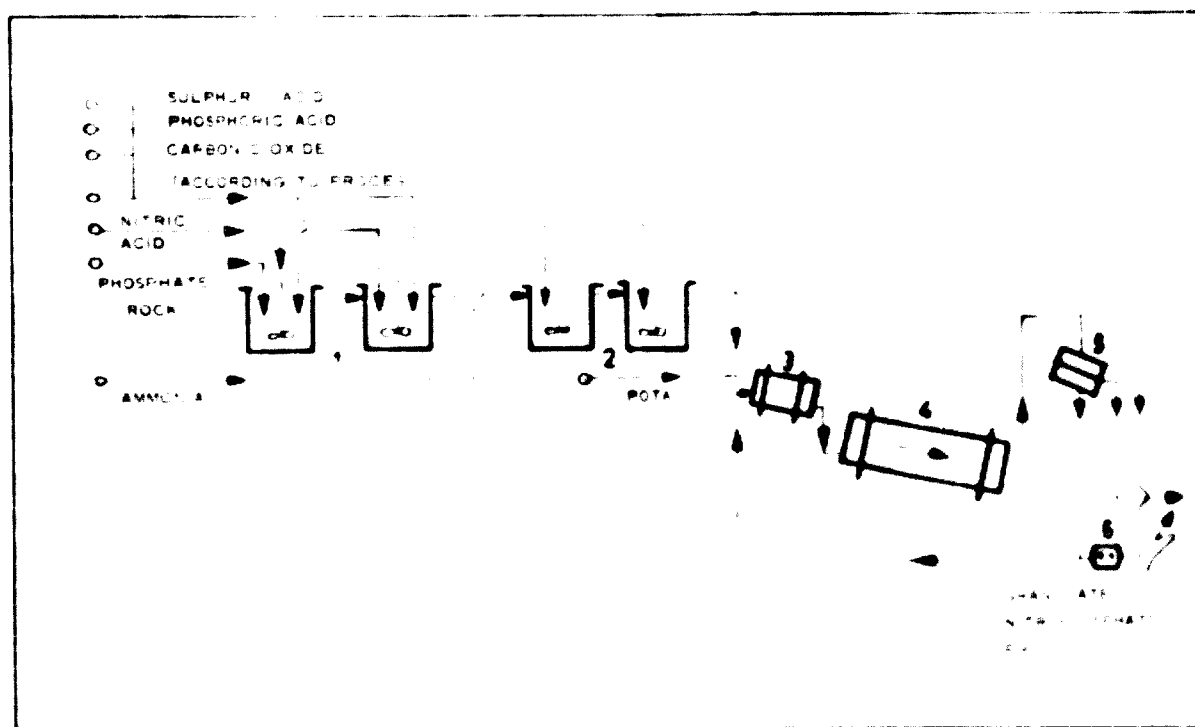
Figures 15 and 16 below show simplified flow diagrams for nitrophosphate processes employing calcium nitrate separation,

Figure 15. Separation type nitrophosphate-ammonium nitrate plant



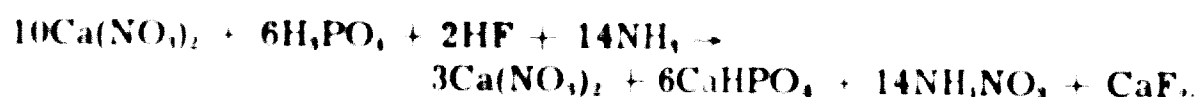
(1) digestion tank, (2) chill tank, (3) $\text{Ca}(\text{NO}_3)_2$ filter, (4) ammoniation tank, (5) carbonation tank, (6) calcium carbonate filter, (7) ammonium nitrate evaporator, (8) prill tower, (9) concentrator, (10) granulator, (11) drier, (12) screens.

Figure 16. Non-separation type nitrophosphate process



(1) digestion tanks, (2) ammoniation tanks, (3) granulator, (4) rotary drier, (5) screens, (6) oversize crusher.

(with recycle) and non-separation, respectively. In each of these processes, nitric acid in concentrations up to about 60 per cent is the principal solubilizing agent. Ammonia is added to the slurry to reduce the calcium-nitrate content, to furnish nitrogen, and to stabilize the phosphates. Thus, the final products will contain dicalcium phosphate, ammonium nitrate, calcium fluoride and perhaps some ammonium sulphate, ammonium phosphate, and a little calcium nitrate, according to the method and materials used. The overall reaction during ammoniation can be expressed as



Potash or potassium sulphate can be added, if desired, to make complete N-P-K fertilizers. Phosphate water-solubility can vary from nearly zero for the carbon-dioxide method to 50 per cent or even higher when substantial amounts of sulphuric acid and or phosphoric acid are used.

In properly made nitrophosphates, virtually all the phosphate is citrate-soluble. The mole ratio of $\text{CaO}:\text{P}_2\text{O}_5$ in phosphate rock is usually between 3.3 and 4.0:1 and for dicalcium phosphate 2:1. Therefore, at least 40 to 50 per cent of the CaO in the rock must be isolated by combination with other anions to prevent the formation of calcium phosphates more basic than dicalcium phosphate.

The chemistry and technology of the various processes are quite complex, and selection of the optimum method depends in each case on several factors. These include:

- (a) Cost and availability of raw materials;
- (b) Agronomic requirements in terms of required N-P-K ratios and concentrations;
- (c) Agronomic requirements regarding minimum P_2O_5 water-solubility;
- (d) Sources of investment capital.

When all these factors have been considered, a choice of the optimum method and raw materials can be made on the basis of the various proprietary processes available (Hignett *et al.*, 1965). Sulphur requirements range from zero for the carbon dioxide and the Uhde-Odda methods to 10 per cent and above when phosphoric acid and/or sulphuric acid are used. In general, existing nitro-phosphate processes represent a compromise in each case between low sulphur needs (as sulphuric acid) and low P_2O_5 water-solubility, or higher sulphur requirements and increased water-solubilities. Table 13 below indicates the various raw material needs for 1-1-1 nitrophosphate fertilizers made by different methods.

Table 13. Raw material requirements and products for selected nitrophosphate and conventional processes

	Product		Basic raw material requirement (tons/day)			Cost of raw materials	
	Grade	Tons per day	Phosphate rock ^b	Sulphur	Ammonia	\$/day	N · P ₂ O ₅
Diammonium phosphate and ammonium sulphate	18 —46—0	217	334	281	251	24,715	82.40
	21 — 0—0	768					
Diammonium phosphate and ammonium nitrate or urea	18 —46—0	217	334	94	261	18,375	61.20
	33.5— 0—0	480					
	45 — 0—0	(358) ^c					
Triple superphosphate and ammonium nitrate or urea	0 —46—0	217	327	67	261	17,360	57.90
	35.5— 0—0	598					
	45 — 0—0	(446) ^c					
Mixed acid nitrophosphate and ammonium nitrate	20 —20—0	500	325	60	259	17,005	56.70
	33.5— 0—0	299					
Modified Odde process	20 —20—0	500	313	0	260	14,830	49.40
	33.5— 0—0	299					
Modified Odde process with sulphate cycle	25 —25—0	400	313	0	260	14,830	49.40
	33.5— 0—0	299					
Sulphate cycle nitrophosphate	28 —14—0	715	313	0	260	14,830	49.40

Source: T. P. Hignett et al. (1965), "Nitrophosphate Processes, Advantages and Disadvantages" in *The Fertilizer Industrial Round Table Annual Meeting*, Washington, D. C.

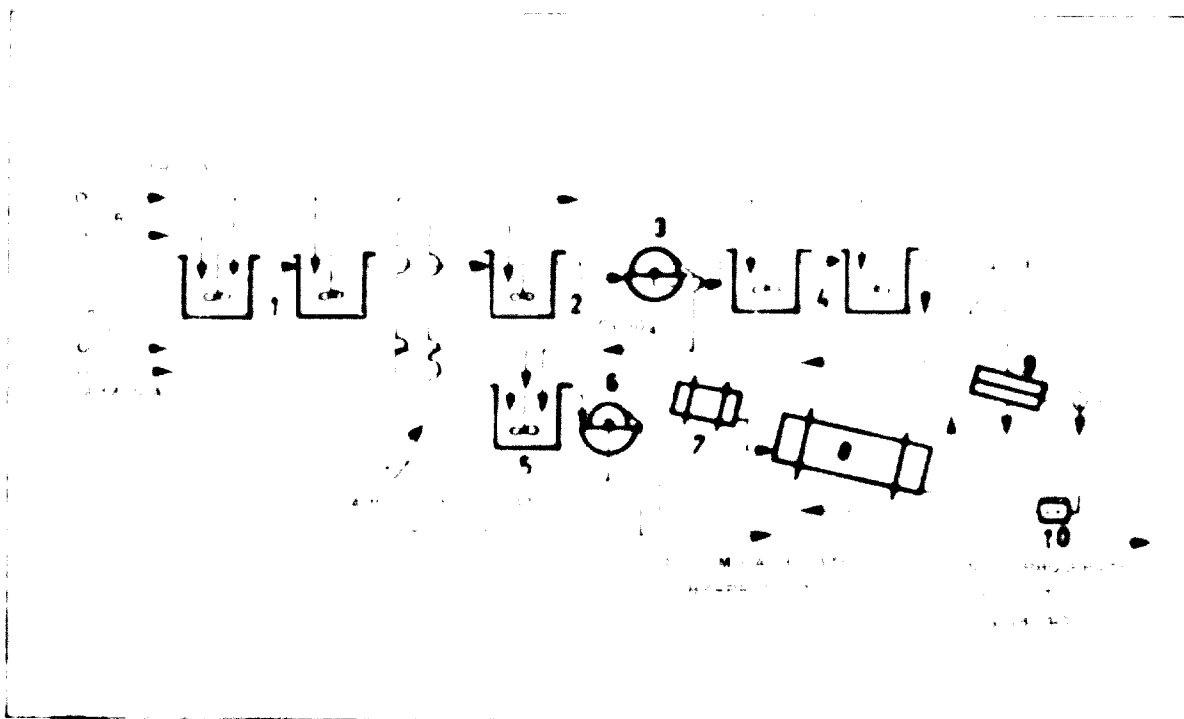
^a Assumed cost per ton: phosphate rock, \$10; sulphur, \$35; ammonia, \$45.

^b 33 per cent P₂O₅.

^c If an equivalent quantity of urea is produced as an alternative to ammonium nitrate.

A nitrophosphate process that eliminates the need for sulphur and at the same time offers high P_2O_5 water-solubility would have many advantages. Several methods for achieving this dual aim have been proposed (Hignett *et al.*, 1965; Weber and Oliver, 1963). In one of these (Weber and Oliver, 1963), phosphate rock is digested with nitric acid, and ammonium sulphate is added to the slurry. The precipitated calcium sulphate is separated by filtration and reacted with ammonia and carbon dioxide to produce ammonium sulphate, which is recycled to the reaction slurry precipitator. Calcium carbonate produced by carbonating the gypsum can be used to regenerate carbon dioxide or sold.

Figure 17. Proposed nitrophosphate-sulphate cycle process



(1) digester tanks, (2) gypsum precipitation tank, (3) gypsum filter, (4) ammoniation tanks, (5) carbonation tank, (6) carbonate filter, (7) granulator, (8) rotary drier, (9) screens, (10) oversize crusher.

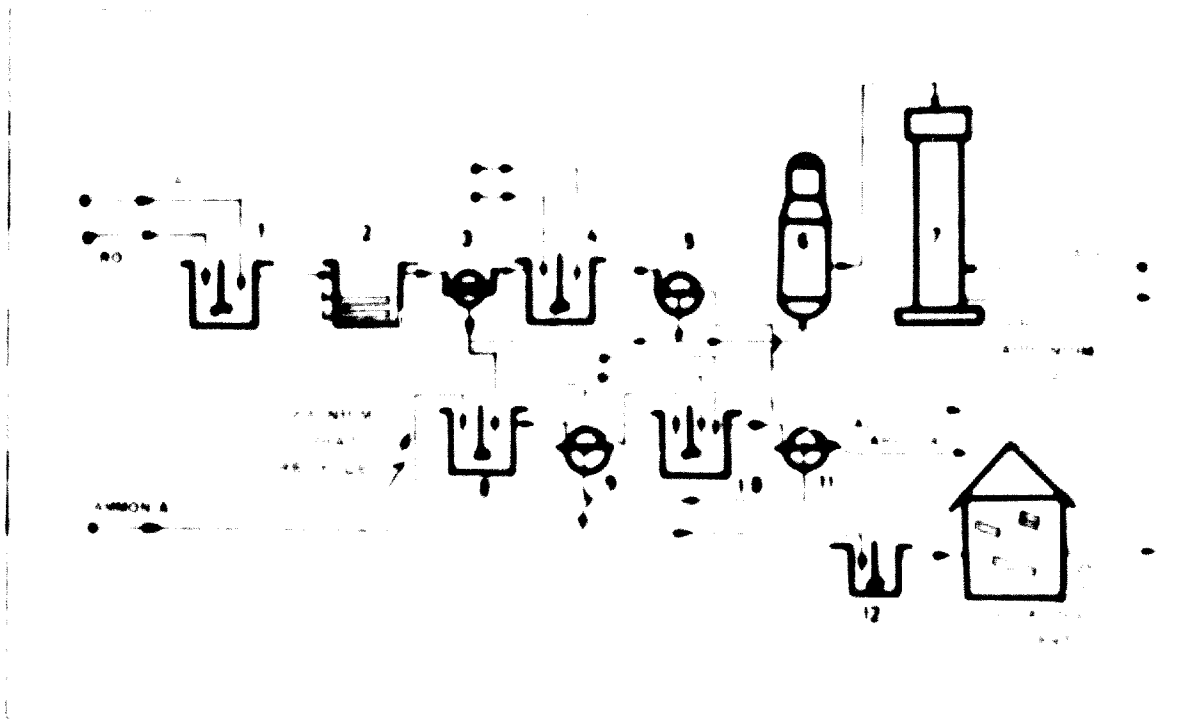
Filtered reaction liquor containing phosphoric acid and ammonium nitrate is ammoniated, evaporated, and prilled or granulated to yield a water-soluble product containing about 28 per cent nitrogen and 14 per cent P_2O_5 . Figure 17 above shows a simplified flow diagram of this process.

The use of a sulphate recycle has also been proposed for the Uhde-Odda process (Hignett *et al.*, 1965). In this method the reaction liquor remaining after separation of some of the calcium nitrate is treated with ammonium sulphate, and the resulting calcium sulphate is used to regenerate ammonium sulphate by ammoniation and carbonation. The reaction liquor is ammoniated, evaporated and

prilled to yield products such as 25-25-0 and 30-10-0. Calcium nitrate crystals separated from the nitrophosphate reaction liquor are also carbonated and ammoniated to produce ammonium nitrate (and calcium carbonate), which can be added to the main reaction liquor or evaporated and prilled separately to produce solid ammonium nitrate (33.5-0-0). Figure 18 below shows a basic flow diagram of this process.

At present no commercial nitrophosphate installation incorporating an internal ammonium sulphate recycle is known. However,

Figure 18. Proposed separation type nitrophosphate process with sulphate recycle



(1) digestion tank(s), (2) chill tank, (3) centrifuge, (4) No. 1 carbonator, (5) No. 1 carbonate filter, (6) evaporator, (7) prill tower, (8) sulphate precipitator, (9) No. 2 CO₂ filter, (10) No. 2 carbonator, (11) No. 2 CO₂ filter, (12) ammoniator.

the techniques of each section have been in large-scale operation in separate plants for many years. Nitrophosphate processes of this type, therefore, are considered to have an excellent future potential, particularly in developing countries where low-cost ammonia is available and elemental sulphur is in restricted supply.

Capital costs of such plants can be higher than those for simpler processes that do not incorporate separation, the ammonium sulphate recycle and the prilling stages. However, associated sulphuric acid and phosphoric acid units are not needed, so the total installed costs for both methods are probably similar.

Agronomic considerations

Sulphur

Sulphur is indispensable to plant life (McVickar et al., 1963, Sulphur Institute), yet soils in many areas of the world are deficient in this element. The continued use of concentrated fertilizers containing little or no sulphur can aggravate this condition. Hence, fertilizers incorporating gypsum, magnesium sulphate or other sulphur-containing radicals, or these materials themselves, may be necessary for agronomic reasons. This might influence the choice of a particular process and type of product, especially in a developing country.

Phosphorus

Total phosphate water-solubility in phosphate fertilizers is held by some agronomists to be essential for effective results, and in certain countries it is the only acceptable criterion. This view, however, is by no means universal, and many authorities claim equally effective results for phosphate fertilizers of limited water-solubility on the basis of extensive agronomic evidence (Mattingley, 1963; Piepers, 1965; Vanden Berg, 1963). This appears to apply particularly to pastures and long-term crops grown on neutral or slightly acid soils.

Thus, when new fertilizer projects in which the production of phosphates with limited water-solubility are contemplated, adequate field testing should be undertaken to ensure that the proposed fertilizers will be suitable for the respective crops, soils and other agronomic requirements. It may be possible in some cases to use totally water-soluble phosphate fertilizers in limited amounts as starter materials, with larger quantities of less water-soluble materials.

One interesting possibility (McVickar et al., 1963) is the use of phosphate rock-sulphate mineral combinations in conjunction with reducing bacteria, either in some type of process or perhaps for application to the soil in granular form.

5.

Summary and conclusions

World consumption and production of fertilizers are at present growing at the unusually high rate of 14 per cent annually. The consumption of nitrogen fertilizer is expanding more rapidly than that of phosphate fertilizer, but even this is increasing by about 11 per cent per year. Ample supplies of natural gas and other feed-stocks are available for ammonia production yet the situation regarding future supplies of phosphate fertilizer is viewed by many with apprehension. This is because sulphuric acid is by far the most popular solubilizer for phosphate rock, and although the sulphur shortage, with correspondingly high sulphur prices, is not so acute as it has been, it appears to be continuing.

Although large reserves of sulphur in non-elemental form exist, these have normally been more costly to use than elemental sulphur when the latter is in ample supply. The price of minerals containing sulphur can be expected to rise in conformity with elemental sulphur prices; and even if substantial new reserves of elemental sulphur should be found, it is unlikely that the prices of sulphur from all sources will revert to their former low levels.

Therefore, to ensure the continued availability at reasonable prices of fertilizers that normally require sulphur for their manufacture, various alternative production methods have been proposed. In addition, several new types of fertilizer using little or no sulphur in their manufacture have been developed. These alternative methods and products arose in some cases out of a sulphur shortage in Europe in the early 1950s and are still in wide use today.

Certain alternative processes for manufacturing fertilizers are of particular importance to developing countries because they offer the possibility of manufacturing other products simultaneously, and this may result in savings or an increase in foreign exchange. Typical examples include the production of phosphorus and corresponding phosphoric acid of high purity; the use of iron-sulphide minerals to make sulphuric acid, blast-furnace feed and electricity; and the use of low-cost minerals such as anhydrite to make sulphuric acid and cement.

It seems evident from this study that the alternative processes available and certain proposed methods (such as nitrophosphate processes incorporating an internal ammonium-sulphate recycle) will enable the fertilizer industry to overcome a sulphur shortage without an undue rise in prices or a reduction of agronomic effectiveness. However, this may entail additional capital investment, a willingness to adopt different techniques and perhaps a compromise on the part of some agronomists regarding optimum N-P-K ratios and degrees of phosphate water-solubility.

Recommendations

Recommended alternative processes and fertilizer products designed to offset a sulphur shortage and rising sulphur prices are summarized in table 14 below.

Table 14. Recommended alternatives for developing countries in the event of a sulphur shortage

Products	Recommended alternatives
<i>Nitrogen fertilizers</i>	
Ammonium sulphate from H_2SO_4 and NH_3	Ammonium sulphate from gypsum, NH_3 and CO_2
<i>Idem</i>	Ammonium sulphate from lean stack gases
<i>Potassium fertilizers</i>	
Potassium sulphate from H_2SO_4 and KCl	Use of natural minerals such as burkeite, langbeinite; alkaline-ion exchange processes
<i>Phosphate fertilizers</i>	
Coarse ground rock	Finely ground rock, granulated to reduce dusting
Single superphosphate	<i>Idem</i>

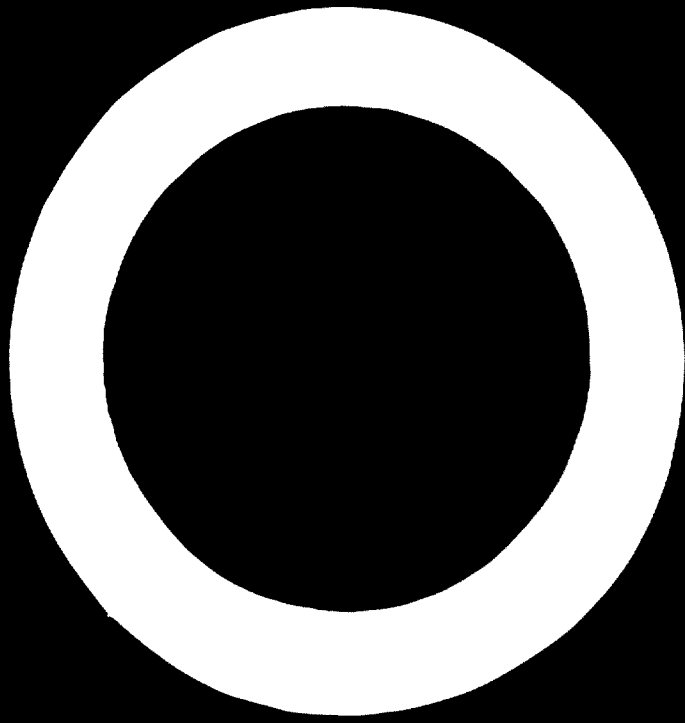
<i>Products</i>	<i>Recommended alternatives</i>
Mixed fertilizers using single superphosphate	Granulated mixed fertilizer using finely ground rock
Deflourinated rock (for animal feed)	Dicalcium phosphate from phosphate rock, mineral acid and lime
Magnesium phosphate	Nitrophosphates
Calcium metaphosphate	Slags from steel works
Other fusion products	
Wet-process phosphoric acid	Phosphorus and furnace-grade phosphoric acid
<i>Idem</i>	Phosphoric acid by HCl digestion and solvent extraction
Sulphuric acid from elemental sulphur	Sulphuric acid from pyrites, smelter gases, etc.
Sulphuric acid from elemental sulphur	Sulphuric acid (and cement) by calcining anhydrite
<i>Idem</i>	Sulphuric acid (plus iron oxide, power and non-ferrous metals) by controlled roasting of sulphide minerals
<i>Idem</i>	External closed-cycle roasting of by-product gypsum
<i>Idem</i>	Spent acid recovery by crystallization, roasting, etc.
Binary and ternary fertilizers (partly or totally water-soluble)	Nitrophosphate processes possibly with interal, closed ammonium-sulphate cycle
Single superphosphate	Bacterial reduction of phosphate rock-gypsum mixtures to make the phosphate soluble

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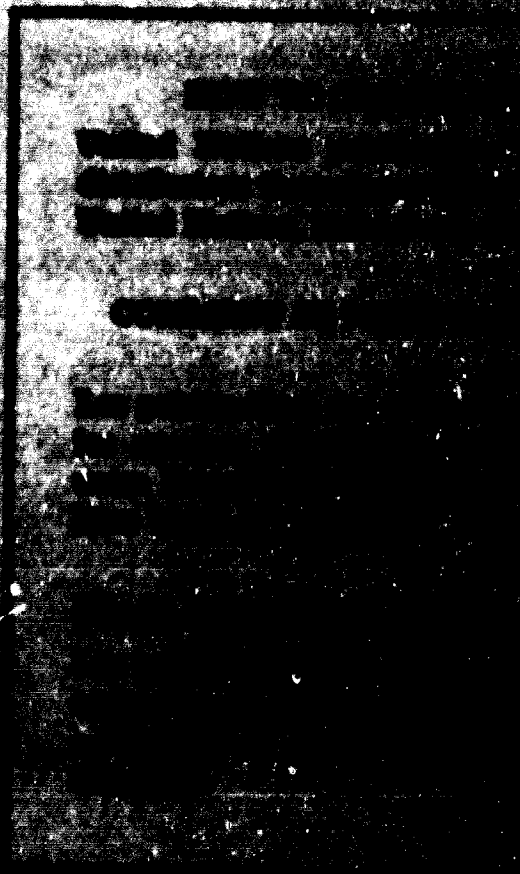
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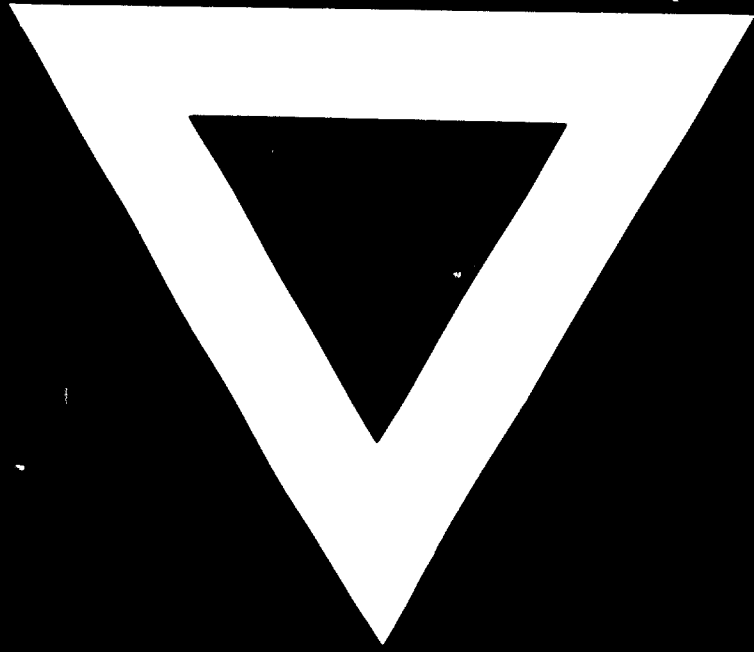




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10. 2. 72