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SYRIAN ARAB REPUBLIC

Technical report: Fertilizer industry pollution control*

Prepared for the Government of the Syrian Arab Republic
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

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* The views expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of the United Nations Industrial Development Organization (UNIDO). Mention of company names and commercial products does not imply the endorsement of UNIDO. This document has not been edited.

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Preface

The reader of this technical report must realize that the current state of affairs at the General Fertilizer Company (GFC) complex near Homs is significantly less than desirable with relatively little regard being paid to either worker health and safety or to the environment. Few emissions, water and wastewater quality, or hazardous waste data are being collected and recorded. Proper sampling techniques, analytical methods and contemporary equipment to utilize such methodologies are practically non-existent and analysts or technicians are either unaware, untrained or unmovitated to perform such tasks. Reliability of existing, documented environmental information is subject to criticism and the accuracy is questionable because, in all instances during the observation phase of the UNIDO expert's tenure, no proper quality assurance/quality control--and hence no statisticall reliability--of data was demonstrated to his satisfaction.

As a result, it is nearly impossible to compare the paucity of emissions data, for example, with existing air pollutant standards; moreover, because this plant represents an integrated fertilizer manufacturing establishment, that is, one production unit more or less dependent upon another for feedstock, intermediate, or product, and because there were very few days in the June-July period when the entire complex was fully operational, it was not possible to substantiate, with any degree of preciseness, individual process production rates--if they existed on a daily basis--particularly since they were not made available to the expert.

But by dwelling on all the negative aspects of what was observed at the fertilizer complex, one might tend to lose sight of the real aim of the mission--to attempt to be as positive as possible and in this manner hopefully motivate or inspire senior management to make those serious and conscious decisions to "turn the complex around." Therefore, every attempt was made to discuss realistic and practical control technology approaches toward minimizing releases of fertilizer feedstocks, intermediates, products, byproducts, and wastes to the environment and accomplish this at acceptable and minimal cost.

One final comment is necessary: The expert is quite cognizant of U. S. air, water, and hazardous waste regulations, standards, and guidelines and has made use of same throughout the report. He has and is currently involved in the development of international standards for toxic and hazardous wastes with several Western European environmental agencies and hence decided to maintain some constancy regarding the regulations and not confuse the reader by intermixing standards of different nations or comparing them--that was not the purpose of this exercise--many of these regulations and standards are similar or nearly similar. The U. S. environmental standards as presented throughout the report are for the reader's benefit and facility of interpretation, and serve merely as examples of what has been and can be achieved. Many may be considered too stringent for application to the GFC fertilizer complex; however, they are given here for illustrative purposes only and, as such, can represent a benchmark or guide for consideration by the responsible environmental authorities and industry. These are in no way intended to compare Syrian and U. S. industries and their respective degrees of environmental difficulties.

Abstract

The assignment of this mission was to provide technical assistance to senior management of the General Fertilizer Company near Homs to minimize product losses from the fertilizer manufacturing establishment and to address directly environmental pollution caused by uncontrolled air emissions, wastewater effluents, and hazardous solid wastes to the battery limits of the plant and the surrounding community near Lake Kattinah and Homs.

The UNIDO project number is DP/SYR/86/009/11-14 and the technical report is titled, "Technical Assistance to Minimize Environmental Pollution from the Fertilizer Manufacturing Facility at Homs" and the assignment was accomplished during the period June-July 1989.

The major conclusions of the project include the fact that many of the environmental problems originate from both feedstock and product losses, which are resulting in plant structural degradation and deterioration of the environment. A majority of these difficulties is caused by both downwash of acid gases and cumulative acidic deposition resulting from uncontrolled emissions from the fertilizer facility and the nearby power plant. The report also discusses the potentially harmful radioactive materials such as radium and radon in phosphate rock storage and milling areas that may cause detrimental effects to workers.

Priority recommendations include addressing a variety of uncontrolled emissions with several control technology methods such special scrubbers with recycle and reuse potential for NO/NO_2 tail gases and N_2O_4 fugitive emissions from HNO_3 storage vessels, baghouses or fabric filters with special applications for prilled products in the CAN and urea units, "double lime" treatment of contaminated gypsum pond water to reduce effectively fluorides, phosphorus, and radium, a process change--utilizing limestone in lieu of phosphate rock--in the manufacture of GTSP from H_3PO_4, and an in-plant good housekeeping program to aid identify and

remedy feedstock and product losses at the source and promote an environmental awareness program and esprit-de-corps among factory employees.

More than forty technical publications, manuals, reports, books, and documents comprising comprehensive, up-to-date environmental and industrial pollution control methods were placed in the GFC library for use by the staff.

Finally, recommendations of GFC staff engineers for UNIDO training and fellowships are detailed and appended.

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INTRODUCTION

The Syrian Arab Republic has establised a policy to increase agricultural production and, in that respect, has constructed an integrated fertilizer complex at Homs under the appellation of the General Fertilizer Company (GFC) under the Direction of the General Establishment of Chemical Industries (GECI).

The GFC complex is located about 10 km southwest of the city of Homs and abuts the shore of Lake Kattinah and the agricultural village of Kattinah. The general layout of the complex is shown in Fig. 1 together with main roads, railroads, power plant, refinery, and agricultural areas adjoining it. The complex is situated within an area of about one square kilometer, 1.2 x 0.8 km. The ground surface gently slopes towards Lake Kattinah on the west and the Assi River to the east. The GFC complex comprises the following manufacturing units*:

- Calcium/Ammonium Nitrate (CAN)
  - Nitric Acid.................... 280 T/d
  - Calcium/Ammonium Nitrate....... 480 T/d
- Ammonia/Urea (natural gas based)
  - Ammonia........................1000 T/d
  - Urea...........................1050 T/d
- Triple Superphosphate (TSP)
  - Sulfuric Acid.................. 850 T/d (2 units)
  - Phosphoric Acid................ 533 T/d
  - GTSP...........................1400 T/d

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* Capacities are based on design.[1/]

Each manufacturing unit has internal to its battery limits the following: water and wastewater treatment, boilers, laboratories and administrative effices. The GFC complex is headed by Dr.-Eng. Ammar Makki, the General Director and the Production Manager is Mr. Ammar D. Alsibai. The administrative and operating staff total some 3000 employees.

Because the Syrian Arab Republic recognized the need to improve the performance of this heavy chemical industry and optimize the

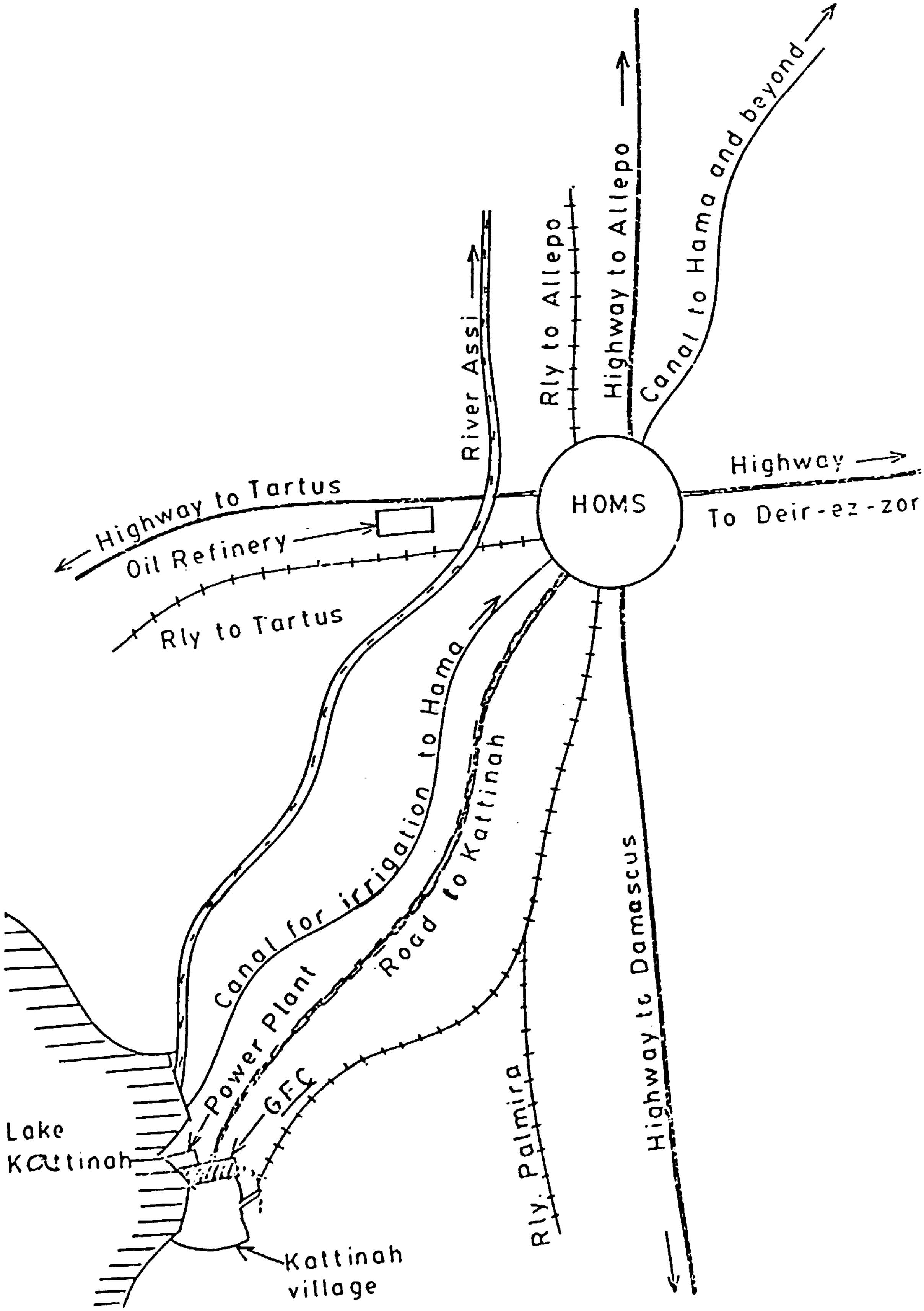

Figure 1. General Location of GFC Facility at Homs.

utilization of existing capacities through improvement of operations and minimization of environmental pollution therefrom, it requested the assistance of UNIDO under the Special Industrial Service program to obtain an expert cognizant of air, water, and hazardous waste pollution probrems, state-of-the-art remedial methods, and possessing the ability to assess the environmental impact of current fertilizer industry practices.

In this respect, his responsibilities are so defined:

- o To assess the environmental impact of air emissions from fertilizer production and recommend remedial actions;
- o To assess the environmental impact on surface and potential groundwater sources and recommend remedial actions;
- o To assess the current disposal of hazardous waste (solid waste) and recommend remedial actions;
- o To provide a socio-economic environmental impact assessment;
- o To provide expertise on the latest methods of environmental impact assessment; and
- o To prepare a technical report containing all of the aforementioned information and provide overall recommendations.

The duty period, as prescribed in the job description, was for two months and transpired during June-July 1989. The senior counterpart staff, titles, and areas of specialization are listed in the Annexes. Recommended fellowships and individuals, together with a list of training courses and curricula, are also contained in the Annexes. Finally, an extensive and comprehensive Bibliography is presented in the Annexes and is divided into areas of general interest, environmental impact assessment, air emissions/control, wastewater effluent limitations/guidelines and standards, remedial actions at contaminated sites, and other reports of interest. Copies of all articles, books, reports, and documents were made available to the GFC technical library for future reference. The final Annex attempts to interconnect defined and assessed environmental problems at GFC with appropriate remedial and control methods.

RECOMMENDATIONS

Recommendations comprise two categories--specific and general:

Specific

1. NO/NO_2 tail gas from the HNO_3 unit contributes significantly to acidic deposition and requires efficient scrubbing with a mildly basic solution of ammonium hydroxide (NH_3 + water) to minimize NH_3 lossess. The resultant NH_4NO_3 solution could be recycled for reuse.
2. The N_2O_4 fugitive emission from HNO_3 storage needs to be controlled. The N_2O_4 should be collected and catalytically converted to NO_2 and recycled to the secondary oxidation unit for reuse.
3. Baghouse or fabric filters need to be installed in both CAN and urea units. Baghouse use in the urea unit, however, should be limited to process airstreams with low moisture contents such as bagging operations only. Urea prills must be controlled through use of wet scrubbers, which allows ease of recycling of dissolved urea collected.
4. Process unit fugitive emissions (loss of feedstock and product) be controlled by initiation of a monthly equipment leak inspection, detection, and repair program. Pumps should be sealless, have dual mechanical seals, or be located within a closed vent system. Valves and compressors also need similar attention.
5. Solid wastes such as ZnS from desulfurization of natural gas, S-based filter cake/sludge and spent V_2O_5 catalyst from H_2SO_4 production, and dewatered gypsum (piles) need to be considered as hazardous wastes and treated and disposed properly in clay-lined, capped and managed landfills.
6. Contaminated gypsum slimes be treated for control of pollution parameters, namely, pH, phosphorus, and fluorides by a "double liming" procedure with final pH maintained at greater than 9.0 to ensure optimal precipitation of phosphorus as dicalcium phosphate (and monocalcium phosphate), fluorides as calcium fluoride, and Radium-226. With proper

management and employment of a spray-packed bed-type scrubber system to control the combined emissions of the WPPA reactor, the filter, and several other miscellaneous sources of SiF_4 and HF emissions, it would be possible to attain the monthly average wastewater effluent guidelines of 35, 25, and 50 mg/l for total P, fluoride, and total suspended solids, respectively.

7. The dry grinding/milling of phosphate rock at the GFC facility be terminated and replaced as soon as practicable by wet-rock grinding in order to reduce feedstock phosphate rock losses, minimize dust emission on-site and environmental contamination off-site, and ensure worker safety from the potentially harmful effects by inhalation and ingestion of radionuclides, such as Ra-226 and radon gas. Furthermore, management should, in the interim, immediately provide workers with surgical-type masks that cover nose and mouth, gloves, and replaceable plastic boots, and require that: (*a*) contaminated working garments be left at the plant and not worn home (to cause secondary contamination) and (*b*) should insist that showers be taken at the plant to remove contaminated soil and dust--this should be GFC policy.
8. Quality control measures be undertaken to improve urea product quality regarding biuret content. Greater than 1.0 percent biuret (urea process logs often show more than 1.3 percent and as high as 1.8-2.0 percent) is inimical to to broadleaf plant growth--in other words, biuret acts as a herbicide--in a product considered to be a fertilizer. The effective operating temperature of the prilling tower should be controlled closely (not to exceed 170°C) to ensure outlet temperatures do not exceed 60°C. Prolonged prilling tower temperature excursions greater than 170°C will cause urea to decompose into cyanuric acid and NH_3. Since the odor threshold for NH_3 is 46 ppm (35 mg/m^3), the shift engineer should be able by organoleptic means (smelling) to recognize the odor of NH_3, provided that fugitive emissions are properly controlled in the work-

place area.

9. Senior management should consider one of two options: (a) Elect to consider a manufacturing process change for GTSP--the Simplot limestone treatment for GTSP production, which eliminates use of pulverized phosphate rock and substitutes milled limestone instead, thus eliminating additional input of fluorides to the GTSP process and product, or (b) transfer GTSP operations to the Khnefis mine site near Palmyra. The latter option allows minimization of uncontrolled emissions of dust and fluorides (in the Homs agricultural area) and offers a further hazardous waste control optional use of phosphate rock excavation, when fully mined out, to be utilized for safe disposal of gypsum tailings.
10. Based on the fact that the NH_3/urea cooling tower is continually having difficulty functioning as designed due to fouling by oil and grease, it must be stressed that the oil and grease separator unit be repaired and made fully operational as soon as practicable.
11. Sludges removed/produced from physical-chemical treatment of process wastewaters should be removed by slurry pumping and dewatered using plate-and-frame filter presses (to 27-70 percent solids content), placed in sludge drying beds (isolated from manufacturing area and identified by plot number) for evaporative drying, analyzed for heavy metals, and, if in the acceptable concentration range, utilized as agricultural soil stabilizer.
12. The nitrification/denitrification biotreatment unit should be made operational by reduction of product NH_3 and urea losses to process wastewater. In other words, the design capacity for NH_3 and urea concentrations should not be exceeded and pilot plant testing data obtained prior to design and construction of the 200 m^3/min wastewater treatment unit should be reviewed for applicability. Plans should be made to supply adequate carbon (CH_3OH or domestic plant (BOD_5) wastewater) to the biotreatment unit.
13. The GFC complex lacks both a separate stormwater runoff sewer and a properly sized emergency receiving and holding

basin to prevent nutrient-rich stormwater from reaching both Lake Kattinah and the Assi River untreated. The use of such a stormwater diversion system should be carefully studied and implemented.

14. A comprehensive GFC manufacturing facility air quality survey needs to be initiated in order to identify and control air emissions that are causing acidic deposition within and around the area.
15. Consideration should be given to desulfurization of the power plant's fossil fuel, conversion to elemental sulfur, and reuse as feedstock to the H_2SO_4 production process. It is estimated that a reduction of up to 12 percent of the elemental sulfur feedstock requirement for GFC could be realized and the major contributor to the SO_x emissions inventory in the area--the power plant--would have its SO_x emissions under control with a concommitant noticeable reduction in acidic deposition.

<u>General</u>

Senior GFC management should:

1. Campaign for a good housekeeping program within the plant. Such a program would entail: (a) a suggestion box for good environmental ideas, and (b) a reward system--either monetary or public recognition of the "GFC environmental employee of the month," or both, for example. In this manner, the employees would feel as members of a "team effort" to control pollution of <u>their</u> environment.
2. Create a highly visible environmental pollution control group within the management.
3. See that the technical staff are effectively trained and educated: (a) in the latest fertilizer manufacturing techniques and (b) environmental control methods.
4. Encourage attendance of technical staff at international conferences, symposia, and meetings dealing with fertilizer production and environmental pollution control methods.
5. Consider integration of all wastewater treatment for the fertilizer complex, not have isolated treatment units and

operational staffs. In this regard, the staffs should have their respective training upgraded routinely to include the latest sanitary and environmental engineering concepts and be fully licensed and certified operators and laboratory technicians. Moreover, the wastewater and product laboratories should both be upgraded to include current analytical methods using proper and statistical sampling methodology.

6. Should initiate a complete fluoride and phosphorus manufacturing process inventory (that is, material balances) to account for feedstock and product losses.
7. Should: (a) identify all waste emissions--quality and quantity--to include water, air, and solids; (b) minimize the number of wastewater effluents and attempt to combine compatible wastes and treat accordingly; (c) reduce/eliminate all untreated wastewater discharges (industrial and domestic) to Lake Kattinah and the Assi River.

The reader should make liberal use of the Table of Contents to help locate specific areas of interest, whether in the area of product manufacture, emissions, or control technologies.

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I. ASSESSMENT OF ENVIRONMENTAL IMPACTS OF UNCONTROLLED AIR EMISSIONS FROM FERTILIZER MANUFACTURING

A. Calcium/Ammonium Nitrate Unit

Nitric Acid Process. The Nitric Acid (HNO_3) unit was inspected on 22 June 1989 and generally conforms with the configuration depicted in Fig. 2. Ammonoxidation is used to produce dilute HNO_3 of 55-65 percent. Ammonia (NH_3) is reacted with air to produce oxides of nitrogen (NO_x):

$$2\ NO + O_2 \longrightarrow NO_2 \qquad (1)$$

$$3\ NO_2 + H_2O \longrightarrow 2HNO_3 + NO \qquad (2)$$

The initial ammonia oxidation takes place in the converter in the presence of a platinum-rhodium catalyst at pressures from atmospheric to 9.2 atm. The exit gases from the converter may range from 705°C to 980°C and are used to superheat steam and preheat process air. The gases then pass through a waste heat boiler to generate steam for the air compressor drive turbine and uses elsewhere. The quantity of steam generated by the process ranges from 500-1000 kg/T HNO_3. By this time, due to the lower temperature, the second reaction involving the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) has begun to occur. Following additional cooling to 38-49°C, where some of the water is condensed and forms HNO_3, the gases pass up through an absorption column. Some additional air is also passed up through the column to oxidize the NO formed during the absorption step (equation 2, above) to NO_2. Water fed to the top of the absorber acts as the absorbant producing product HNO_3 out the bottom of the column. The absorption unit temperature is held constant by cooling water (isothermal absorption) to improve the absorption efficiency. Cooling water requirements range from 104,000 to 146,000 liters/T HNO_3 product.

Gases leaving the top of the absorber are fairly low in NO_x, but may be catalytically reacted to further reduce the levels and then, depending on the process pressure, passed through a hot gas expander unit to recover some of the energy required to drive the process air compressor. (The differential energy required for the air compressor can be supplied by a helper

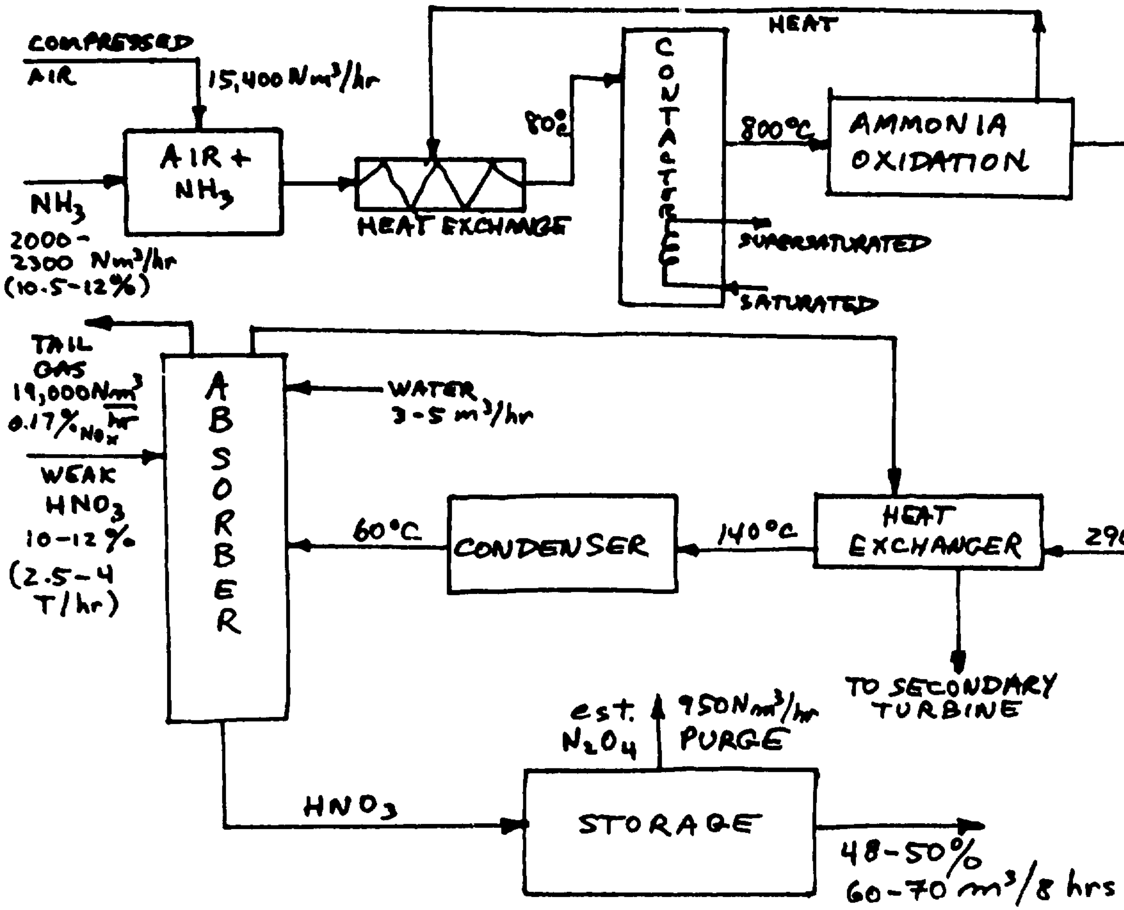

Figure 2. Process Schematic for Nitric Acid.

turbine driven by the steam generated by the process.)

Nitric Acid Observations. Two significant uncontrolled emission sources were apparent: (*a*) Uncontrolled tail gases from the absorption unit containing approximately 0.17 percent NO_x in an emission rate of 19,000 Nm^3/hr ($NO + NO_2$) or 150 kg/T HNO_3 and (*b*) intermittant emissions of N_2O_4 from the HNO_3 storage tank purge estimated at a minimum of 15 kg/T HNO_3. N_2O_4 is formed from the dissociation of HNO_3 according to:

$$HNO_3 \rightleftarrows H_2O + NO_2 \qquad (3)$$

$$2\ NO_2 \rightleftarrows N_2O_4 \qquad (4)$$

The N_2O_4 emission from the HNO_3 storage tank should be recovered and converted to NO_2 catalytically, and recycled to the secondary oxidation unit. Several sources of fugitive emissions, that is, leaking valves, fittings, tanks, and so forth, were also noted.[2/] No attempt at NO_x control was observed. Analyses of tail gases were made between 0 and 3 times per day for NO and NO_2 only--no other emission parameters were analyzed for on a routine basis. (See Section I. D. Emission Control Methods: Wet Scrubbers, pp. 52-54)

Nitric Acid Air Emission Standards. In the United States, emissions of NO_x and the so-called "criteria air pollutants" (those pollutants designated as capable of endangering the public health and welfare) are controlled through the Clean Air Act and National Ambient Air Quality Standards (NAAQS)(see Table 1).

Table 1. NAAQS for Criteria Air Pollutants.[3/]

Pollutant/Averaging Period	Primary Standard ($\mu g/m^3$)	Primary Standard (ppm)	Secondary Standard ($\mu g/m^3$)	Secondary Standard (ppm)
Sulfur dioxide				
Annual arithmetic mean	80	0.03		
24-hour	365	0.14		
3-hour			1,300	0.5
Particulate matter, as PM_{10}^{a}				
Annual arithmetic mean	50		same	
24-hour	150		same	
Carbon monoxide				
8-hour	10,000	9	same	
1-hour	40,000	35	same	
Ozone				
1-hour	235	0.12	same	
Nitrogen dioxide				
Annual arithmetic mean	100	0.05	same	
Lead				
Maximum quarterly average	1.5		same	

[a] PM_{10} = particulate matter with an aerodynamic diameter equal to or less than 10 µm

Ammonium Nitrate/Calcium-Ammonium Nitrate Process. The Calcium/Ammonium Nitrate (CAN) unit was observed on 19 June 1989 and the process flowsheet is shown in Fig. 3. Ammonium Nitrate (AN) is produced by neutralization of HNO_3 and NH_3:

$$HNO_3(aq) \quad + \quad HN_3(g) \longrightarrow NH_4NO_3(aq) \quad + \quad heat$$

Typically, a 45-60 percent solution is mixed with gaseous NH_3 in a ratio of 3.55-3.71 to 1 by weight. The reaction is carried out in a low pressure vessel termed the neutralizer. The feed ratio produces up to an 83 percent by weight AN product. The high heat of reaction causes flash vaporization of water with some NH_3 and NO_3^- going overhead. The reaction liberates 46.5-52.4 MJ (11,000-12,600 kcal/mole of AN formed), depending on the

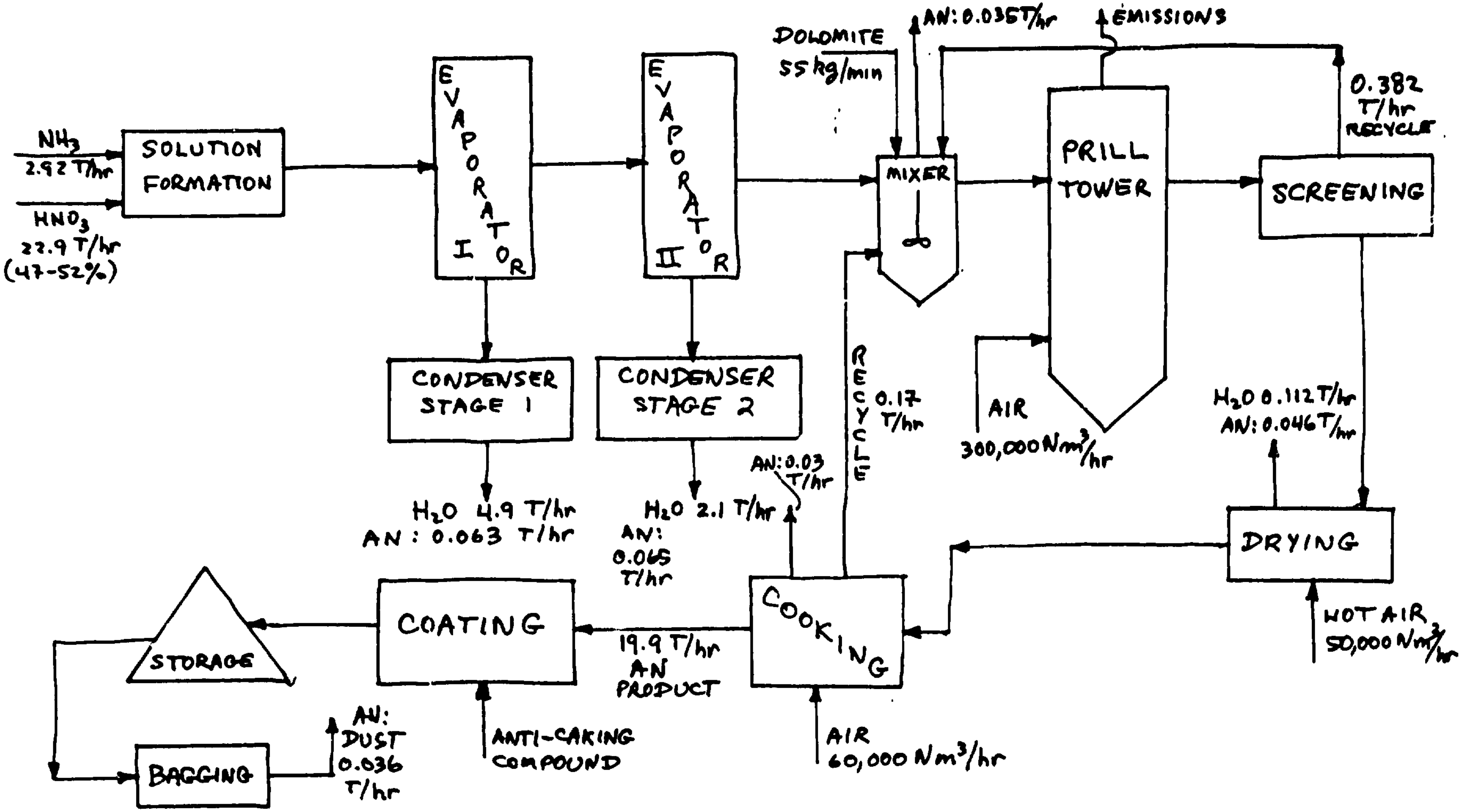

Figure 3. Process Schematic for Ammonium Nitrate/CAN.

original concentration of HNO_3 feed. The temperature range is 132-149°C. The overhead vapors from the neutralizer often lead to an air pollution problem or, if condensed, must be treated prior to being discharged to the atmosphere.

AN contains up to seven unit operations:

- Solution formation or synthesis
- Solution concentration
- Solids or prill formation
- Solids finishing (drying and/or cooling)
- Solids screening
- Solids coating
- Bagging

The AN solution is concentrated in one or two evaporators using heat to drive off additional water. A melt containing 95-99.8 percent AN at approximately 149°C is produced and is then used to make prilled AN. To produce prills, concentrated AN melt is sprayed into a prill tower. AN droplets form in the tower and fall countercurrent to a rising air stream that cools and solidifies the falling droplets into spherical "prills". High density prills are formed from a 99.5-99.8 percent AN melt; they are less porous than low density prills.

Two breakdown reactions can occur:

- Decomposition:

$$NH_4NO_3(s) \xrightarrow{T > 232^\circ C} N_2O(g) + 2H_2O(g) + \text{heat}$$

- Dissociation:

$$NH_4NO_3(s) \rightleftharpoons NH_3(g) + HNO_3(g) - \text{heat}$$

The dissociation reaction (an equilibrium, reversible reaction) is favored by increasing temperatures and <u>is responsible for NH_4NO_3 fume, a significant contributor to emissions</u> during solids formation (prilling).

Furthermore, AN possesses five crystalline states of matter and rapid transitions among the various crystalline states can result in fracturing of the AN particles, which leads to AN dust emissions (see Table 2).

Table 2. Properties of Solid Ammonium Nitrate.

Melting point: 170.6°C
Solubility : 118 g/100 g water @ 0°C
843 g/100 g water @ 100°C

Crystal States	Temperature, °C	Morphology
I	170 - 125	ε cubic
II	125 - 84	δ tetragonal
III	84 - 32	γ rhombic
IV	32 - -18	β rhombic
V	< -18	α tetragonal

GFC injects milled dolomite into the melt stream at a rate of 55 kg/min, which results in a 14 weight percent quantity of dolomite additive in the final CAN product. This additive serves three purposes:

- It raises the crystalline transition temperature of the solid, final product
- It acts as a dessicant, drawing water into the final prills to reduce caking
- It allows prilling to be conducted at a lower temperature by reducing the freezing point of the molten AN

Concentrator and prill tower emissions contain significant amounts of fine particulate AN, which can represnt both a serious air pollution problem and an indirect water pollution problem source via runoff and washoff.

Following screening, the prills are coated with a French-supplied product--a proprietary anti-caking agent--a fatty amine-based compound at the rate of approximately 50 l/hr.

CAN Observations. The most apparent uncontrolled emission sources concern AN and CAN particulate (dust) emissions: open-topped prill tower, grinding of dolomite coating material, screening operations, cooling chamber, thick layers of AN/CAN dust everywhere--these particulate emissions account not only for air pollution problems, but are major sources of loss of product. Neither wet scrubbers nor fabric filters or baghouses were observed; in fact, no air pollution control devices were noted. Severe corrosion of equipment, apparatus, concrete foundations and stairwells were seen. In the United States, there is an agency responsible for worker safety and health in chemical manufacturing facilities--the Occupational Safety and Health Administration (OSHA). If this CAN unit were located in the United States, OSHA would have no option but to seek complete shutdown of such an operation. One only needs to recall the disasterous explosion of an AN tanker in port at Texas City, Texas, in the 1950s. The investigation concluded that the violent explosion was caused by excessively dry and dusty AN fines, which underwent spontaneous combustion and detonation.

Ammonium Nitrate Air Emission Standards. AN production processes emit particulates (AN and CAN), NH_3, and HNO_3. Particulate emissions, consisting primarily of AN and CAN, are emitted from neutralizers, evaporators/concentrators, prilling towers, solids finishing, bagging and handling operations. AN emissions from individual sources range from 0.03 to 147.2 kg/T of AN produced for the granulation technique. Uncontrolled NH_3 emissions from neutralizers, evaporators/concentrators, prilling towers, and granulators range from 0.03-29.7 kg/T of AN. When operating under acidic conditions, neutralizers emit HNO_3 ranging from 0.004-0.08 kg/T of AN.[4/]

The most commonly used control system for high density prill towers is a collection hood and a wetted, fibrous-filter scrubber. For AN high density prill towers, uncontrolled particulate emissions range from 0.81-2.74 kg/T of AN, whereas controlled emissions range from 0.03-0.85 kg/T of AN. Some treatment systems only treat a portion of the total prill tower emissions; reported controlled emissions for these systems are the sum of the treated air emissions and the baghouse emissions.

In the United States, AN emissions from the production unit must be less than an opacity of 20 percent. Limits on particulate emissions from AN production facilities are usually based on the plant's production rate. For example, a 181 T/d AN plant would have an emission factor range of 3.58-12.14 kg/hr (0.47-1.61 kg/T), whereas a 1089 T/d AN plant has an emission factor range of 5.97-35.49 kg/hr (0.13-0.78 kg/T). New source performance standards (NSPS) vary from state to state and change dependent on the size of the AN plant. Table 3 shows the allowable emission rates versus plant size for 21 states where AN plants exist in the United States.

Table 3. Allowable Particulate Emission Factors by Plant Size (ref. EPA-450/3-81-002)

Plant Size	Average Emission Rates		Range*
T/d	kg/hr	kg/T	kg/T
181	7.10	0.941	0.899-1.16
362	11.30	0.749	0.688-1.009
724	16.71	0.554	0.507-0.737
1089	18.51	0.408	0.370-0.543

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* Range for low density prill, high density prill, and granulation AN-forming processes

B. Ammonia/Urea Unit

Ammonia Process. The ammonia unit was seen on 20 June 1989 and the process flowsheet is delineated in Fig. 4. M.W. Kellogg with Technip of France recently completed the conversion of the NH_3/urea unit from naphtha to natural gas feedstock. The natural gas is supplied from the Jubeisseh field to the northeast. The production of NH_3 from natural gas comprises six basic steps:

- Desulfurization (to prevent poisoning the Ni-catalyst in the reformer
- Reforming of CH_4 to H_2 and CO
- Shifting of CO with water to produce additional H_2
- Absorption of CO_2
- Methanation of residual CO_2 prior to NH_3 synthesis

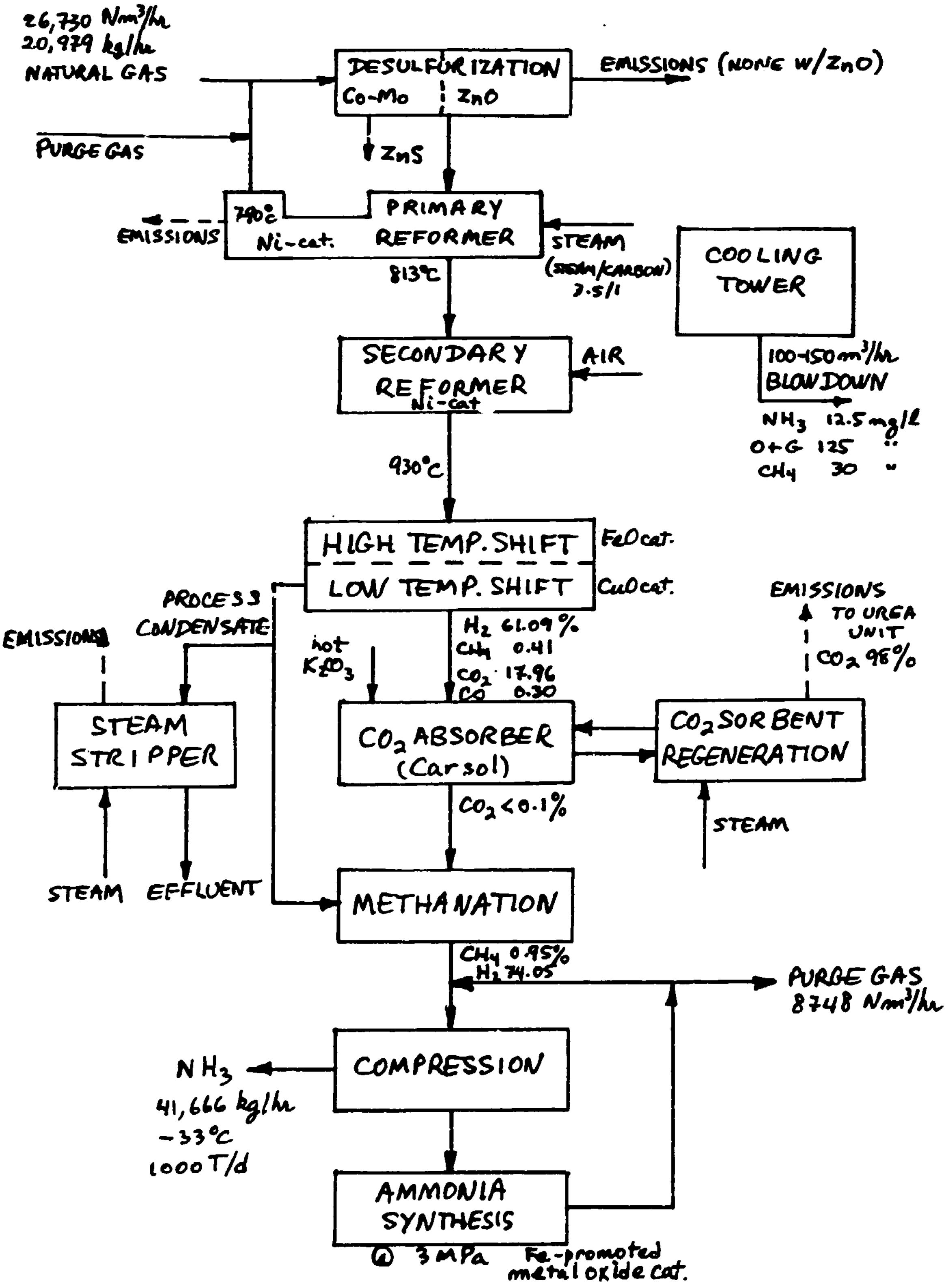


Figure 4. Process Schematic for Ammonia.[5]

- Synthesis of NH_3 from H_2 and N_2

In the sulfur removal and gas reforming section, natural gas at medium pressures of 14.6-41.8 atm is treated to remove sulfur by passing the gas through a dual bed of Co-Mo catalyst followed by ZnO. There are basically three advantages to the ZnO bed: energy in the form of steam regeneration is not required, there are no air emissions, and higher molecular weight hydrocarbons are not removed, which would result in a reduction of the heating value of the gas.

Steam reforming occurs in two steps. In the primary reformer (the radiant energy section of the reformer), methane (CH_4) reacts with steam in the presence of a Ni-catalyst at temperatures around 790°C according to:

$$CH_4 + H_2O \dashrightarrow CO + 3H_2 \quad \text{(reform)}$$

$$CO + H_2O \dashrightarrow CO_2 + H_2 \quad \text{(shift conversion)}$$

Gas exits the primary reformer at 750-850°C and 2900-3600 kPa and contains about 10 percent unreacted CH_4, depending on operating temperatures and pressures. Partially reformed gas flows to the refractory-lined secondary reformer, where it is mixed with air (the quantity of which is fixed by the requisite H_2/N_2 ratio of 3 to 1) in the final synthesis gas. Fuel for the primary reformer consists of 7/8 natural gas and 1/8 purge gas from the NH_3 synthesizer. The oxygen (O_2) from the air is combusted with the fuel to provide additional heat in the secondary reformer. Reformed synthesis gas at temperatures in excess of 930°C, which produces sufficient heat to supply from 50-100 percent of the 10.3 MPa steam required in the plant; CH_4 content at this point is around 0.34 percent. The synthesis gas is then cooled to about 370°C.

The gas now enters the high temperature shift converter, which contains a chromium-oxide-promoted iron oxide shift catalyst, where the shift reaction occurs:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

The forward reaction is favored by higher temperatures, but is only partially completed under these conditions. Most of the reaction is allowed to take place at relatively high temperature (330-550°C) to take advantage of higher rates of reaction. At the point where the CO_2 concentration builds up to where the reverse reaction begins to proceed at appreciable rates, the gas is fed to the low temperature shift converter (200°C) to take full advantage of higher equilibrium CO_2/H_2 concentrations. The CO concentration is reduced from 12.8 percent to 3 percent in the high temperature shift converter and from 3 percent to <0.5 percent in the low temperature shift converter.

Unreacted steam is condensed and separated from the gas in a knockout drum. A typical NH_3 plant recovers approximately 40 m^3/hr of process condensate for a 900 T/d plant.[6/]

The gas now contains from 17-19 percent CO_2, which must be removed because it can poison the NH_3 synthesis catalyst--an iron-promoted, metal oxide type. The Kellogg process at GFC employs a hot potassium carbonate solution called Carsol. CO_2 is absorbed in the absorber by the Carsol according to:

$$CO_3^{=} + CO_2 + H_2O \longrightarrow 2\ HCO_3^{-}$$

The scrubbing solution is regenerated in a CO_2 stripper by heating with steam, which generates a 98.5 percent CO_2 stream. This CO_2-rich stream serves as feedstock for the urea plant.

All remaining traces of CO_2 and CO must be removed from the synthesis gas at this point. This is accomplished in a methanation unit, which is simply a reverse of the catalytic steam reforming of CH_4, where the gas is passed through a bed of Ni-catalyst resulting in the following reactions:

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

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

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

The exit gas from the methanator contains less than 10 ppm CO and CO_2 and about 1.3 percent CH_4 plus argon. The requisite H_2/N_2 ratio of 3 to 1 is attained.

Compression of synthesis gas occurs in two stages. After the first stage, water is removed and the gas is cooled to increase volumetric efficiency. Furthermore, the synthesis gas is combined with recycle from the NH_3 synthesizer, which contains 12 percent NH_3, which is further reduced to 9.9 percent when mixed with fresh feed. Following the final compression, the gas is cooled to -33°C and the NH_3 product is removed together with water plus any residual CO/CO_2. Synthesis gas is reheated to 140°C and is then fed to the NH_3 synthesizer, which operates at 14 kPa. The gas exiting the reactor is recycled as described previously. A small amount of the gas is purged to prevent buildup of inert gas, such as argon, in the reaction cycle. The purge gas is refrigerated to remove NH_3 and then fed to the primary reformer along with natural gas. Table 4 gives typical purge gas composition, which is compared to design specifications of Kellogg.

Table 4. Typical NH_3 Synthesis Purge Gas Compared to Kellogg Design for the GFC NH_3 Unit

Composition Component	Concentration, mole % Typical	Kellogg
H_2	60	74.05
N_2	20	24.69
A	3.5	0.31
CH_4	16.5	0.95
NH_3	50 ppm	N/A

N/A = not available

Ammonia Observations. The conversion from naphtha feedstock to natural gas apparently has reduced significantly uncontrolled emissions from this process unit, essentially eliminating SO_x emissions. ZnS solid waste will amount to approximately 43 m^3/yr and must be handled in an environmentally safe manner.

Purge gas is vented to the primary reformer as fuel. Since the 275 kg/hr purge stream contains approximately 70-75 percent H_2, this may be too valuable a resource to use as fuel and might be removed and added to the synthesis gas; recovered H_2 can increase NH_3 plant capacity by as much as 6 percent. Fugitive emissions were noted by the strong odor of NH_3 (NH_3 threshold is 46 ppm (35 mg/m^3)), which arise from leaking compressors and pump seals, NH_3 tank vents, and pressure relief valves. Such emissions can represent an appreciable loss of product NH_3. Also noted was the fact that the oil separator unit was nonfunctional, which is probably one of the causes of poor cooling tower performance. (See Section III.B Disposal Methods, pp.87-89)

Ammonia Air Emission Standards. Table 5 contains a summary of emission factors for both uncontrolled and controlled cases.

Urea Process. The urea unit was reviewed on 20 June 1989 and the process flow diagram is shown in Fig. 5. Urea or $(NH_2)_2CO$ is formed by reacting NH_3 and CO_2 at 175-200°C and 19.2-23.2 MPa (191.5-232 atm) to form ammonium carbamate, $NH_4CO_2NH_2$. The carbamate is then dehydrated to form urea and water. The reaction sequence can be represented thusly:

$$2\ NH_3 + CO_2 \longrightarrow NH_4CO_2NH_2 + \text{heat}$$

$$NH_4CO_2NH_2 \longrightarrow NH_2CONH_2 + H_2O - \text{heat}$$

The carbamate formation step is highly exothermic releasing 150-160 kJ (16,250-17,340 kcal) per mole of $NH_4CO_2NH_2$ formed. This reaction is favored by high pressures. The dehydration step is slightly endothermic, consuming 32 kJ (3,480 kcal) per mole of urea formed. This step is favored by high temperatures. Under reactor operating conditions, the dehydration reaction proceeds to 40-60 percent completion resulting in an overall, net exothermic heat effect. After separation of the NH_3, CO_2 and $NH_4CO_2NH_2$, the resulting solution is about 70-77 percent urea.

Urea, a solid, has a melting point of 133°C and a specific gravity of 1.335 at 20°C. Aqueous urea solutions begin to

Table 5. Emission Factors for Ammonia Production. (ref. EPA-450/3-80-014)

	SO_2	NO_x	CO	TSP	VOC	CH_3OH	MEA	NH_3
Emission factors, kg/T								
Desulfurizer[a] (carbon)	0.006		6.9		3.6			
Controlled (ZnO)	0		0		0			
Reformer[b]	0.0024	2.7	0.068	0.072	0.012			
Δ for stripper overhead to stack		+1.1				+0.15		+0.44
Steam stripper[c]						0.6		1.1
Controlled (to reformer stack)						0		0
CO_2 absorber[d]			1.0		0.47		0.05	1.0
If feedstock used for urea unit			0		0		0	0
Annual emissions: 900 T/d NH_3 Plant, T/y								
(CH_3OH and MEA based on CH_4 equiv. and included with VOC)								
Uncontrolled	0.0025	0.826	2.438	0.022	1.346			
Controlled	0.0007	1.163	0.327	0.022	0.175			
Controlled with on-site urea plant	0.0007	1.163	0.021	0.022	0.027			

---

[a] Since activated carbon has been replaced by ZnO to desulfurize the natural gas feedstock, there are no air emissions, only ZnS waste sludge.

[b] Process heat from the primary reformer is supplied by burning natural gas or fuel oil. Emissions are the combustion products: NO_x, which can be reduced by NH_3 injection into the combustion zone.

[c] CH_3OH contained in overheads from condenstae stripper in annual VOC (volatile organic compounds) emission of about 92 T; when gas stream injected into base of of the reformer stack, the VOC emission is reduced to 23 T/y.

[d] The 98% CO_2 gas stream is commonly vented to atmosphere. Since the gas contains CO and VOC, an alternative is desirable. Since the CO_2-rich stream can be used in urea production, this emission point can be eliminated.

Source: EPA-450/3-80-014. 14.

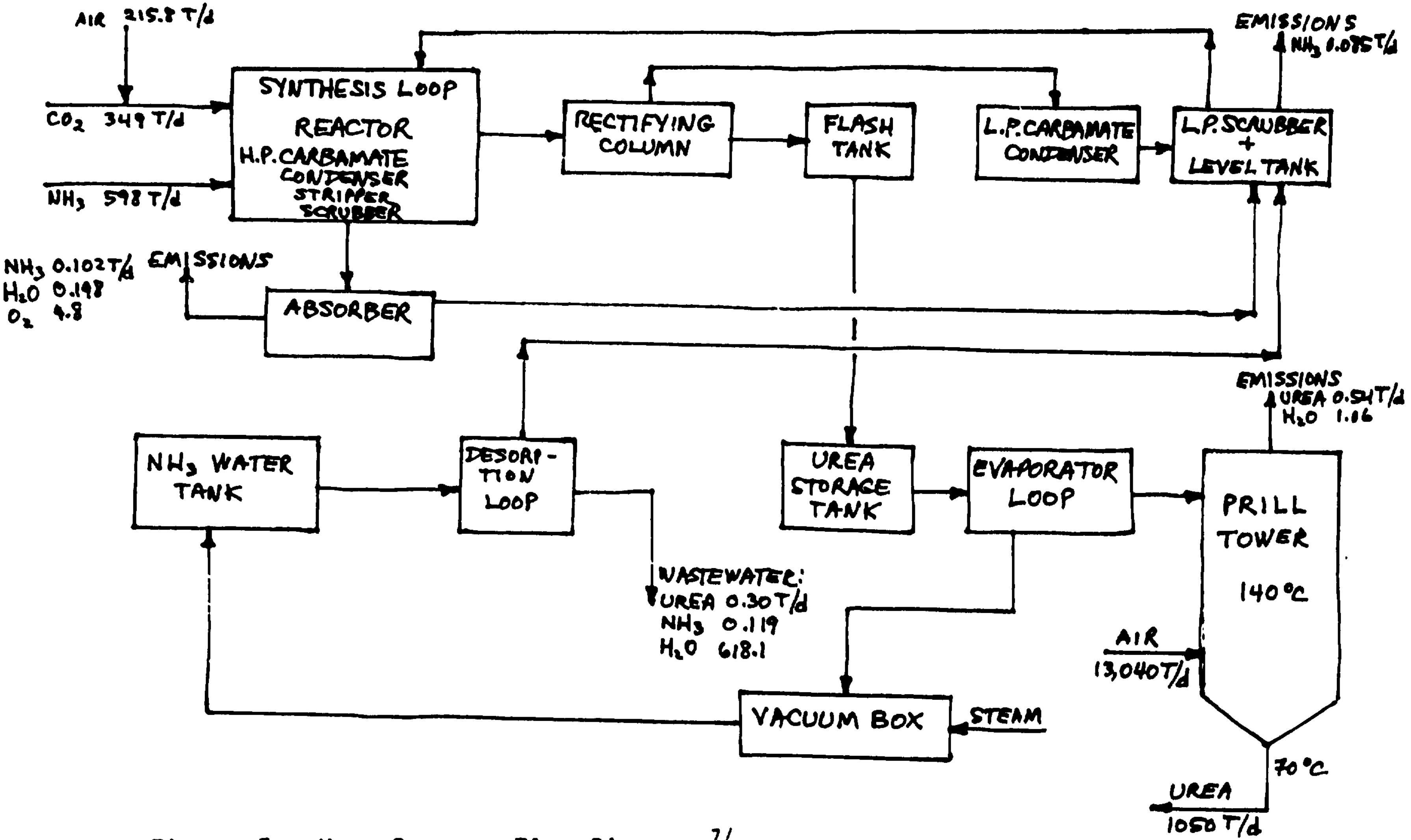


Figure 5. Urea Process Flow Diagram.[7]

decompose at 60°C to biuret, $NH_2CONHCONH_2$, and NH_3 according to:

$$2\ NH_2CONH_2 \longrightarrow NH_2CONHCONH_2 + NH_3$$

Above 170°C, the primary decomposition products of urea are cyanuric acid $(NHCO)_3$ and NH_3. The biuret reaction/concentration in urea must be monitored closely, as it is a plant herbicide. Biuret concentrations in urea solids are 0.1 percent or less in crystals, 0.3 percent in solids formed from crystal remelt, and 1.0 percent in solids formed from concentrated urea solution.

The total recycle process (carbamate plus NH_3) provides benefits of higher yields and lower energy consumption.

Emission sources from synthesis processes are typically noncondensible vent streams from ammonium carbamate decomposers and separators. Emissions from synthesis processes are generally combined with emissions from the solution concentration operation. Combined particulate emissions from urea synthesis and concentration are small compared with particulate emissions from a typical solids-producing urea plant.

Urea Observations. Besides the unending and extremely high noise levels, the consistent problems appear to be particulate emissions from the prilling tower. Review of product urea quality logs in the laboratory showed consistently high biuret concentrations (1-2 percent). Biuret concentrations from prilling must be maintained at or below 1 percent. Typical GFC exit temperature of urea prills was 70°C, with 140°C within the tower. Recall that biuret at $>$ 1 percent concentration in urea becomes a herbicide inimical to broadleaf plants and vegetation. This is contradictory to the main function of urea as a fertilizer. Operating conditions within the prill tower must be adjusted such that the urea prill temperature does not exceed 60°C when exiting the tower. Also, prilling gives a product of about 1 percent biuret, whereas crystallization only has 0.1 percent; a combination of the two operations results in a biuret of about 0.5 percent, a tolerable amount.

Urea Air Emission Standards. Uncontrolled emission rates from prill towers may be affected by the following factors:

- o Product grade being produced (agricultural or feed)
- o Air flow rate through the prilling tower
- o Type of prilling tower
- o Ambient air conditions
- o Melt spray conditions

The existing level of control (ELOC) is defined as that level of control that is currently being applied to emissions from solid urea producing operations within the urea industry. Moreover, standards limiting particulate emissions are also in effect, which cover opacity limits--20 percent maximum, exhaust gas particulate concentration limits, and particulate emission limits calculated from process weights. The process weight regulations can take the form of an allowable emission factor expressed as kg of particulate allowed per ton of production. Particulate emissions from a 363 T/d plant are limited to a range of 5.19-71.44 kg/hr (0.34-4.72 kg/T). The states of Illinois and California in the United States have the most stringent process weight regulations limiting a 363 T/d plant to emissions of 5.19 and 5.97 kg/hr (0.34-0.40 kg/T), respectively. Table 6 presents data on allowable particulate emission factors as a function of size of plants (used in 20 of 23 states). (See Table 11, p. 55, for urea emissions control equipment effectiveness.)

Table 6. Allowable Particulate Emission Factors by Plant Size.

Plant Size	Average Emission Rates	
T/d	kg/hr	kg/T
182	7.29	0.96
364	11.90	0.79
737	17.66	0.59
1091	19.57	0.43

(ref. EPA-450/3-81-001) 7/

C. Triple Superphosphate Unit

Sulfuric Acid Process. The Sulfuric Acid (H_2SO_4) unit (2 x 850 T/d) was observed on 21 June 1989 and a process schematic is presented in Figure 6. The direct contact H_2SO_4 process is so named because of the use of a catalyst surface to accelerate the oxidation reaction between sulfur dioxide (SO_2) and O_2, which occurs when the two gaseous components contact each other on the surface of pelletized vanadium pentoxide (V_2O_5) catalyst to form the resultant sulfur trioxide (SO_3) gas. In turn, the SO_3 gas is hydrolyzed through the addition of water to form H_2SO_4.

Feedstocks are elemental sulfur (S), air, and water. Molten, elemental sulfur is sprayed into a dry air-stream inside a furnace. The elevated furnace temperature auto-ignites the atomized liquid sulfur to oxidize it to SO_2 with the release of a large quantity of heat, which causes the temperature of the resultant SO_2-excess air mixture to rise to 900-1140°C as it exits the furnace and flows to a boiler for heat removal. Sufficient heat is removed to reduce the gas mixture temperature to the initial reaction condition for optimal chemical conversion of SO_2 to SO_3, which takes place in a series of three or four steps. After the conversion stages, SO_3 flows to the bottom of the first absorption tower upwards through ceramic packing in countercurrent flow to downward 98-99 percent H_2SO_4. The SO_3 is easily hydrolyzed to H_2SO_4 by the water in the acid. More heat is released.

In the double absorption process, a second absorption tower is installed at a point intermediate between the first and final $SO_2 \rightarrow SO_3$ catalytic conversion steps. Utilization of this second absorption tower permits the achievement of a greater SO_2 conversion to SO_3 and thus *a significantly reduced quantity of SO_2* in the plant emission stream. Double absorption plants realize SO_2-conversion efficiencies of 99.5+ percent compared to single absorption plant efficiencies of approximately 98 percent. Both processes have the same effluent with respect to both quality and contaminant levels.

Sulfuric Acid Observations. Large, high piles of elemental S feedstock, due to their wind silhouette, present potential for wind-borne processes to cause particulate emissions and resultant loss of feedstock. The H_2SO_4 unit was operational during the morning (but down in the afternoon) and SO_x emissions were noted in the vicinity of the converter; it appeared that the converter

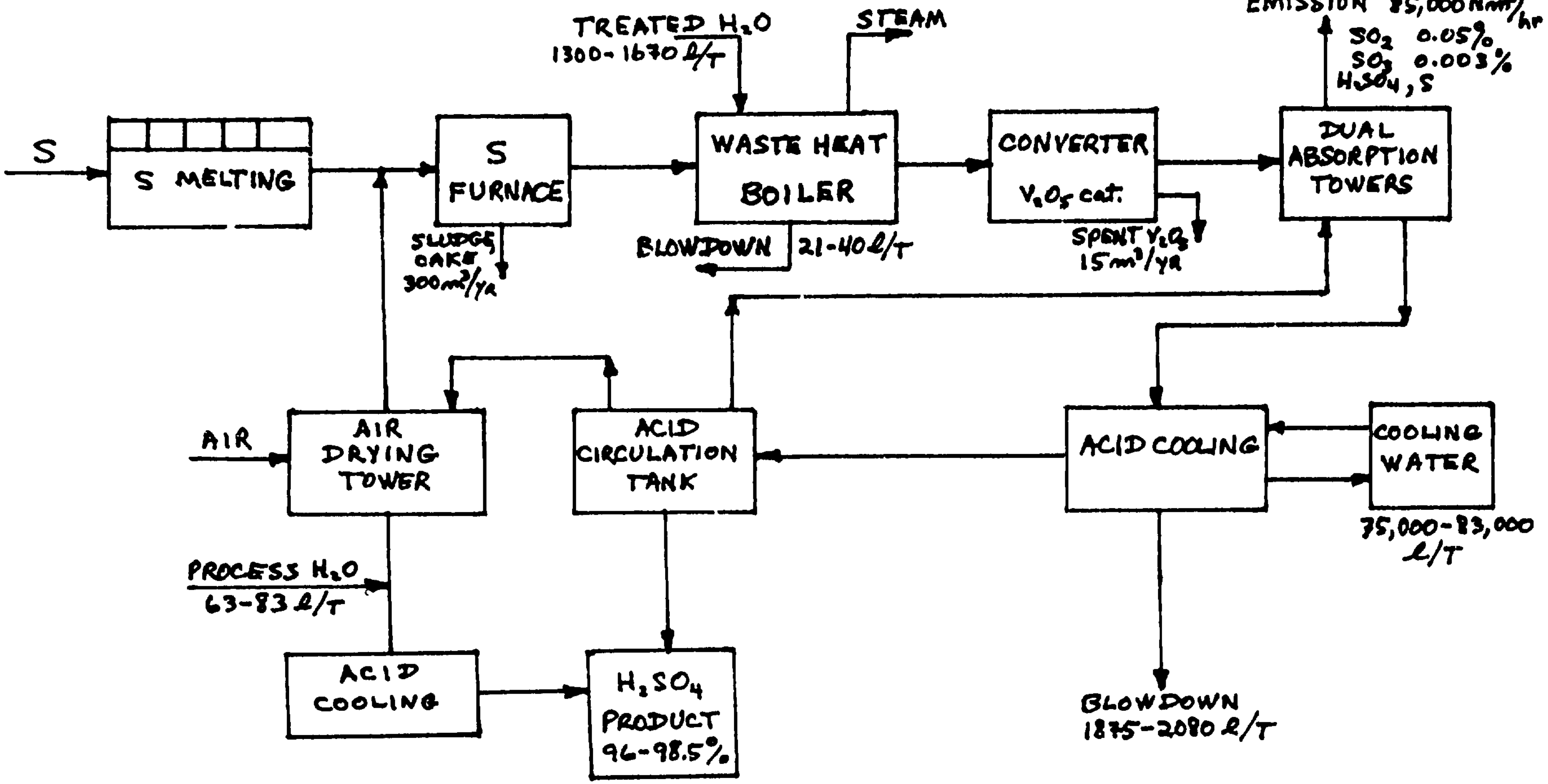


Figure 6. Process Schematic for Sulfuric Acid Manufacture.

suffers from several corrosion spots, which present opportunities for uncontrolled emissio . The converter is filled with four beds of V_2O_5 with a silica carrier and a Na_2O promoter. V_2O_5 catalyst is eluted based on percent conversion and pressure drop. V_2O_5 is reactivated on-site and new catalyst charges are stored nearby. Spent V_2O_5 is generated at the rate of 15 m^3/y and is bagged in polyethylene sacks and disposed in the desert. Conversion rates continue to decline to 90.3 percent. There are obvious uncontrolled SO_x emissions, submersible pumps underspecified and, hence, are overloaded, the effectiveness of the absorption towers is less than design causing significant losses of SO_2 (0.05 percent) and SO_3 (0.003 percent), and the boiler suffers from both internal and external corrosion resulting in serious fugitive emissions. (See Annex V, pp. 125-6.)

Sulfuric Acid Air Emission Standards. The only significant air emission standards for H_2SO_4 plants are as follows:

Parameter	Emission Factor
SO_2	1.81 kg/T of 100% H_2SO_4
Particulates	150 µg/Nm^3

See also Table 1.

Phosphoric Acid Process. The Phosphoric Acid (H_3PO_4) unit (533 T/d as 100% P_2O_5) was inspected on 24 June 1989 and the process is detailed in the flowsheet shown in Fig. 7. Wet process phosphoric acid (WPPA) is produced by reacting H_2SO_4 with fluorapatite, $Ca_{10}(PO_4)_6F_2$, or phosphate rock. In the process, calcium sulfate dihydrate or gypsum, $CaSO_4 \cdot 2H_2O$, is also formed. The overall reaction is shown as follows:

$$3\ Ca_{10}(PO_4)_6F_2 + 30\ H_2SO_4 + SiO_2 + 58\ H_2O \longrightarrow 30\ CaSO_4 \cdot 2H_2O + 18\ H_3PO_4 + H_2SiF_6$$

Table 7 lists the composition of three Syrian phosphate rock supplies employed at GFC. Finely ground phosphate rock is continuously metered to single-tank reactors, usually with two concentric cylinders (a typical design). The reactants are then added to the annulus and digestion occurs in this outer

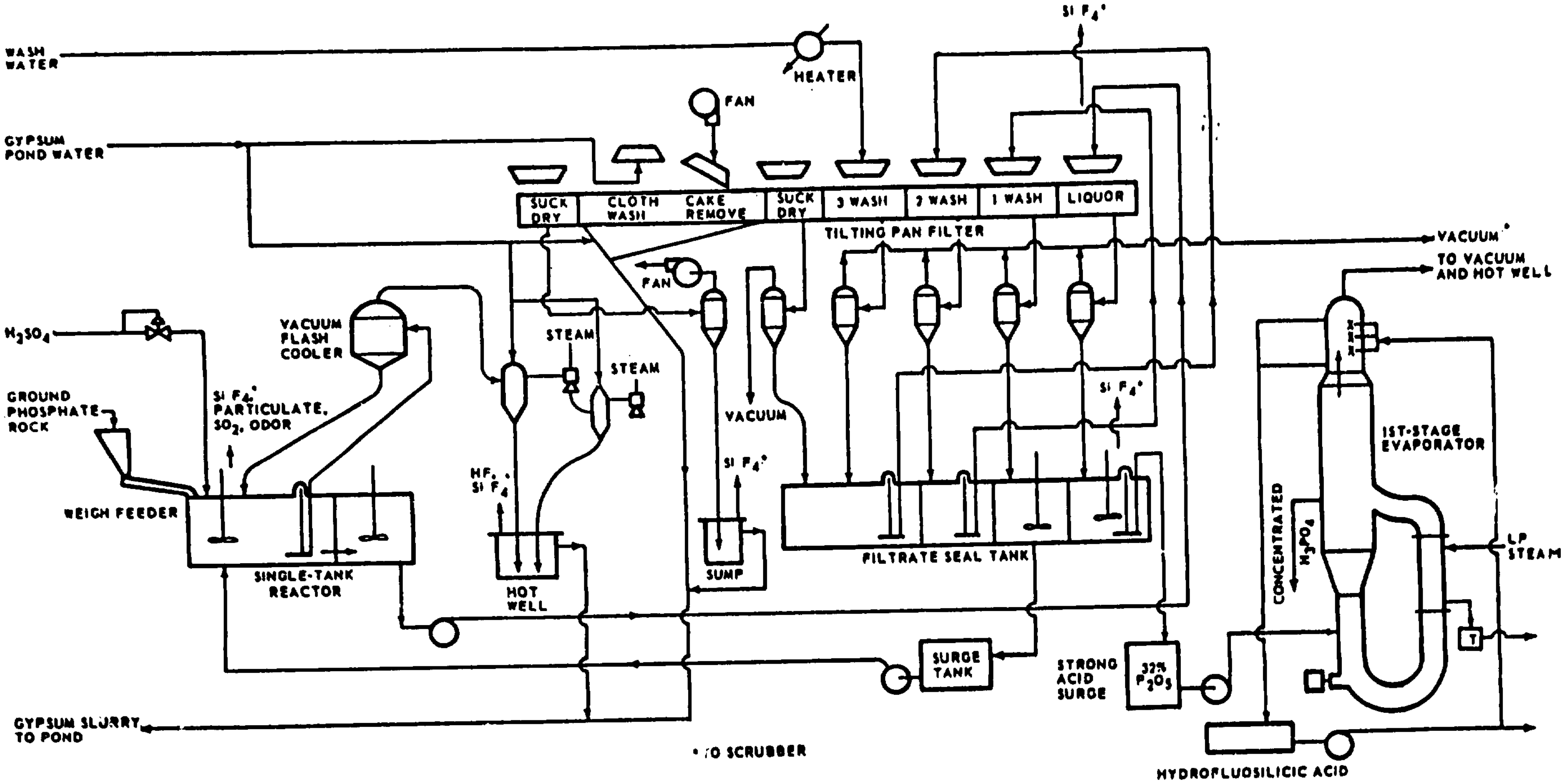


Figure 7. Wet Process Phosphoric Acid Process Flowsheet.

compartment. The second or central compartment provides retention time for gypsum crystal growth and prevents short-circuiting of rock. Concentrated H_2SO_4 is usually fed to the reactor; the only other water entering the reactor is the filter-wash water. A large quantity of heat of reaction is generated in the reactor and must be removed. In modern plants, this is accomplished by vacuum-flash-cooling a part of the slurry and returning it to the reactor (as in the GFC unit, see Figure 7).

The reaction slurry is maintained within the reactor for up to 8 hours before being sent to the filter. The most common filter design is the rotary, horizontal, tilting-pan vacuum filter--a series of individual filter cells mounted on a revolving annular frame. Product slurry from the reactor is introduced into a filter cell and vacuum is applied. After a dewatering period, the filter cake undergoes two- or three-stages of washing with progressively weaker solutions of H_3PO_4. Washwater flow is countercurrent to the rotation of the filter cake with heated, fresh water, or barometric condenser water, used for the last wash; filtrate from this step is used as the washing liquor for the preceding stage, and so on. After the last washing, the cell is subjected to a cake dewatering step and then inverted to discharge the gypsum. Cleaning of the filter media commences at this time and the cell is returned to its upright position to begin a new cycle.

The 32 percent P_2O_5 acid thus obtained from the filter generally is concentrated to 54 percent in a two- or three-stage vacuum evaporation system. In the evaporator, provision is normally made for recovery of fluoride as fluosilicic acid. Inclusion of this recovery feature is dependent on economics and environmental concerns.

Phosphoric Acid Observations. Phosphate rock, pre-ground at the mine, is further milled to reduce coarseness. Emissions of SO_2 and dust with radioactivity (Ra-226) occur during drying, grinding, and transport of phosphate rock. Heavy dust generation from the dry grinding operation was apparent. No controls were observed. Since operation of the Chemie-Linz aluminum fluoride (AlF_3) recovery unit was terminated, no SiF_4/HF recovery currently exists, resulting in uncontrolled SiF_4/HF emissions from the digester/acidulator, hot well, pan filters, sump, filtrate tank, and H_3PO_4 product storage tanks. The P_2O_5 content of the final H_3PO_4 ranges from 45-50 percent. Fluoride in the product H_3PO_4 ranges from 2.5-3.5 percent, which is quite high compared to that found in typical WPPA and averages 0.9 percent. Even the weak acid stream contains 1.25-1.85 percent F^-. (See Section I. D. Emission Control Methods, pp. 46-47; pp. 49-52; and pp. 90-93.

Table 7. Phosphate Rock Analyses.

% Composition	Eastern A or B	Khnefis Mine
P_2O_5	min 29	min 31.35
CaO	47-51	48
SiO_2	3-8	3.25
F	2-4	3
Cl	0.15-0.25	0.2
Fe_2O_3	0.1 -0.6	0.35
MgO	0.2 -0.5	0.35
Calcination loss	7.5 -11	max 10
Moisture	max 2	max 2
Granular size, mm	0 -3	0-2
>2 mm, %	max 5	max 3

Eastern A or B for H_3PO_4; Khnefis for GTSP

This high F^- content of the product should be ample reason for F^- control within the process--to produce a higher quality product. Moreover, no particulate control systems are currently utilized to reduce dust generation within or outside the H_3PO_4 unit. Phos gypsum is no longer transported to the slime pond near the lake. This solid waste is now taken by truck to a disposal area 40 km away on the road to Damascus. It is unknown whether proper control measures are in existence at this site. For proper disposal and management practices, see Section III. B. Disposal Methods, pp. 87-94; and Storage Piles, pp. 56-59.

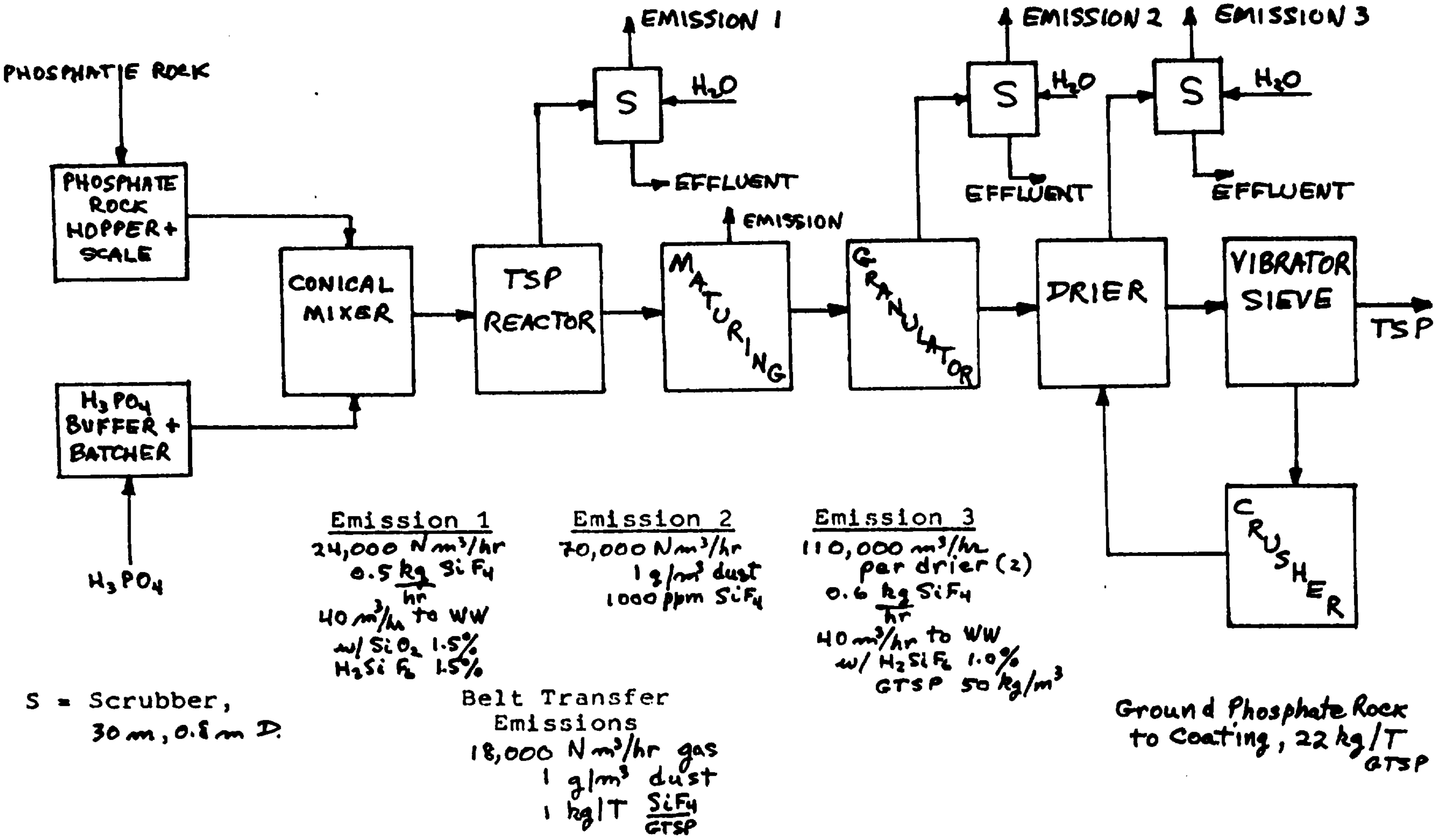
Phosphoric Acid Air Emission Standards. Emission standards for wet process phosphoric acid production are designed primarily to control uncontrolled emissions of F^-, which are limited to 10 g F^-/T of P_2O_5 equivalent input feed and is considered to be quite stringent to account for the seriousness of potential health and environmental effects of uncontrolled F^- emissions.

Triple Superphosphate Process. The Triple Superphosphate (TSP) unit (3 x 500 T/d) was visited on 24 June 1989. A simplified flow diagram is shown in Fig. 8. TSP is a high analysis phosphate fertilizer containing 46.0-48.5 percent P_2O_5. It therefore provides transportation economy and can be most economically produced close to the phosphate rock source. Granular TSP (GTSP) is a hard, uniform, pelletized granule produced in process equipment that normally permits ready collection and treatment of dust and fumes. H_3PO_4 (45-50 percent P_2O_5) and milled phosphate rock (70 percent on 50 µ sieve) are mixed together in a stirred reactor:

$$Ca_{10}(PO_4)_6F_2 \quad + \quad 14\ H_3PO_4 \quad + \quad H_2O \longrightarrow$$
$$10\ CaH_4(PO_4)_2 \cdot H_2O \quad + \quad 2\ HF$$

(Actually three reactors are used: Charges amount to approximately 100 T H_3PO_4 and 100 T phosphate rock every 8-hours, which produces about 200 T of TSP in 8-hours.) The reaction slurry then flows to a maturation tank where it is held for 4-6 days before being discharged to a series of 12 rotating-disc granulators, which produce each about 12 T/hr of GTSP. The next step is a coating operation that involves the addition of milled phosphate rock at the rate of 22 kg/T P_2O_5, followed by drying to further the chemical reaction and screening before returning the product GTSP to the phosphate rock storage shed for final maturation prior to bagging and shipping. The GTSP so produced contains approximately 45 percent available P_2O_5.

Triple Superphosphate Observations. Major uncontrolled emissions of milled phosphate rock dust and product GTSP noted in storage shed (this will include F^- emissions also). If scrubbers



Emission 1
24,000 Nm^3/hr
0.5 $\frac{kg}{hr}$ SiF_4
40 m^3/hr to WW
w/ SiO_2 1.5%
H_2SiF_6 1.5%

Emission 2
70,000 Nm^3/hr
1 g/m^3 dust
1000 ppm SiF_4

Emission 3
110,000 m^3/hr
per drier (2)
0.6 $\frac{kg}{hr}$ SiF_4
40 m^3/hr to WW
w/ H_2SiF_6 1.0%
GTSP 50 kg/m^3

S = Scrubber,
30 m, 0.8 m D.

Belt Transfer
Emissions
18,000 Nm^3/hr gas
1 g/m^3 dust
1 kg/T $\frac{SiF_4}{GTSP}$

Ground Phosphate Rock
to Coating, 22 kg/T_{GTSP}

Figure 8. Process Flowsheet for GTSP Production.

from the one operational reactor were functional, it was not apparent.[8] Maturation time of 4-6 days appears too lengthy compared to other similar processes employed elsewhere. Only three of 12 rotating, granulator discs functional--all disc units covered with thick layers of fine GTSP dust; large clumps (10-25 cm) of GTSP observed within and near the disc units. No dust controls evident. The AlF_3 recovery unit was shut down due to severe corrosion of pumps and silica buildup; hence, no removal of SiF_4/HF presently exists at the plant. Again, the dust also contains radioactive Ra-226 and the air possibly some low levels of decay products or progeny such as radon gas. (See Section I. Fluoride Emissions and Control Techniques, pp. 40-46; Section II. B., pp. 64-75; Section III. A., pp. 83-87 and Section IV, pp. 94-9.

Granular Triple Superphosphate Air Emission Standards. Fluoride emission guidelines for existing GTSP facilities allow up to 100 g F^-/T P_2O_5 input feed and for GTSP storage facilities, 0.00025 g F^-/hr-kg P_2O_5 in storage. Again, these are very stringent standards that recognize the potential health hazards and environmental consequences of contamination that could ensue from uncontrolled emissions of F^-.

D. Emission Control Methods[9]

In this section, several examples will be given that describe control methods and technologies for emissions including physical, chemical, and process changes to reduce product loss. Specific applications to the fertilizer manufacturing industry will be detailed.

Fluoride Emissions and Control Techniques. Gaseous fluorides emitted from phosphate fertilizer processes are primarily SiF_4 and HF, their origin being the digestion of fluorapatite with H_2SO_4 to produce H_3PO_4 and H_2SiF_6, fluosilicic acid. Under existing conditions of temperature and acidity, excess H_2SiF_6 decomposes as follows:

$$H_2SiF_6(l) \longrightarrow SiF_4(g) + 2\,HF(g)$$

At high levels of excess SiO_2, HF evolved will react to form SiF_4 according to:

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O$$

At low levels of SiO_2, emissions will be rich in HF. Not all of the fluorides are emitted during the digestion of phosphate rock. A certain amount is retained in the product H_3PO_4 depending on the rock type treated and the processes used. Scrubbing with water is an effective fluoride control technique because of the high water solubility of most gaseous fluorides. This straightforward approach is somewhat complicated, however, by the presence of SiF_4. SiF_4 will react with water to form hydrated silica and fluosilicic acid:

$$3\ SiF_4 + 4\ H_2O \longrightarrow 2\ H_2SiF_6 + Si(OH)_4$$

$Si(OH)_4$ precipitates forming deposits on control equipment surfaces that plug passageways and tend to absorb additional SiF_4. The nature of the precipitate, in the presence of HF, is temperature dependent: Below 52°C, the precipitate is in the form of a gel; above 52°C, it is a solid. Entrainment of scrubbing solutions must be kept to a minimum to prevent the escape of absorbed fluorides.

Fluoride emissions from WPPA manufacture are gaseous SiF_4 and HF. The reactor is the major source of fluoride emissions from the process accounting for as much as 90 percent of the fluorides from an uncontrolled plant. Additional sources include the filter, the filtrate feed and seal tanks, the flash cooler seal tank, the evaporator system hotwell, and the H_3PO_4 storage tanks. Table 8 lists reported emission factors for various sources.

Table 8. Fluoride Emissions from an Uncontrolled WPPA Unit.

Source	Emission Factor (kg/T P_2O_5)
Reactor	0.016-0.91
Filter	0.004-0.025
Miscellaneous (filtrate feed and seal tanks, hotwells, etc.)	up to 0.11

To prevent an excessive temperature rise in the reactor, the heat of reaction is removed by cycling a portion of the reaction slurry through a vacuum flash cooler. Vapors from the cooler are condensed in a barometric condenser and sent to a hotwell, whereas the noncondensibles are removed by a steam ejector and also vented to the hot well (see Fig. 7). The majority of the fluorides evolved in the flash cooler are absorbed by the cooling water in the barometric condenser. If air cooling is utilized, fluoride evolution can be considerably greater than indicated in Table 8.

The filter is the second largest source of emissions. Most of the fluorides are evolved at the points where the feed acid and wash liquor are introduced to the filter. These locations should be hooded and vented to the digester scrubber. A third source of fluoride emissions is the evaporator used to concentrate the H_3PO_4 from 30 to 54 percent P_2O_5. It is estimated that 20-40 percent of the fluorine originally introduced into the process with the phosphate rock is vaporized during this operation. Most of these fluorides are collected in the system's barometric condensers. The remainder exist with the noncondensibles and are sent to the hot well, which then becomes the emission source for this operation. As shown in Fig. 7, the vapor stream from the evaporator is scrubbed with a 15-25 percent solution of fluosilicic acid at a temperature at which water vapor, which would dilute the solution, is not condensed. The water vapor is then removed by a barometric condenser before the noncondensibles are ejected from the system. All of the fluoride is recovered as byproduct H_2SiF_6.

Several additional minor sources of fluorides also exist: Sumps, clarifiers, and acid tanks. Collectively, these sources can be significant and should be ducted to a scrubber.

Table 9 illustrates a typical material balance for the fluorine originally present in phosphate rock. Fluorine distribution varies and will depend on the type (and source) of rock treated, process used, and operation employed.

Most WPPA plants constructed since the 1970s have installed the spray-crossflow packed-bed scrubber (see Fig. 9) as part of the original design. Improvements in this scrubber have alleviated the initial problem of plugging and allow a greater solids

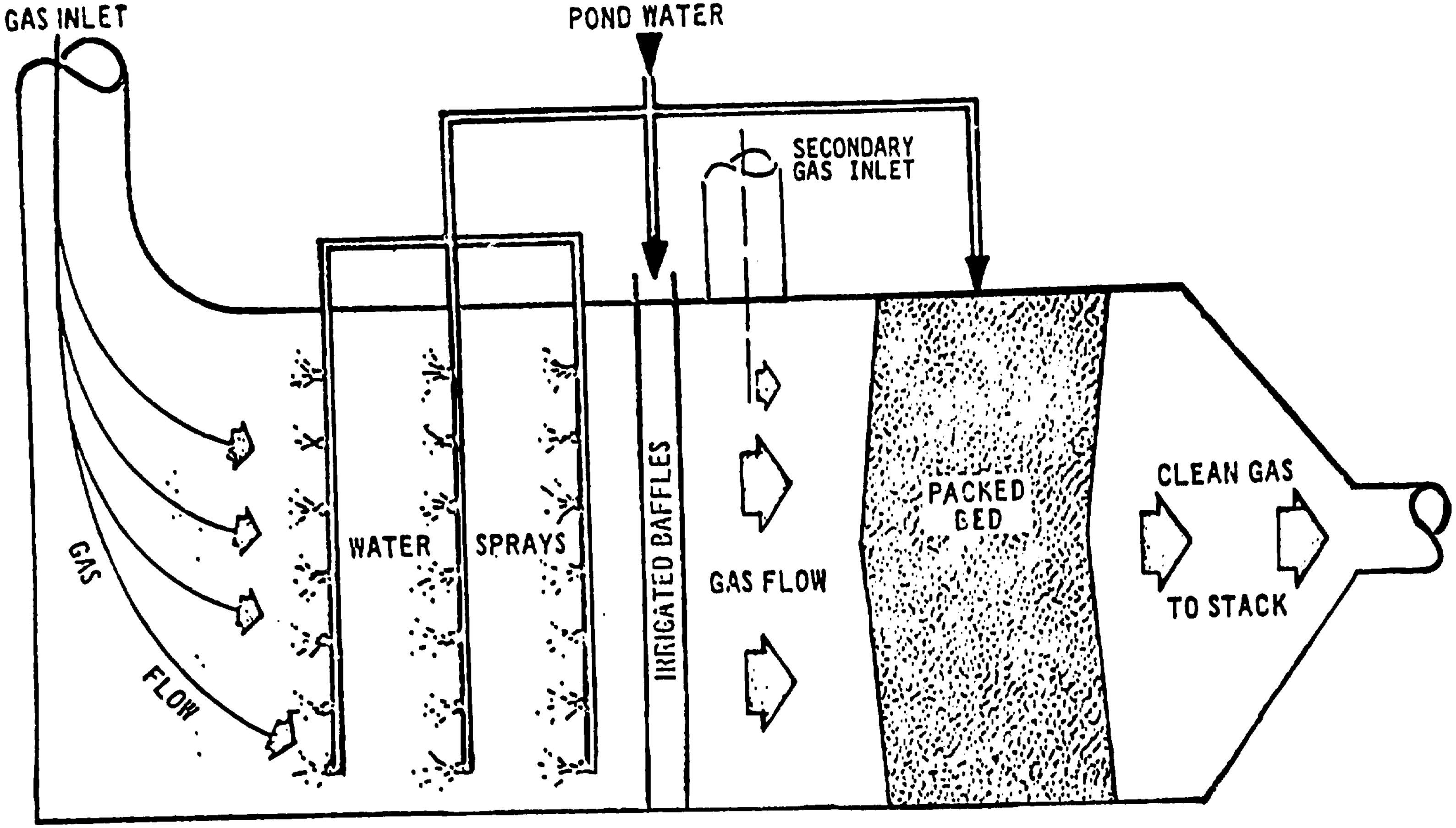


Figure 9. Spray-Crossflow Packed-Bed Scrubber.

handling capacity. It consists of two sections--a spray chamber and a packed bed--separated by a series of irrigated baffles. Scrubber size depends primarily on the volume of gas treated. A typical unit, capable of treatment of effluent streams from a WPPA plant (560 m^3/min), is 2.75 m wide, 3 m high, and 9 m long.

Table 9. Typical Material Balance of Fluorine in the Manufacture of WPPA

BASIS: 1000 kg (1 Ton) Phosphate Rock

Fluoride-bearing Material or Source		Fluoride, kg
Phosphate rock		39
Product H_3PO_4		10
Gypsum		12
Barometric condensers		16.7
Air		0.3
	Total F^-	39

All internal parts of the scrubber are constructed of corrosion-resistant plastics or rubber-lined steel. Teflon can be used for high temperature service. General maintenance consists of replacement of the packing once or twice each year. Expected life of the scrubber is 20 years.

Both the spray and the packed section are equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations--particularly those rich in SiF_4--are treated in the spray chamber before entering the packing. This preliminary scrubbing removes SiF_4 thereby reducing the danger of plugging the bed. Concurrently, it reduces the loading on the packed stage and provides some degree of solids handling capacity. Gases low in SiF_4 can be introduced directly to the packed section.

The spray section accounts for approximately 40-50 percent of the total length of the scrubber. It comprises a series of countercurrent spray manifolds with each pair followed by a system of irrigated baffles, which remove precipitated silica and prevent the formation of scale deposits in the spray chamber. Packed beds of both cocurrent and crossflow design have been tested with the crossflow design proving to be the more dependable. The crossflow design operates with the gas stream moving horizontally through the bed, whereas the scrubbing liquid flows vertically through the packing. Solids tend to deposit near the front of the bed where they can be washed off by a cleaning spray. This design also allows the use of a higher irrigation rate at the front end of the bed to aid in solids removal. The rear portion of the bed is usually operated dry to provide mist elimination.

The bed is seldom more than 1-1.2 meters in length, but this can be increased if necessary with little change in capital or operating cost. Several types of ceramic and polyethylene packing are in use with Tellerettes probably the most common. Pressure loss through the scrubber ranges from 2.5 to 20 cm H_2O with 10-15 cm being average.

Recycled gypsum pond water (see Section II) is normally employed as the scrubbing liquid in both the spray and packed sections. Filters are located in the water lines ahead of the spray nozzles to prevent plugging by suspended solids. The ratio of scrubbing liquid to gas ranges from 0.00015-0.00052 liters per min/Nm^3 per min (0.02-0.07 gpm/acfm), depending on the fluoride content--particularly the SiF_4 content--of the gas stream. Approximately one-third of this water is used in the spray section, whereas the remaining two-thirds is used in the packing.

The packed bed is designed for a scrubbing liquid inlet pressure of about 1.27-1.34 atm (4-5 psig). Water at this pressure is available from the pond water recycle system. The spray section requires an inlet pressure of 2.36-3.04 atm (20-30 psig). This normally necessitates the use of a booster pump. Spent scrubber water is collected in a sump at the bottom of the scrubber and pumped to the gypsum pond.

Process Changes--Wet-Rock Grinding for Phosphate Rock. Particulates in the form of dust result from the drying and grinding of phosphate rock and often escape if drier gases are uncontrolled, as well as during grinding, especially when the materials are very dry. Hence, dust can be a significant problem at each point of transfer of the materials. The size of the dry, ground phosphate rock particle is less than 0.07 mm. The world's primary phosphate occurrences are of sedimentary origin and contain radioactive materials, predominantly uranium and its decay products. Uranium, along with a very small amount of thorium, is thought to have been deposited contemporaneously with the phosphate. It is a fact that the phosphate industry currently mines more total uranium than does the uranium industry.

Under the Environmental Impact Statement for the Central Florida Phosphate Industry, the proposed action will eliminate rock drying. This will result in a decrease in SO_2 and dust emissions in Polk County, Florida, caused by drying, grinding, and transportation as mines in that county are depleted and new mines open elsewhere. Since the new mines will ship wet rock, an estimated 1140 T/y of dust and 7090 T/y of SO_2 emissions from driers in Polk County will not migrate into adjoining areas. The emissions from existing rock drying will decrease as the driers are phased out.

Reduction in radiation levels will occur as dry-rock grinding is replaced with wet-rock grinding and driers are eliminated. This will lower fugitive dust levels and result in a commensurate decrease in escaping radionuclides, and also reduce radiation levels in the immediate vicinity of the grinders and the eliminated driers.

Wet-rock grinding has four inherent advantages:

- Reduces by about half the capital expense--from receipt of underground wet-rock through the point of feeding it into the acid processing system

- Eliminates dry-rock dust pollution
- Improves fuel economy by 24 liters/T of phosphate rock ground, which combines with electrical power savings to reduce operating costs per ton of P_2O_5
- Improves reliability, therefore, reducing the required amount of surge of ground rock. If a plant is located near a phosphate mine, a rock slurry can be pumped directly to the plant from the mine eliminating rail or truck transportation and belt conveyors

<u>Process Changes--Simplot Limestone Treatment for GTSP</u>. In the Simplot process, when H_3PO_4 in WPPA reacts with limestone ($CaCO_3$) to make GTSP, fluorides are present only in the WPPA. Hence, the only fluorides that might be emitted are the residual fluorides (H_2SiF_6 or SiF_4 and HF) in the WPPA:

$$2\ H_3PO_4 + CaCO_3 \longrightarrow CaH_4(PO_4)_2 \cdot H_2O + CO_2$$

The product contains 45-50 percent available P_2O_5. In the old GTSP process, the fluorides present comprise both the native fluorapatite fluoride content and the WPPA residual fluorides. It is therefore logical that the Simplot process would emit much less fluoride (uncontrolled) that the old GTSP process for each mole of monocalcium phosphate ($CaH_4(PO_4)_2 \cdot H_2O$) in the GTSP produced. However, the phosphate content of each monocalcium phosphate molecule, produced in either process, is derived ultimately from fluorapatite. Therefore, the emittable fluorides from the total processing of fluorapatite to make one mole of $CaH_4(PO_4)_2 \cdot H_2O$ is the same regardless of whether the old process or the Simplot process is employed. Potential fluoride emissions from the Simplot process are lower only in the absence of the WPPA plant.

This process provides a means of reducing local fluoride emissions at the plant where it is applied. <u>Fluorapatite is not used as a feedstock</u>, so this fluoride source is eliminated. Excess $CaCO_3$ can be fed also to precipitate the fluoride in the

WPPA as insoluble calcium fluoride (CaF_2). In contrast, the WPPA process emits more fluorides, which require more scrubbing water and therefore larger gypsum pond areas. The amount and complexity of emission control equipment are reduced by the Simplot process. The firm has found that the only gas cleaning devices necessary are a scrubber on a drier and conventional baghouses on the other system components such as screens and elevators.

Results of recent New Source Performance Standards (NSPS) compliance testing at the Simplot plant in Idaho showed average emissions of 0.085 kg F^-/T P_2O_5 fed. The requirement for NSPS compliance in GTSP production is 0.09 kg F^-/T P_2O_5 fed.

Process Changes--Hemihydrate Process for WPPA. It appears that solutions to three WPPA production problems are possible through use of the two-stage hemihydrate (hemidihydrate or HDH) process:(1) Energy comsumption; (2) gypsum removal; and (3) fluoride emissions. Energy consumption is reduced by avoiding the need for evaporative concentration of product acid. The gypsum produced is reported to be of sufficient purity for use in building material (wall board)*. Gypsum from conventional dihydrate processes cannot be used because of its level of radioactivity. Fluoride emissions are controlled by recovery reported to be greater than 99 percent in a co-installed, on-line system. The recovered fluoride may be concentrated to 20-24 percent H_2SiF_6.

Capital cost savings are reported for the HDH process compared to the dihydrate process in rock grinding, steam used for acid concentration, weak acid intermediate storage, and product acid clarification. These savings are partially offset by a larger reaction volume filter area requirement. The capital cost for recrystallization and dihydrate filtration approximately equals that for acid concentration in dihydrate processes. An overall

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[*] Blumrich, W.E., Koening, H.J. and Schwehr, E.W. (1978). The Fisons HDH Phosphoric Acid Process. Chem. Engr. Prog., 74, 58-61, November.

5-10 percent capital cost reduction for the HDH process, compared to the dihydrate process, is reported. Operating costs are also reported lower, mainly because of P_2O_5 recovery exceeding 98 percent and low steam consumption. In the HDH process, recrystallization depends largely on phosphate rock composition. Morocco rock is used at the Trepco, Yugoslavia, plant (Lurgi Chemie and Huettentechnik GmbH) and the Whitehaven, UK, plant (Albright & Wilson) is designed for use with either Morocco or Florida rock. HDH plants are also in commercial use in Japan.

Fabric Filters for Ammonium Nitrate and Urea. Fabric filters or baghouses are high efficiency collection devices used quite extensively in the NH_4NO_3 and urea industries for control in bagging and coating operations. An average removal efficiency for a fabric filter is 99 percent. A typical fabric filter system is shown in Fig. 10. Design variables for baghouses include method of cleaning, choice of fabric, size of the unit, air-to-cloth ratio, and whether the baghouse is a pressure or suction unit. In the type of design shown, the airstream enters the baghouse and is pulled up into fabric sleeves located throughout the baghouse. The air pulled through these fabric sleeves is exhausted to the atmosphere, whereas dust remains trapped within the weave of the fabric, forming a layer of dust on the bag. The pressure drop through the bag increases as this dust layer builds up. The dust eventually is removed from the bag by one of several bag cleaning methods.

Two methods of cleaning are shaking or rapping and reversing the airflow through the bag by air jets or pulses. Shaking consists of manually or automatically shaking the bag hangers or rapping the side of the baghouse to free the dust from the bags and into a receiving hopper below. In the jet pulse method, compressed air is released at regular intervals into a group of bags, causing the bags to pulse and the dust to be released. Cleaning can be either continuous or intermittent. Intermittent cleaning consists of shutting down the baghouse when it reaches its

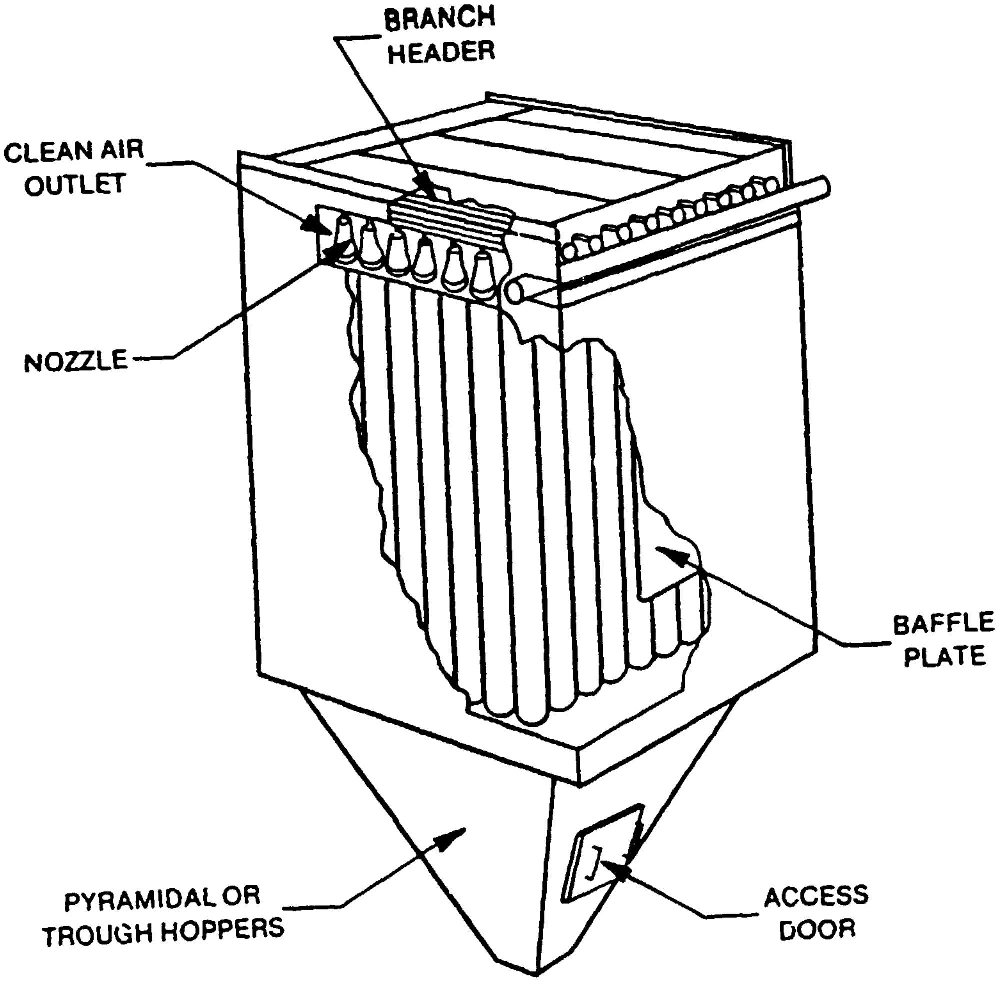


Figure 10. Fabric Filter (Baghouse).

highest design pressure drop. For continuous cleaning, individual bags are cleaned at regular time intervals.

An important operating principle for fabric filters is that effective filtration of the dusty airstream is accomplished, not only by the fabric, but also by the dust layer that forms on the fabric. This dust layer bridges the gaps between adjacent fibers and increases the opportunities for impaction and interception of small particles. For this reason, too frequent cleaning can actually decrease efficiency by not allowing a dust layer to accumulate between cleaning cycles. The urea dust layer can cause problems in urea plant applications due to the hygroscopic nature of urea particulate. The dust layer can absorb moisture from the air and cause the formation of a sticky cake. This cake increases the pressure drop and can cause difficulties in cleaning. For this reason, use of baghouses in urea plants is currently limited to process airstreams with low moisture contents, such as bagging operations. Therefore, with the exception of bagging operations, urea emission sources are typically controlled with wet scrubbers. The preference toward scrubbing systems as opposed to dry collection systems is primarily due to the ease of recycling dissolved urea collected in the device. Scrubber liquors are recycled back to the solution concentration process, eliminating potential waste disposal problems and recovering the urea collected. (See Wetted Fibrous Filter Scrubber for additional information.)

Materials available for bag construction are numerous. They include cotton, Teflon, fiberglass, orlon, nylon, dacron and wool. The type of material selected depends on many factors, including temperature, frequency of cleaning, ease of particle removal, resistance to chemical attack, and abrasion characteristics of the collected particles. Factors affecting baghouse performance include air-to-cloth ratio, type of fabric used, method and interval of cleaning, pressure drop, and the properties of the exhaust being cleaned. Air-to-cloth ratio, defined as $A/C = Q_{ESA}/A_{NC}$, where Q_{ESA} is the emission stream flow rate at actual conditions in Nm^3/m and A_{NC} is the net cloth area in m^2, is dimensionally equivalent to a velocity in m/min and it indicates the average face velocity of the gas stream through the effective area of the fabric. An excessive A/C ratio results in excessive loss, reduced collection efficiency, rapid bag blinding, and increase wear on the fabric. Too low an A/C ratio results in an oversize unit and can also reduce collection efficiency since an adequate filtering dust layer may not be allowed to accumulate between cleaning cycles. Table 10 lists some recommended A/C ratios for various dust and fumes as a function of cleaning method. Pressure drops in baghouses depend on a variety of factors including the A/C ratio, fabric type, and cleaning cycle. Pressure drops typically increase between cleaning cycles as the dust layer builds. Pressure drops from 0.5-2 kPa are common for many applications.

Table 10. Recommended Air-to-Cloth Ratios for Various Dusts and Fumes by Cleaning Method

Dust or Fume	A/C Ratios Recommended for Cleaning Method (m/min)		
	Shaker	Reverse Air	Pulse Jet
Abrasives	0.6 - 0.9	•	2.7
Fertilizer	0.6 - 1.1	0.5 - 0.6	2.4 - 3.0
Gypsum	0.6 - 1.1	0.5 - 0.6	3.0 - 4.9
Limestone	0.6 - 1.0	•	2.4 - 3.7
Metal fumes	0.5	0.5 - 0.6	1.8 - 2.7
Silica	0.7 - 0.9	0.4 - 0.5	2.1 - 3.7

• No information available

A/C ratios range from 0.6 to 3.0 m/min with 0.9 m/min being the typical ratio reported for the urea industry.

Wet-Scrubbing--Wetted Fibrous Filter Scrubbers. A wet scrubber is a device in which a particle-laden gas stream is brought into intimate contact with a liquid for the purpose of transferring particulates from the gas to the liquid stream. The wetted fibrous filter scrubber is coming more into practice and is discussed here in more detail. It is typically used in conjunction with a collection hood, but it can also be used to control the entire exhaust flow. The scrubber consists of two series of filter elements separated by an atomizing spray chamber (see Fig. 11). Each filter drum or element, made of compressed glass fibers (fiberglass) is irrigated to remove captured particles by rotation through a shallow liquor bath. The exhaust stream first encounters a set of elements of relatively low fiber density, designated "spray catcher" elements. These elements collect the large, insoluble particulates (>3 µ) that may clog the second set of filter elements. It appears that the dominant collection mechanism for these elements is inertial impaction. The pressure drop across the "spray catcher" elements ranges from 0.25-0.50 kPa.

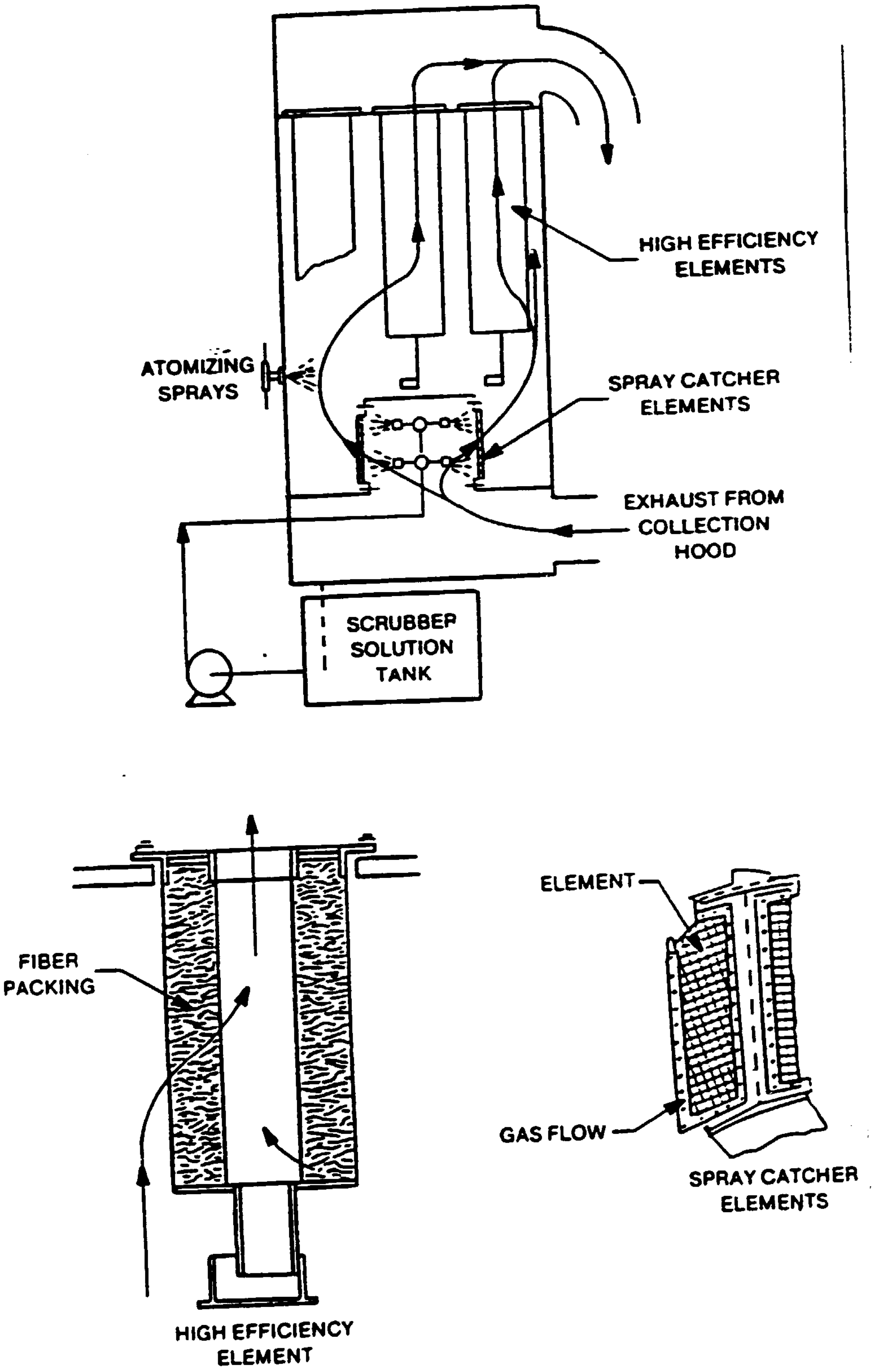


Figure 11. Detail of a Wetted, Fibrous Filter Scrubber

The remaining particulates in the gas stream flow into the spray chamber where some of them impinge on the water droplets, which are then removed from the gas stream by the second set of filter elements that are designed as high efficiency elements. These high efficiency elements contain fibers that are compressed to a greater density that the "spray catcher" elements. The pressure drop across these elements is about 1-5 kPa for prill tower applications. The dominant collection mechanism for these elements is Brownian movement of the particles, which causes the particles to collide with the dense glass fiber mat (for prill tower control, a Teflon mat is used) where they are collected. A collection efficiency is reported for particles less than 3 µ in diameter, as well as 100 percent collection efficiency for particles larger than 3 µ.

The design of the wetted fibrous filter allows the pressure drop to be adjusted readily while the scrubber is in operation. This adjustment is possible through the use of a moving, semi-cylindrical baffle plate that may be used to cover a fraction of the filtration drum. By covering a portion of the drum face, the airflow is forced to travel through a smaller area on the drum, which increases face velocities. These higher velocities result in greater impingement of particulates on the filter mat and increase removal efficiency at the expense of higher pressure drop. The baffle may also be used to hold the pressure drop constant at various airflows through the scrubber. This feature allows collection efficiencies to be maintained while producing different grades of product that require different airflows.

Table 11 delineates control equipment performance parameters from urea prill tower, granulator, and cooler emission sources.

Fugitive Emissions Control. Process fugitive emissions can be defined as emissions from a process or piece of equipment that are being emitted at locations other than the main vent or process stack. Process fugitive emissions include fumes or

Table 11. Emissions Control Equipment Effectiveness in Urea Manufacturing Facilities

			Performance Parameters		
Emission Source	Control Option	Control Device	Removal Efficiency (%)	Pressure Drop (kPa)	Liquid/Gas Ratio (l/m^3)
Prill tower	ELOC	Spray tower	a	a	0.40
	Option-1	Entrainment scrubber	85	1.3	0.87
	Option-2	Wetted fibrous filter	98	3.1	0.27
Granulator	ELOC	Entrainment scrubber	99.9	4.1	0.87
Cooler	ELOC	Plate impingement (tray type) scrubber	98	1.3	0.40

[a] Removal efficiency and pressure drop vary according to the specific Model Plant selected for analysis.

ELOC = Existing Level of Control (see Section B: Urea Process--Urea Air Emission Standards).

Table 12. Currently Employed Control Methods for Various Inorganic Vapors

	Absorption		Adsorption	
Inorganic Vapor	Removal Efficiency %	Solvent	Removal Efficiency %	Adsorbent
Hg	95	brine, hypochlorite solution	90	sulfur-impregnated activated carbon
HCl	95	water	-	-
H_2S	98	Na_2CO_3/water	100	NH_3-impregnated activated carbon
CaF_2	95	water	-	-
SiF_4	95	water	-	-
HF	85-95	water	99	calcined alumina
HBr	99.95	water	-	-
$TiCl_4$	99	water	-	-
Cl_2	90	*alkali solution*	-	-
HCN	-	-	90	NH_3-impregnated activated carb.

gases that escape from or through ports and feed and/or discharge openings to a process. Examples include the open top of a vapor degreaser, the slag or metal tap opening on a blast furnace, and the feed chute on a ball mill. Process fugitive emissions sources include vent fans from rooms or enclosures containing an emissions source. Other examples include cooling towers or process drains.

These sources can be controlled by add-on control devices once the emissions from the sources are captured by hooding, enclosures, or closed vent systems and then transferred to a control device. Because of the nature of the opening (for example, for access or maintenance), sometimes the opening through which emissions escape cannot be totally enclosed or banked off. Operators have to access the equipment or materials have to be fed or discharged from the process. For this reason, hoods or partial enclosures are used to control emissions from such openings. Table 12 (previous page) lists current control methods for several inorganic vapors.

Fugitive emissions of organic vapors occur in plants processing organic liquids and gases, such as petroleum refineries, chemical and fertilizer plants, and plants producing chemically-based products such as plastics, dyes, and drugs. One group of emission sources found in plants of this type is referred to as equipment leaks. Fugitive emissions of this type result from incomplete sealing of equipment at the point of interface of process fluid with the environment. Control techniques for such leaks include leak detection and repair programs and equipment installation or configuration. Control techniques and control efficiencies for common types of processing equipment are summarized in Table 13.

Storage Piles--Wind Erosion and Dust Control Methods. Most dust arises from stockpile areas as the material is dumped from the conveyor or chute onto the pile, and as bulldozers move the pile. During periods with high wind speeds (greater than 5.3 m/sec) or

Table 13. Control Effectiveness of Control Methods for Organic Area Fugitive Emissions

Emission Source	Control Technique Equipment Modification	Control Effectiveness %
Pumps	Monthly leak detection and repair	61
	Sealless pumps	100
	Dual mechanical seals	100
	Closed vent system[a]	100
Valves		
- gas	Monthly leak detection and repair	73
	Diaphragm valves	100
- light liquid	Monthly leak detection and repair	46
	Diaphragm valves	100
Pressure relief valves	Rupture disk	100
	Closed vent system[a]	100
Open-ended lines	Caps, plugs, blinds	100
Compressors	Mechanical seals with venting degassing reservoirs	100
	Closed vent system[a]	100
Sampling connections	Closed purge sampling	100

[a] Closed vent systems are used to collect and transfer the fugitive emissions to add-on control systems such as flares, incinerators, or vapor recovery systems.

low moisture, wind erosion of a nonweathered surface may also cause serious emissions and loss of feedstock or product or both (including gypsum piles). Wind erosion of exposed areas or piles occurs in the following ways: soil transport by surface creep, saltation, and suspension. Wind erosion is usually an intermittent activity that occurs above a threshold wind velocity as indicated above. The following emission factor equation is the most commonly used for estimating erosion from storage piles:

$$E = 1.9 \times \frac{S}{1.5} \times \frac{365 - P}{235} \times \frac{f}{15}$$

where E = total suspended particulate emission factor, kg/day-hectare

S = silt content of aggregate, %

P = number of days/year with ≥ 0.025 cm of rain

f = percent of time that the unobstructed windspeed exceeds 5.3 m/sec at the mean pile height

The premise of the equation is that wind erosion emissions vary with soil particle size, moisture, and windspeed.

Control systems function in one of two ways: by reducing windspeed on the soil surface, or by forming a new, less-erodible soil surface. The following methods are used to reduce windspeed at the soil surface:

- Covering the pile with a wind-impervious fabric or vinyl
- Erecting a windscreen
- Pile orientation and silhouette (pile shape)

Methods for forming a new, less-erodible surface include:

- Water spraying to compact and weight soil particles
- Application of chemical dust suppressants to form a crust over the existing soil or to bind the upper soil particles
- Establishment of a vegetative cover. Roots bind soil together and stems reduce windspeed at the surface.

Products for dust control of exposed areas and undisturbed storage piles are identical. Product categories are as follows:

- Liners and geotextiles that are impermeable to liquids
- Windscreens that decrease windspeed on the downwind or leeward side
- Spray systems that spray foam every few hours to cover or moisten the soil
- Application of liquid chemicals to form a soil admixture. These products, which are sprayed on every few weeks, include bitumens, adhesives, salts, or binders with grass seed.

Applicable control techniques for open storage piles are presented in Table 14.

Table 14. Control Technology Applications for Open Storage Piles

Emission Points	Control Procedure	Efficiency %
Loading onto piles	Enclosure	70-90
	Chemical wetting agents or foam	80-90
	Adjustable chutes	75
Movement of pile	Enclosure	95-99
	Chemical wetting agents	90
	Traveling booms to distribute material	(no estimate)
Wind erosion	Enclosure	95-99
	Wind screens	$\leq$ 70
	Chemical wetting agents or foams	90
	Screening of material prior to storage, with fines sent directly to processing or to a storage silo	(no estimate)
Loadout	Water spraying	50
	Gravity feed or to conveyor	80
	Stacker/reclaimer	25-50

Acid Gases Reduction--An Example of Environmental Control. GFC complex air quality data obtained in 1982 demonstrate the signicicance of the effect of the adjacent power plant's SO_2 emissions. Air quality improves dramatically during periods of power plant shutdown. Data recently obtained (on 26 June 1989) from power plant officials shows that the four units have a fossil fuel combustion capacity of 799 T/d with the fossil fuel currently supplied from the Homs refinery containing about 5 percent sulfur. If all four units were operational, the daily fuel combusted would contain about 40 tons of sulfur or 20 tons of sulfur at 50 percent capacity. Repowering and retrofitting this power plant with an innovative, clean fossil fuel technology (a fuel oil treatment technology to remove and recover elemental sulfur) has the potential for significantly reducing SO_2 (and NO_x)(along with ozone formation) emissions in the region. Any reductions in such emissions would diminish the potential exposure and possible damage to terrestrial ecosystems from acidic deposition, not to mention corrosive effects on GFC manufacturing equipment, buildings, piping, and most importantly, employees.

The advanced fossil fuel cleaning technologies can be characterized by physical and chemical removal operations and processes. Generally, 40-70 percent of the total sulfur can be removed by advanced physical cleaning. Chemical cleaning processes are able to remove over 90 percent of the total sulfur from certain feedstocks.

What is further proposed is the removal and recovery of a significant portion of the total sulfur content of the fossil fuel and the reuse of this elemental sulfur as feedstock in GFC's H_2SO_4 unit. Currently, the H_2SO_4 unit uses 168 T/d of S, with one line operational. If up to 20 tons of S were covered and transported for use in the H_2SO_4 unit, at its present capacity, this would reduce daily sulfur feedstock requirements by 12 percent. The savings in S-feedstock may even balance the cost to the power plant of cleaning the fossil fuel--but the environment would be the winner in the battle to reduce acidic deposition in the area. (Another alternative is to use low sulfur fossil fuel.)

II. ASSESSMENT OF ENVIRONMENTAL IMPACT ON SURFACE AND GROUNDWATER SOURCES

A. Standard Industrial Classification and Fertilizer and Phosphate Manufacturing Point Source Categories for Effluent Limitation Guidelines

This industrial manufacturing group includes establishments primarily engaged in manufacturing nitrogenous and phosphatic basic fertilizers and are broken down into two Standard Industrial Classifications: SIC No. 2873, Nitrogenous Fertilizers or establishments producing fertilizers from nitrogenous materials such as ammonia fertilizer compounds and anhydrous ammonia, nitric acid, ammonium nitrate, ammonium sulfate and nitrogen solutions, urea, and natural organic fertilizers and mixtures; and SIC No. 2874, Phosphatic Fertilizers or establishments producing phosphatic materials that include phosphoric acid; normal, enriched and concentrated superphosphates; ammonium phosphates; nitro-phosphates; and calcium meta-phosphates.

Under authority of the Clean Water Act, the Environmental Protection Agency (EPA) has promulgated Effluent Limitation Guidelines for these fertilizer categories accordingly (only those applicable to GFC's processes):

- Fertilizer Manufacturing Point Source Category
    - Subpart A--Phosphate Subcategory
    - Subpart B--Ammonia
    - Subpart C--Urea
    - Subpart D--Ammonium Nitrate
    - Subpart E--Nitric Acid
- Phosphate Manufacturing Point Source Category
    - Subpart D--Defluorinated Phosphate Rock Category

These Effluent Limitation Guidelines are presented here in order to present, for the reader's consideration, how EPA regulates pollutants in wastewaters from the fertilizer industry. The figures shown can be considered too stringent for application to the GFC complex; however, they are given here for illustrative purposes and can represent a benchmark or guide for future attainment.

The term "process wastewater" means any water that, during manufacturing or processing, comes into contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product. The term "non-process wastewater" means any water including precipitation runoff that, during manufacturing or processing comes into accidental contact with any raw material, intermediate, finished product, byproduct, or waste product by means of: (1) Precipitation runoff; (2) accidental spills; (3)

accidental leaks caused by the failure of process equipment; and (4) discharges from safety showers and related personal safety equipment. The term "calcium sulfate storage pile runoff" means the calcium sulfate transport water runoff from or through the calcium sulfate pile, and the precipitation that falls directly on the storage pile, which may be collected in a seepage ditch at the base of the outer slopes of the storage pile. The term "non-contact cooling water" means water that is used in a cooling system designed so as to maintain constant separation of the cooling medium from all contact with process chemicals, but which may on the occasion of corrosion, cooling system leakage, or similar cooling system failure contain small amounts of process chemicals. N.B.--Best Practicable Control Technology Currently Available (BPCTA) limitations are considered the least stringent of all guidelines proposed by EPA. The figures shown are not to be exceeded.

Fertilizer Point Source Category, Subpart A--Phosphate Subcategory, Calcium Sulfate Storage Piles

BPCTA Process Wastewater Limitations, mg/l	Max Daily	Monthly Average*
Total phosphorus (as P)	105	35
Fluoride (as F)	75	25
Total Suspended Solids	150	50
BPCTA Non-Process Wastewater Limitations, mg/l		
Total phosphorus (as P)	105	35
Fluoride (as F)	75	25

* Monthly average = average of daily values for 30 consecutive days.

Subpart B--Ammonia Subcategory

BPCTA Wastewater Limitations, kg/T NH_3	Max Daily	Monthly Average
Ammonia (as N)	0.1875	0.0625
pH units	6.0-9.0	6.0-9.0

Subpart C--Urea Subcategory

BPCTA Wastewater Limitations, Urea Solutions, kg/T

	Max Daily	Monthly Average
Ammonia (as N)	0.95	0.48
Organic-N	0.61	0.33

BPCTA Wastewater Limitations, Urea Prills/Granulation, kg/T Urea

	Max Daily	Monthly Average
Ammonia (as N)	1.18	0.59
Organic-N	1.48	0.80

Subpart D--Ammonium Nitrate Subcategory

BPCTA Wastewater Limitations, kg/T NH_4NO_3

	Max Daily	Monthly Average
Ammonia (as N)	0.73	0.39
Nitrate (as N)	0.67	0.37

Subpart E--Nitric Acid Subcategory

BPCTA Wastewater Limitations, Gaseous NH_3 Feed, kg/T HNO_3

	Max Daily	Monthly Average
Ammonia (as N)	0.007	0.0007
Nitrate (as N)	0.33	0.044

BPCTA Wastewater Limitations, Liquid NH_3 Feed as Shipped, kg/T HNO_3

	Max Daily	Monthly Average
Ammonia (as N)	0.08	0.008
Nitrate (as N)	0.33	0.044

Phosphate Point Source Category

Subpart D--Defluorinated Phosphate RockSubcategory

BPCTA Process Wastewater Limitations, mg/l

	Max Daily	Monthly Average
Total phosphorus	105	35
Fluoride	75	25
Total Suspended Solids	150	50
pH units	6.0-9.5	6.0-9.5

Non-process wastewaters have the same effluent limitations except the Total Suspended Solids limit is dropped.

B. Fluoride Emissions/Gypsum Pond Water Treatment Emissions Reduction. The use of gypsum pond water as the scrubbing solution complicates the task of fluoride removal regardless of the scrubber design. Gypsum pond water can be expected to contain from 0.2-1.5 percent fluosilicic acid (2,000-15,000 mg/l F^-) or typically, 5,000-6,000 mg/l F^-. Decomposition of H_2SiF_6 to SiF_4 and HF results in the formation of a vapor-liquid equilibrium that establishes a lower limit for the fluoride concentration of the gas leaving the scrubber. This limit will vary with temperature, pressure, and fluosilicic acid concentration of the water. Table 15 contains equilibrium concentrations calculated from experimentally obtained vapor pressure data at three temperatures and several fluosilicic acid concentrations.

Table 15. Equilibrium Concentrations of Fluorine in Vapor Phase over Aqueous Solutions of Fluosilicic Acid.

Fluosilicic Acid Solution Content Wt. %	Total Vapor Phase Fluorine Conc. (ppm F)		
	50°C	60°C	70°C
0.105	2.4	3.8	-
0.550	3.8	4.4	10.5
1.000	4.4	7.1	15.4
2.610	-	9.8	20.7
2.640	5.6	-	-
5.050	8.2	14.2	54.1
7.470	12.4	19.4	208.5
9.550	13.5	25.6	-
11.715	19.1	34.6	-
14.480	-	83.5	-

(ref. EPA-450/2-77-005)

Provided that the solids loading of the effluent stream has been reduced sufficiently to prevent plugging, the fluoride removal efficiency of the spray-crossflow packed-bed scrubber (see Fig. 9) is limited only by the amount of packing used and the scrubbing liquid. Efficiencies as high as 93.5 and 99.9 percent have been measured for scrubbers installed at separate WPPA plants. Table 16 lists fluoride levels reached by four WPPA plants tested by EPA. All plants used a spray-packed bed-type scrubber to control the combined emissions from the reactor, the filter, and several miscellaneous sources and were considered to represent the best controlled segment of the industry. Gypsum pond water was used as the scrubbing medium. Emission rates ranged from 0.0008-0.0062 kg F^- per ton of P_2O_5 input to the process.

Table 16. Scrubber Performance in WPPA Plants.

Plant	Scrubber Design	Fluoride Emissions (kg/T P_2O_5)
A	Spray-cocurrent packed bed	0.0062
B	same	0.0025
C*	same	0.0008, 0.0049
D	same	0.0045

* Two separate tests performed. (ref. EPA-450/3-79-038F)

Most control systems now in use utilize recycled process water (gypsum pond) as the scrubbing medium thereby eliminating the creation of additional effluent. Phosphate fertilizer plants do not need to discharge gypsum pond water continuously. The pond water is re-used in the process and a discharge is required only when there is rainfall in excess of evaporation. Hence, the volume of effluent from phosphate fertilizer plants is almost exclusively a function of rainfall conditions.

WPPA processes discharge the following wastewater streams:

- o Gypsum slurry--filter cake slurried with pond water--contains about 2.5 kg of gypsum per kg of 100 percent H_3PO_4 or 1.2 kg of gypsum per kg of 30 percent H_3PO_4
- o Wastewater from barometric condensers that treat gas from: (1) the reactor vacuum cooler, and (2) the vacuum evaporators that concentrate the WPPA. (At some plants, the gas from the WPPA evaporators can be treated for H_2SiF_6 recovery prior to entering the barometric condensers.)
- o Wastewater discharged from the scrubber that treats gases from the acidulation reactor, filters, hot wells, and

filtrate seal tanks

GTSP processes discharge streams include wastewaters from the scrubbers that treat gas from the reactor, granulator, drier, cooler, and screens.

Gypsum ponds are generally diked areas. In the past, unfortunately, they have usually not been lined to prevent seepage. The gypsum pond serves two purposes: (1) As a settling and storage area for waste gypsum, and (2) as an area for cooling process water prior to reuse. Fig. 12 is a simplified representation of a typical gypsum pond serving a 900 T/d P_2O_5 WPPA unit. This pond, handling both slurry and process water, would have about 140 hectares of wet area and a water depth of 3 m. Most likely it would be located adjacent to the WPPA facility and surrounded by mined-out land of sparse vegetation. Assuming that the pond is used for both gypsum settling and cooling, there is a region where the stream from the sluicing operation joins the pond. This area, known as the gypsum flats, is where the gypsum settles out. It is constantly worked by draglines, which remove settled, wet gypsum and transfer it onto an active gypsum pile to dry. The gypsum pile would be about 25 m high and about 60 hectares adjacent to the wet pond.

Fluorides in the gypsum slurry, in the water from the barometric condensers, and in the scrubber that treats process emissions to air go to the gypsum pond. It follows, therefore, from Table 9, that over 70 percent of the fluorine content of the rock used in the WPPA process may pass to the pond. When the same plant also produces TSP (as does GFC), a large part of the fluorine content of the H_3PO_4 will also pass to the gypsum pond through the water scrubbers in these additional processes. Thus, 85 percent or more of the fluorine originally present in the phosphate rock may find its way to the gypsum pond. Fluoride associated with the gypsum is, however, in an insoluble form, probably as CaF_2, before being sent to the pond. It is believed that fluorides from the barometric condensers are the primary

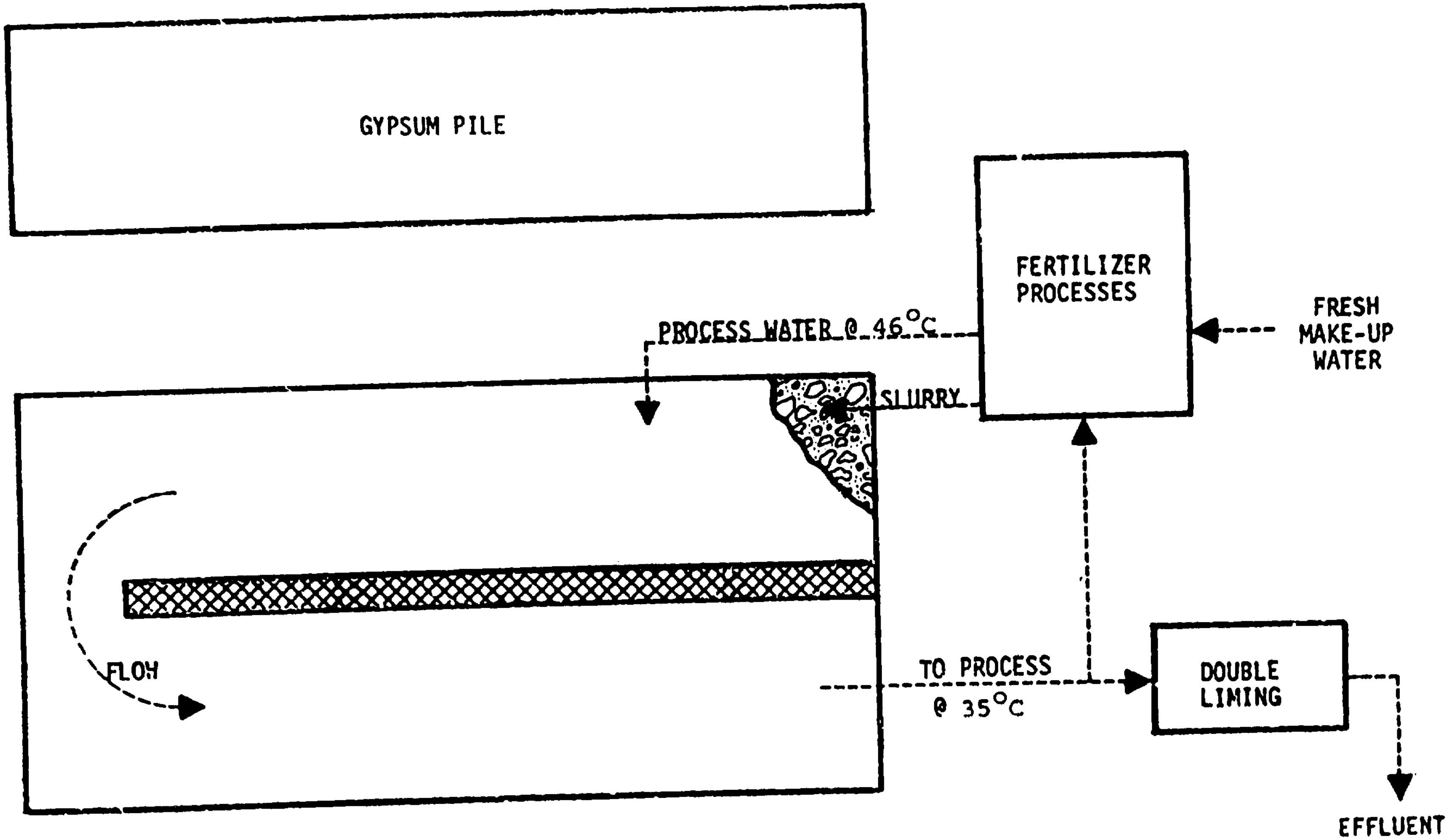


Figure 12. Typical Gypsum Pond for a 900 T/d P_2O_5 Plant.

source of pond emissions.

In gypsum ponds, approximately 1360 m^3 of disposal volume is required per year for each daily ton of P_2O_5 produced by the plant. Based on WPPA production, plants have gypsum ponds with surface areas in the range of 0.044-0.18 hectare per daily ton of P_2O_5 produced.

The water within pond systems is normally acidic, having a pH in the neighborhood of 1.5. This acidity is probably due to mostly inclusion of H_3PO_4 in the washed gypsum from the gypsum filter. The fluoride concentration of a given pond does not continue to rise as fluorides are added, but tends to stabilize. This action may be due to precipitation of complex calcium silicofluorides in the pond water. Published emission factors from gypsum ponds range from 0.22-11.2 kg/ha-day. Table 17 gives the emission factors attained from a comprehensive investigation.

Table 17. Fluoride Emission Factors for Selected Gypsum Ponds.
(Temperature = 32°C; kg/ha-day)

F^- Concentration	Wind Velocity at 5 m elevation, m/s			
	1	2	4	5
Pond A (6,400 mg/l)	0.9	1.5	2.6	-
Pond B (12,000 mg/l)	0.9	1.5	2.6	3.6

The most recent measurements of fluoride emissions from gypsum ponds indicate fluoride concentrations above the pond of 18-46 µg/l (ppb), consisting almost entirely of HF, as measured by the EPA Remote Optical Sensing of Emissions (ROSE) system. Emission rates of 0.22-8.2 kg/ha-day were determined by concurrent wet sampling and analysis.

Gypsum Pond Wastewater Treatment. Contaminated water can be treated effectively for control of pollution parameters, namely, pH, phosphorus, and fluorides. Treatment involves "double liming" or a two-stage lime neutralization/precipitation procedure. The first treatment stage provides sufficient neutralization to raise the contaminated water, containing up to 9,000 mg/l F^- and up to 6,500 mg/l P, from pH 1-2 to pH 3.5-4.0. The resultant treatment effectiveness is, to a significant degree, dependent on the mixing efficiency at the point of lime addition and the constancy of the pH control. At a pH level of 3.5-4.0, the fluorides will precipitate principally as CaF_2:

$$H_2SiF_6 + 3\ CaO + H_2O \longrightarrow 3\ CaF_2 + 2\ H_2O + SiO_2$$

This mixture or slurry is then held quiescently to allow the CaF_2 floc to settle. Equipment employed for neutralization ranges from crude, manual distribution of CaO (lime) with localized agitation to a well-engineered lime control system with a compartmented mixer. Similarly, the quiescent areas range from a pond to a controlled thickener or settler. The partially neutralized water, following separation from the CaF_2, now contains 30-60 mg/l F^- and up to 5,500 mg/l P. This water is again treated with lime sufficient to increase the pH to 6.0 or higher. At this pH level, calcium compounds, primarily dicalcium phosphate (Ca_2HPO_4), plus some monocalcium phosphate and additional quantities of CaF_2, precipitate from solution.

As before, this mixture must undergo quiescent settling to allow the Ca_2HPO_4 and minor amounts of $Ca(H_2PO_4)_2$ and CaF_2 to settle. The reduction of phosphorus is strongly dependent on the final pH, holding time, and quality of the neutralization facilities, principally mixing efficiency. Fig. 13 is a diagrammatic representation of a well-designed "double lime" treatment facility. Laboratory and treatment plant data for phosphorus and fluoride removal are presented in Table 18. Phosphorus concentrations were shown, in another series of tests, to be settling-time sensitive as expected. Note data shown in Table 19, for example. Radium-226 is also effectively precipitated by double lime treatment as demonstrated by data in Table 20. Double lime treatment will not, however, reduce the nitrogen (N) quantity, although at pH greater than 9.0, significant NH_3

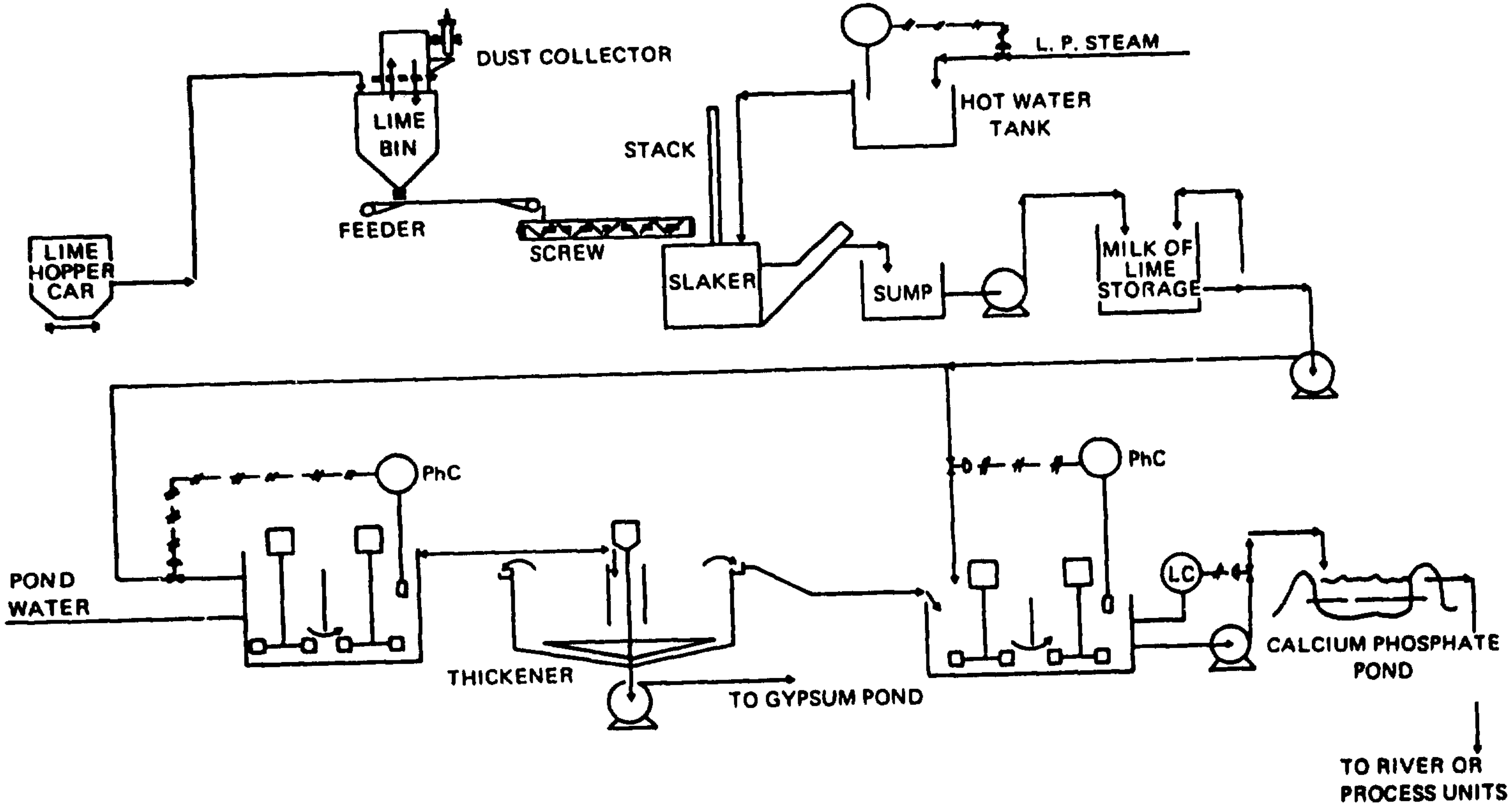


Figure 13. **POND WATER TREATMENT**

loss to ambient air can occur.

Table 18. Phosphorus and Fluoride Reductions as a Function of pH. (ref. EPA-450/1-74-006)

pH	Phosphorus, mg/l		Fluoride, mg/l	
	Laboratory	Plant	Laboratory	Plant
5.5	-	-	-	17
6.0	-	42	-	14
6.5	-	24	-	12.5
7.0	500	18	13	12.5
7.5	330	14	8.5	12.5
8.0	200	12	6.8	12.5
8.5	120	8	5.8	12.5
9.0	20	6	5.2	12.5
9.5	3	3	4.8	12.5
10.0	1.2	1.2	4.6	12.5

Table 19. The Effect of Settling Time on Phosphorus Reduction by Lime Treatment.

Time hr	pH	P Concentration mg/l
0	7.35	60
5	7.6	29
22	6.7	19
46	6.4	9

Table 20. Effect of Lime Treatment on Radioactive Radium-226.

pH	Radium-226 Concentration pCi/l
2.0	91
1.5	65
4.0	7.6
8.0-8.5	0.04

The most effective method to maintain low NH_3-N contaminant levels in wastewater is to prevent its entry into the sewer system. The following technology is considered to be the Best Available Technology Economically Achievable (BATEA):

- o Ammonia steam stripping followed by either high-flow NH_3 air stripping or biological nitrification-denitrification (discussed later in this Section II)
- o Continuous ion exchange followed by denitrification. This treatment system can provide the proper technology

to maintain the NO_3-N within effluent limitation guidelines

- Advanced urea hydrolysis followed by high-flow, NH_3 air stripping. The urea hydrolysis technology is rapidly improving and should eventually be capable of meeting the proposed effluent limitation guidelines

Gypsum Pond Water Seepage Control. The contaminated gypsum pond storage areas are surrounded by dikes and the bases of these dikes are normally natural soil from the immediate surroundings. As the need develops to increase the height of the retaining dikes, gypsum is dug from inside the diked area and added to the top of the earthen base. Dikes in Florida now extend to a 30.5-36.5 meters vertical height. These combined earthen/gypsum dikes tend to have continual seepage of contaminated water through their walls. In order to prevent this seepage from reaching both surface streams and groundwater, it is necessary to collect and re-impound it.

Seepage collection and re-impoundment is best accomplished by construction of a seepage-collection ditch all around the perimeter of the diked area. This ditch needs to be of sufficient depth and size to not only collect contaminated water seepage, but to permit collection of seepage surface water from the immediate outer perimeter of the seepage ditch. This is best accomplished by erection of a small secondary dike as shown in Fig. 14. This secondary dike also serves as a backup or reserve dike in the event of a failure of the primary or main dike.

The design of the seepage ditch with respect to distance from the main impounding dike and depth is a function of the geology of the area and the type of material used to construct the dike. Some data suggest that gypsum pond bottoms tend to be self-sealing, that is, compacted gypsum plus clay fines or silt and aluminum and iron silicates forced into interstices may form an artificial "cement-like" layer at the base of the old gypsum

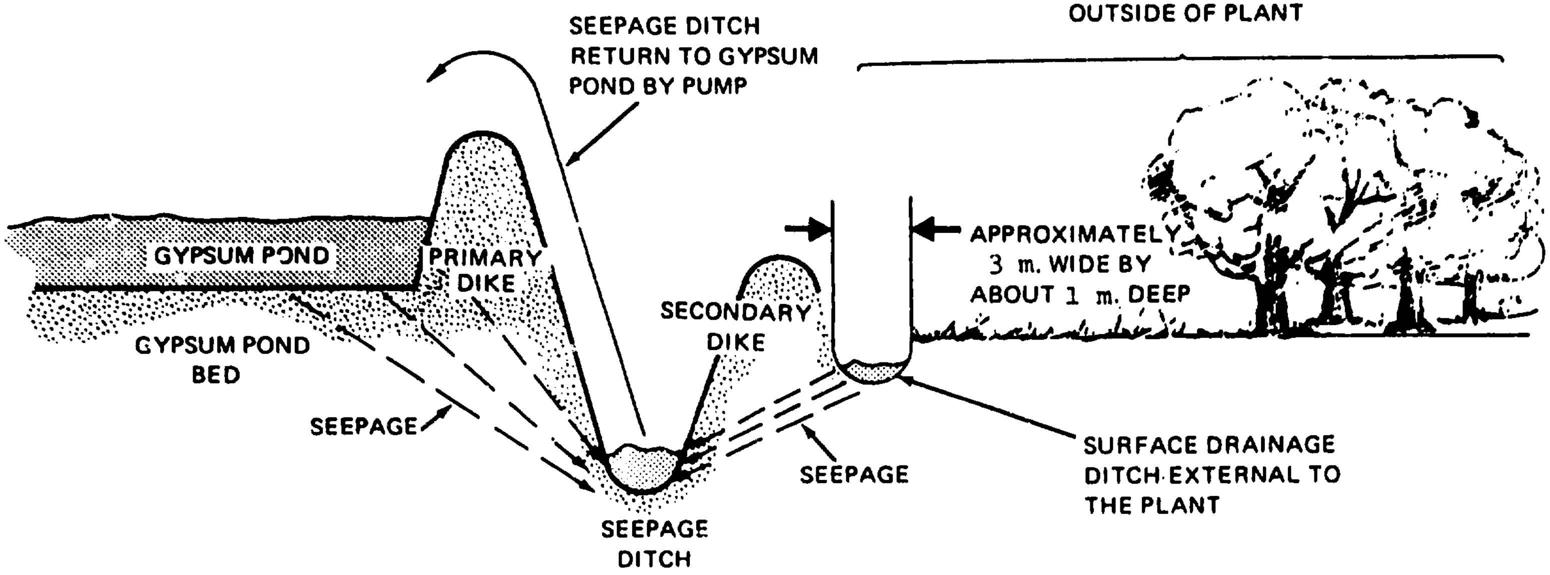


Figure 14. GYPSUM POND WATER SEEPAGE CONTROL

ponds, which is both acid-resistant and of very low permeability. In conclusion, the design of seepage ditches must consider the areal geology and the phreatic or vadose water level of the impounding dike material to achieve an effective seepage control system. An installation of a pump station at the low or collection point of the seepage ditch completes this seepage control system. The pumps serve to move the collected seepage water back into the contaminated water storage area. Normally these pumps are operated only a few hours per day, but this is entirely dependent on the seepage and rainfall conditions prevailing.

Gypsum Pond Area Reduction by Cooling Towers/Fluoride Recovery. WPPA plants utilize a wide variety of gypsum cooling pond arrangements. In most cases, process and gypsum sluicing waters are transferred to a common pond allowing these waters, which are vastly different in properties, to mix, with the ultimate result that both process and gypsum pond waters become highly contaminated with H_3PO_4, H_2SO_4, and H_2SiF_6.

In some cases, separate cooling and gypsum ponds are employed. All process waters except gypsum sluicing water are sent to cooling ponds. Gypsum slurry is pumped from the filtration operation to a gypsum pile where the gypsum is allowed to settle. The supernatant water is subsequently recycled through the cooling pond, thus contaminating it with H_3PO_4, H_2SO_4, and fluorides from the filtered gypsum.

The required size of the gypsum slurry pond is small--about 2 hectares--since no area is required for cooling. This water would be the most contaminated and acidic water in the plant because of the presence of H_3PO_4, H_2SO_4, iron and aluminum complexes, and fluorides from the filtration operation.

The pond area required for the barometric condensers is determined by the cooling duty requirements. This area is estimated to be 360 m^2 per ton of P_2O_5 per day. Since the cooling pond receives condensed vapors from the flash cooler and evaporators, entrained H_3PO_4 often is present as a contaminant. This occurrence, however, can be minimized by entrainment separators so that the main contaminant entering the cooling pond could be limited to fluorides.

Cooling towers now have replaced the cooling pond area. Gases from the WPPA vacuum cooler and vacuum evaporators are scrubbed to recover fluorides as H_2SiF_6 prior to final scrubbing in the process barometric condensers. Water from the WPPA reactor's scrubber is utilized to scrub the vacuum cooler/evaporator gases, thus effecting further fluoride recovery. Recovery efficiencies as high as 99 percent are reported. The water from the barometric condensers is cooled in closed-loop cooling tower systems. In some of these systems, the scrubbing water in the closed-loop is limed to precipitate the fluorides for disposal and to regenerate the caustic. With cooling pond areas, therefore, mostly redundant, pond systems are reduced to the principal function of handling gypsum slurry.

From Table 9, it can be seen that most of the soluble and potentially emittable fluorides are contained in the gases routed to the barometric condensers. Additional fluorides are contained in the gases from the WPPA reactor. Since the fluorides from both of these sources are sufficiently recovered and converted to the saleable H_2SiF_6 byproduct, and since pond area is reduced by removal of the pond's thermal loading by cooling towers, pond area and pond fluoride emissions can be reduced by at least one-half.

C. Treatment Systems for Fertilizer Wastewaters

Oil and Grease Reduction. Oil and grease in wastewater from nitrogen fertilizer process units can present problems especially when large rotating machinery, such as reciprocating compressors in NH_3 and urea units are employed. Oil and grease can be removed from the wastewater effluents to levels below 25 mg/l in properly designed and operated American Petroleum Institute (API) or equivalent separators (see Fig. 15). To assist in the

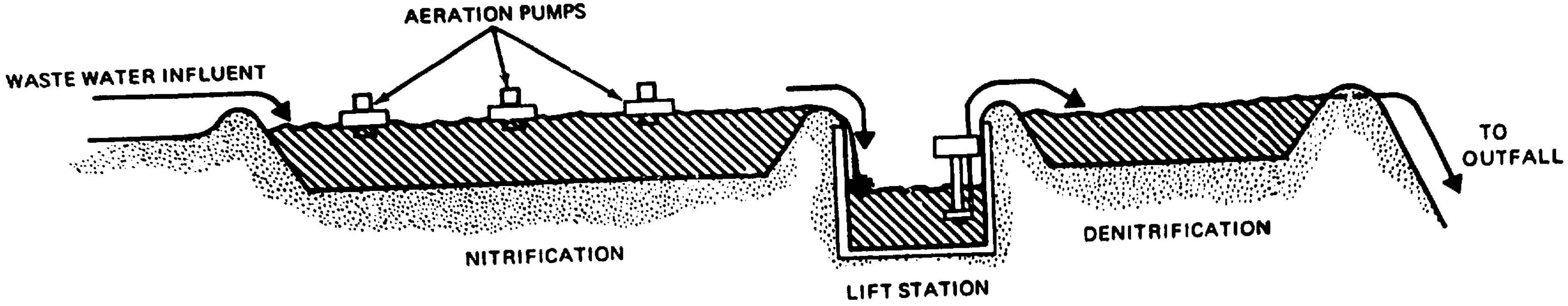


Figure 16. BIOLOGICAL TREATMENT

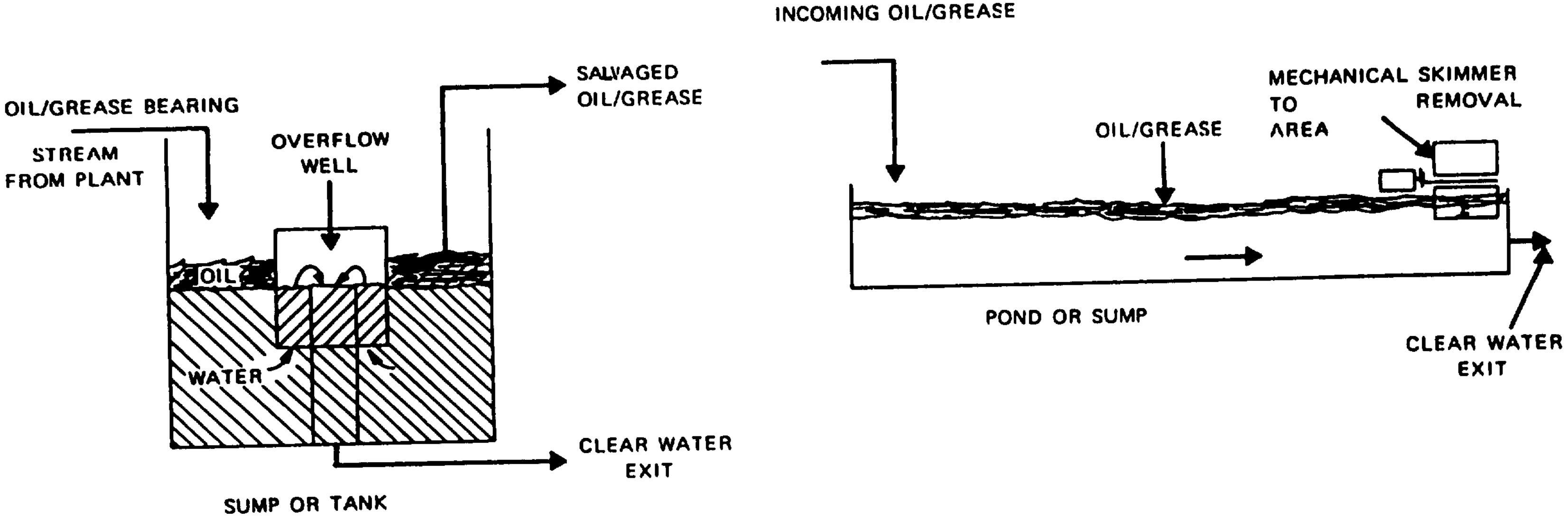


Figure 15. OIL/GREASE REMOVAL SYSTEMS

design of these separator units, the American Petroleum Institute in Washington, DC, has published a "Manual on Disposal of Refinery Wastes." The information contained in this manual is directly applicable to treatment of wastewater effluents from the nitrogen based fertilizer unit processes and operations. Oil and grease from many such sources can be prevented from escaping to these effluents by "housekeeping" techniques at the source. This can be effectively accomplished by such containment devices as drip pans.

Biotreatment for Urea Wastewaters (Nitrification/Denitrification). This treatment technique is based on the reaction of NH_3-N with oxygen in an aerated basin to form NO_3-N through biochemical oxidation (see Fig. 16). The NO_3-N in turn is metabolized in an anaerobic basin in the presense of a biodegradable carbon source to form N_2-N. The first step--nitrification--takes place in the presence of nitrifying aerobic bacteria, which convert the NH_3-N to NO_3-N. This biochemical reaction is promoted by the degree of aeration and warm temperatures. This step can be carried out in a lagoon, pond, trickling filter, or activated sludge basin according to the following:

$$2\ NH_3 + 3\ O_2 \longrightarrow 2\ NO_2^- + 2\ H^+ + 2\ H_2O$$

(nitrite formation)

$$2\ NO_2^- + O_2 \longrightarrow 2\ NO_3^- \quad \text{(nitrate formation)}$$

The denitrification step is an anaerobic process that occurs when the microorganisms metabolize the NO_3-N and the carbon source (urea and methanol, for example) into N_2 gas and CO_2. The initial breakdown of the NO_3-N requires that an organic carbon source is available. This can be in the form of methanol to give:

$$6\ NO_3^- + 5\ CH_3OH \longrightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6OH^-$$

This denitrification reaction must occur in the presence of denitrifying bacteria under anaerobic conditions. It is essential that maximum nitrification be obtained in the first basin prior to commencement of the denitrification process; this usually requires longer retention times and lower loading factors (that is, kg BOD_5 or COD per kg MLVSS-day) than are found in conventional activated sludge plants. Continuous addition of an organic carbon source (methanol) and inorganic carbon (bicarbonate) to accelerate the rate of denitrification is possible with concurrent increases in operational costs.

The overall oxidation-reduction reaction functions optimally with initial NH_3-N concentrations around 25 mg/l, but expected removals of 90 percent can be achieved with carefully controlled operations in order to depress the formation of H_2S if any sulfur source is present such as $SO_4^=$. Therefore, care should be taken when considering the installation of a denitrification process as to the siting of the biotreatment facility in relation to the wind rose and the nearest area of inhabitants.

Prior to full-scale design and ultimate construction of such a wastewater treatment facility, good engineering practice and common sense dictate that pilot plant studies and evaluation precede any major engineering decisions. Such pilot-scale evaluations should be representative of both concentrations of industrial and domestic wastes to be treated together with proportionally envisioned flowrates. Such a pilot plant should be scaled in the 10-100 m^3/day range. Such an investigation should consider as necessary the obtaining of data on the following design parameters:

- Removal efficiency for the parameter chosen, for example, BOD_5, COD, and so forth
- Optimum temperature for nitrification/denitrification stages
- Allowable temperature range of operation
- Nutrient requirements, if any
- BOD_5, COD, NH_3-N, NO_3-N, etc. removal rates
- Oxygen utilization
- Oxygen transfer (α and β)
- Sludge production, removal, dewatering, and disposal
- Optimum loading range, that is, kg BOD_5 or COD/kg MLVSS per day (MLVSS = mixed liquor volatile suspended solids)

- o Bacterial species identification

Consideration should also be given to the installation of an equalization basin prior to the primary clarifier to the nitrification step to retain shock loads of high strength wastes that could be inimical to bacterial species present and could also be used to dampen or even-out unexpected large wastewater flows or stormwater runoff.

Wastewater Treatment Sludge. After inspection of the GFC complex's three wastewater/water treatment facilities, it appears that a considerable quantity of sludge is wasted to Lake Kattinah or the Assi River. This cannot be tolerated indefinitely. If the clarifier units are designed and operated properly (design overflow rates for a sedimentation tank range from 24.5-40.8 m^3/day-m^2 (600-1000 gal/day-ft^2) and for a thickener is 8.2 m^3/day-m^2 (200 gal/day-ft^2) and also that correct doses of coagulant aids are administered to effect proper flocculation and settling, then the sludge generated can be pumped as a slurry to either a standard plate-and-frame filter press or a vacuum rotary filter for dewatering to about 27- 70 percent solids. The dewatered sludge can then be placed in sludge drying beds to reduce further its moisture content. If chemical analysis verifies the absence of toxic concentrations of heavy metals such as Hg, Pb, Cr, Co, Cd, Ni, etc., then the dried filter cake can be utilized for agricultural soil stabilization. Therefore, what is proposed is to collect sludge from each of the three industrial wastewater treatment units and the domestic wastewater treatment unit, dewater using plate-and-frame filter presses, remove sludge cake and place in individual sludge drying beds (appropriately labeled), analyze each of the four dried sludge cakes for toxic concentrations of heavy metals and, if acceptable, utilize for soil stabilization.[10/]

Emergency Holding Basin for Stormwater Runoff. Table 21 lists results of a water quality survey conducted in 1982 of the stormwater discharge to and in the Assi River, downstream of the entry of wastewater from the GFC complex.

Table 21. 1982 Water Quality Survey--Stormwater and Assi River.

Parameter mg/l	Stormwater Discharge to Assi River 14/8	 10/10	Assi River• 14/8	 10/10
pH units	9.3	8.9	7.7	8.1
Conductivity, µmhos/cm	580	480	600	370
TDS	330	288	360	222
Total Hardness[a]	205	208	240	165
Ca Hardness[a]	126	130	134	70
M.O. Alkalinity[a]	238	278	151	157
Cl^-	40.8	38.7	29.1	18.5
NO_3^-	85.8	49.6	66	60.5
NO_2^-	28.7	8.7	0.4	0.8
NH_4^+	87.6	1677	19.7	2.7
$SO_4^=$	29.8	58.1	400	23
$PO_4^{\equiv}$	0.2	0.5	0.14	0.45
Dissolved oxygen	6.9	7.8	7.7	8.7
BOD_5	26	110	26.8	37.6
COD	1160	2580	93	142
Oil & Grease	115	160	-	-
Turbidity	22	48	58	58

• Downstream from wastewater entry; a Expressed as $CaCO_3$.

This 1982 survey gives strong justification to the concept of installing separate stormwater collection and treatment systems in order to protect the Assi River, the water in the irrigation canal, and eventually the agricultural crops from uptake of pollutants being discharged to the environment during rainfall periods. This significant pollutional load is also being distributed to Lake Kattinah and is at least partially responsible for initiating eutrofication and subsequent algal blooms as evidenced by the viable algal community present in the lake, the river, and the irrigation canal.

Wastewater Effluent Stream Identification, Pollutant Inventory, and Good Housekeeping Practices at GFC. Senior management at the GFC complex must authorize the initiation of a comprehensive in-depth, in-plant air emissions, wastewater effluents, hazardous wastes environmental survey to cover the CAN, Ammonia/Urea, and WPPA/GTSP units, the three industrial wastewater and one domestic wastewater treatment plants. In only this way can senior management be able to identify feedstock and product losses, which appear to be extensive. Material balances of key pollutant parameters such as fluoride, P_2O_5 or total phosphorus (as P), sulfate or total sulfur (as S), and NH_3-N and NO_3-N. Workers and plant operators should be instructed to be conscious of fugitive emission sources (see Table 14) and immediately report such occurrences to their respective shift supervisors, who, in turn,should have the leaks repaired as soon as possible. Pumps should either be sealless or possess dual mechanical seals. Drip pans should be installed under compressors to prevent oil and grease from leaving the process unit battery limits. Establishment of good housekeeping practices with the endorsement and full support of senior management and staff will go a long way to minimizing many losses from the GFC complex. The employee suggestion box technique has worked well at the Dow Chemical and Union Carbide Companies particularly when employees were rewarded for worthwhile suggestions that resulted in cost saving to the firms.

D. Contaminated Groundwater Remedial Actions

What follows is a guide regarding remedial action planning for contaminated groundwater.

Scoping of Groundwater Remedial Activities:

- Site management planning
- Project planning
    - Characterization of the hydrogeology
    - Characterization of the contamination
    - Evaluation of pollutant plume movement and response
    - Assessment of design parameters for potential treatment technologies
- Remedial action objectives
    - Cleanup levels of pollutants (maximum contaminant levels allowed)
        - Risk-specific doses
        - Reference doses
        - Lifetime health advisories
        - Maximum contaminant level goals
        - Water quality criteria
    - Area of attainment

- Groundwater remediation process
  - Response objectives
  - Potential remedies identified (air stripping, carbon adsorption, oxidation, ion exchange)
    - Natural attenuation with monitoring
    - Active restoration with extraction of groundwater for on-site treatment
  - Scoping
  - Remedial investigation/Feasibility study (RI/FS)
  - Data collection
  - Remedial action objectives
  - Interim action
  - Selection of remedy
- Restoration time frame
- Documentation
  - Number of extraction wells
  - Treatment process
    - Control of cross-media (air, land, water) impacts
    - Expected pumping/flow rates
    - Management of residuals produced
    - Gradient control system
    - Type of institutional controls and the implementing authority (the state, the region)
- Evaluating performance and modifying remedial actions
  - Discontinue operations
  - Upgrade or replace remedial action
  - Modify remedial action
  - Performance monitoring (frequency, length of time)
- Multiple sources strategy (for sites with different sources of waste)
  - Survey contributors
  - Survey of potential sources

III. ASSESSMENT OF CURRENT DISPOSAL PRACTICES OF HAZARDOUS WASTES

A. Health Concerns--Radioactive Contamination

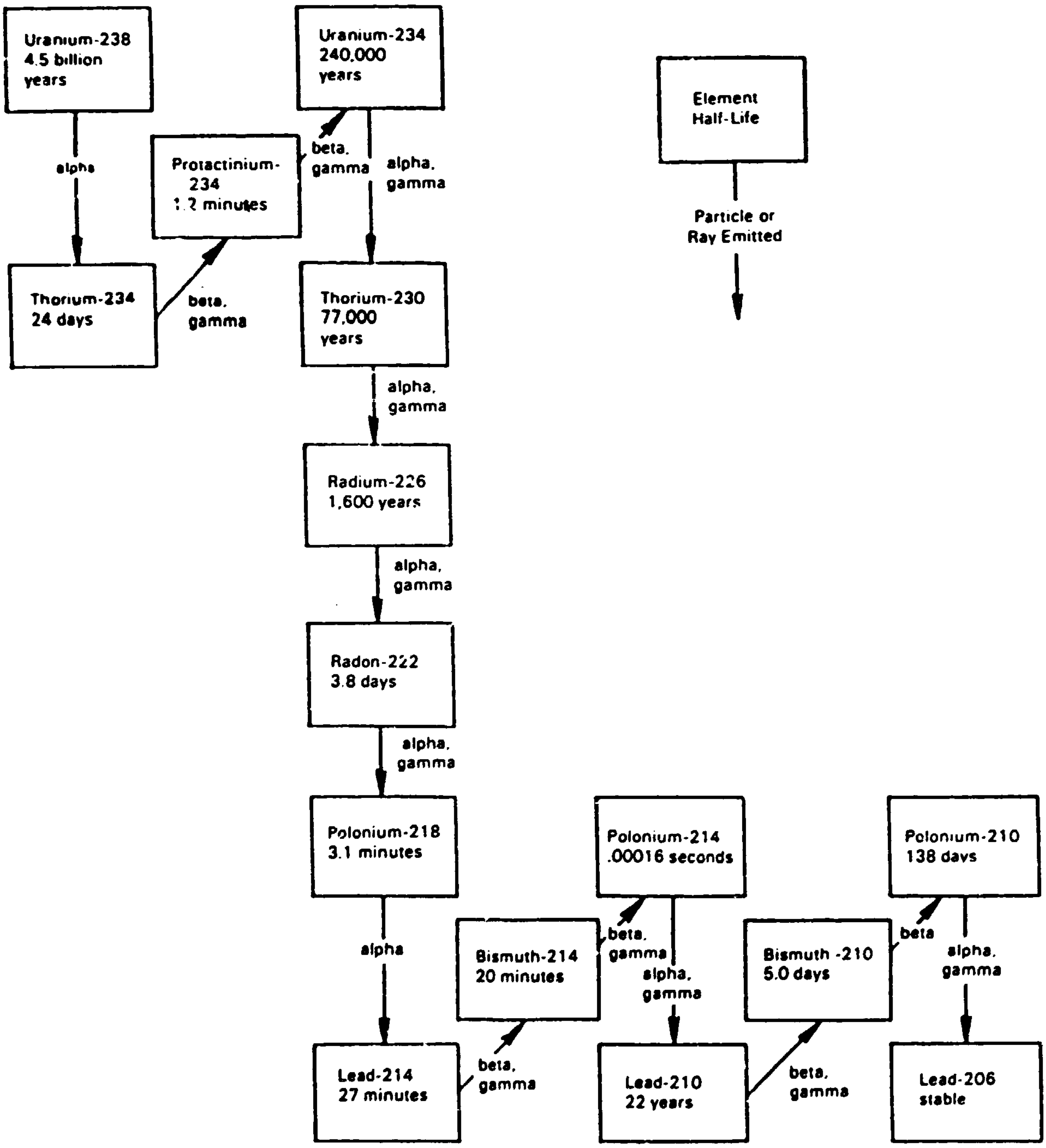
The feedstock phosphate rock and the gypsum sludge produced as a result of processing this rock into WPPA and GTSP contains radioactive materials consisting primarily of radium, thorium, and uranium. Both feedstock dust (and particulates) and gypsum wastes contain residual quantities of these elements and their radioactive decay products, which have remained not only as contaminants within the GFC complex, but in the gypsum pond tailings and disposal areas. Contaminated soils have sometimes been utilized as fill material on private roads and public properties for various purposes. There are many other radionuclides that may also be impacted by selection of proper control technologies to be discussed.

The radioisotopes of concern belong to the uranium-238 and thorium-232 decay series (see Fig. 17). Hazards to the local population of the Lake Kattinah area, Homs and beyond, and GFC workers could occur through several pathways, including:

- Inhalation of radon decay products, particularly where radon is concentrated within building structures
- Inhalation of particulates (dust) or ingestion of materials, such as vegetables grown in the vicinity, containing radioisotopes of the two decay series
- Ingestion of radionuclides via drinking water and food
- External body exposure to gamma radiation

In the absence of any remedial action, these potential health hazards could persist for extremely long periods (millions of years) because of the long half-lives of the controlling isotopes. There are three types of radiation believed to pose health hazards. One is alpha radiation (positively charged nuclear particles) associated with radioactive decay of radon gas and other radioactive elements, such as radium and uranium. Although alpha radiation cannot penetrate the outer layers of skin (epiderma), it can enter the body via inhalation and

Figure 17. Uranium-238 decay series.



ingestion routes. Inhalation of alpha-emitting particles is a major health hazard and may contribute to lung cancer. Ingestion of water, dust, plants, or animals that contain alpha-emitters may contribute to cancer in the target organs of the body where the alpha-emitters lodge.

The second type of radiation that may pose a health hazard is gamma radiation. Gamma-emitters can contribute to external exposure, since they are able to irradiate the human body. Such exposure can contribute to cancer in various parts of the body. Different measures may be required to reduce exposure to alpha and gamma radiation.

The third type of radiation is beta radiation (electrons). Energetic beta particles can pass through the skin. The primary hazard from beta radiation, however, is internal deposition by ingestion or inhalation. Although decay of radium to radon does not produce beta radiation, a subsequent portion of the decay chain produces beta radiation. The beta radiation is of secondary concern relative to the alpha and gamma radiation, as the associated risks are typically much lower.

The principal health concern at sites or areas containing radioactive wastes has been radon, radon progeny, and gamma radiation from radionuclide decay. The primary gamma radiation source at waste sites is radium in the soil. In addition, radon gas is continually produced by radioactive decay of radium, as indicated in Fig. 17. Radon and its decay products (radon progeny or duaghter-products) are alpha emitters that are potentially injurious if they become lodged in the respiratory system. Radon in the soil can penetrate through fractures and porous building materials and accumulate unsafe concentrations within homes and other buildings and enclosures.

Radon has a half-life of 3.8 days; its progeny are radioactive particles, which can attach to dust and other particulate materials. If they are inhaled, either attached or unattached to other particulates, they may deposit in the respiratory system, where they emit alpha particles, which may be damaging to the adjacent tissue. Alpha-emitting particles from decay of radon and progeny are considered to be a cause of lung cancer.

Residences and other buildings (for example, GFC's industrial buildings and enclosures) have been located on and near some waste disposal (and feedstock) sites contaminated with radioactive materials. The radiation hazard derives from elevated outdoor and indoor gamma radiation levels that approach and sometimes exceed the radiological standards for the general public. It is important to note that there are average background radiation levels associated with these materials. Typical levels are shown in Table 22; they may not be the same as the average level in any particular location.

Table 22. Typical Background Radiation Levels.

Component	Typical Background
Gamma radiation	8-13 μR/hr
Ra-226 or Ra-228 in soil	~1 pCi/g
Uranium in soil	~1 pCi/g
Th-232 in soil	~1 pCi/g
Ra-226 in water with Ra-228	~1 pCi/l
U-238 in water	~1 pCi/l
Radon in air (outdoor)	0.2 pCi/l
Radon in air (indoor)	~1 pCi/l

Sites that contain certain radioactive wastes may also contain other types of hazardous waste. Some sites, for example, contain various types of hazardous waste and the radioactive portion may pose a relatively small threat by comparison. However, regarding waste generated from a nitrogenous/phosphatic fertilizer complex such as GFC, there do not appear to be any wastes that would be more hazardous as a constituent than the radioactive components of phosphate rock dust and dewatered gypsum tailings, except possibly for spent V_2O_5 catalyst, S-sludge and cake, and ZnS from natural gas desulfurization.

Radioactive wastes at uncontrolled sites come from a variety of sources. Some of the most common have been residual material derived from the beneficiation of uranium-, radium-, and thorium-bearing ores and from the process use of these elements or from phosphate rock used to produce WPPA and TSP. It appears that most of the contaminated wastes are in tailings, a soil-like matrix.

The following public comments were recorded in the Environmental Impact Statement for the Central Florida Phosphate Industry and are included here for instructional purposes: "With respect to fluoride and uranium, recovery of these two compounds, based solely on economic consideration .... is totally unacceptable in view of the documented damage caused by these compounds. They should be removed from the wastewater as a simple matter of health protection. If a profit results, so much the better for the industry. But placing such an emphasis on profit is neither justifiable nor desirable from the public or environmental health standpoint. We suggest that you include the information that Florida has the highest rate of lung cancer in the United States."

B. Disposal Methods

It may be possible to deal with radioactive waste materials by control methods that do not remove either the soil or the radionuclides from the site. Such methods include capping and vertical barriers or quite possibly mine disposal (see also Table 20).

Capping. This concept involves covering the contaminated site with a barrier sufficiently thick and impermeable so as to minimize the diffusion of radon gas. Barrier materials can be either natural low-permeability soils, for example, clay, or synthetic membrane liners, or both. Both types of materials are generally available. A barrier might consist of a meter or two of compacted clay, depending on radiation levels, and extending a few meters beyond the perimeter of the contaminated area.

Cap design must consider the need to: (1) Confine radon until it has essentially decayed to its progeny (for normal soils, the depth of cover required is about 150 cm for Rn-222 and 5 cm for Rn-220; (2) attenuate the gamma radiation associated with all the radionuclides present (for normal soils, the depth of cover required for gamma radiation shielding is on the order of 60 cm); (3) provide long-term minimization of water infiltration (rainfall or groundwater influent flow) into the contaminated material; (4) function with minimal maintenance; (5) promote drainage and minimize erosion; and (6) have a permeability less than or equal to the permeability of any bottom liner system present or the natural subsoils. The technology of caps is well developed and is available from the EPA Risk Reduction Engineering Laboratory in Cincinnati, Ohio. All reasonable steps should be taken to prevent or prohibit construction of buildings on capped wastes.
<u>Vertical Barriers</u>. Vertical barrier walls may be installed around the contaminated zone to help confine the material and any contaminated groundwater that might otherwise flow from the site. The barrier walls, which might be in the form of slurry walls or grout curtains, would have to penetrate an impermeable natural horizontal barrier, such as a clay zone or aquiclude, in order to be effective in impeding or deterring groundwater flow. A barrier wall in combination with a surface cap could produce an essentially complete containment structure surrounding the waste mass.

Slurry walls are constructed by excavating a trench beneath a slurry. The slurry could be bentonite clay and water or it could be portland cement, bentonite clay, and water. In cases where strength is required of a vertical barrier, disphragm walls are constructed with pre-cast or cast-in-place concrete panels. An illustration of the slurry wall construction process is shown in Fig. 18.

Grout curtains are constructed, however, by pressure-injecting grout directly into the soil at closely spaced intervals around the waste site (see Fig. 19). The spacing is selected so that each "pillar" of grout intersects the next, thus forming a continuous wall or curtain. Various kinds of grout can be utilized, such as portland cement, alkali silicates, and organic polymers.

Figure 18. Slurry trench construction operations

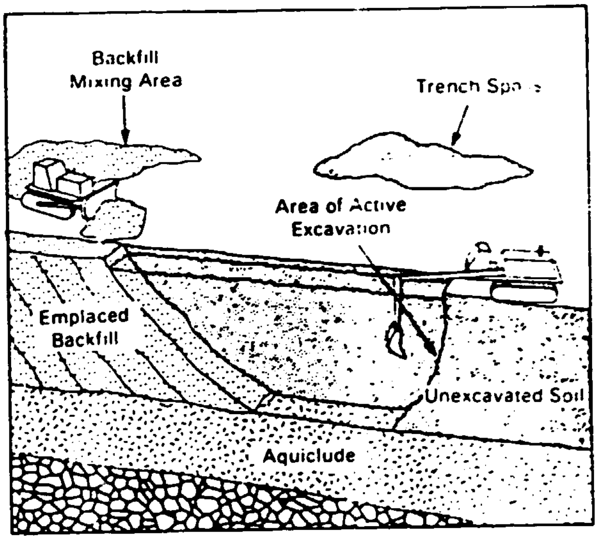
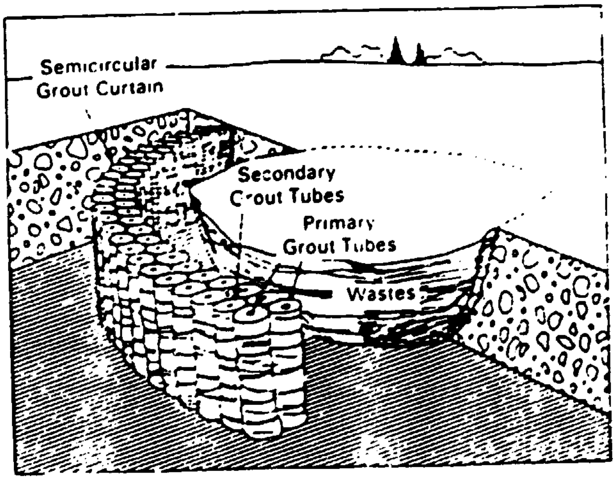


Figure 19. Grout curtain around waste site.



Underground Mine Disposal. Both active and inactive mines (particularly phosphate rock mines) could provide sites for the permanent disposal of radiologically contaminated wastes. A conceptual representation of a mine disposal facility is shown in Fig. 20. This is one way to plan for a safety zone of distance between the radioactively contaminated material and the human population at risk, although groundwater could provide a route for transport of contamination. As one cell of phosphate rock becomes depleted, the second cell is explored and excavated. This then allows the vacated and empty first cell to be filled with dewatered, spent gypsum tailings, and so on. After the first cell is effectively filled, the requisite thickness of clay cap is applied, and the surface vegetated with native plants or grasses.

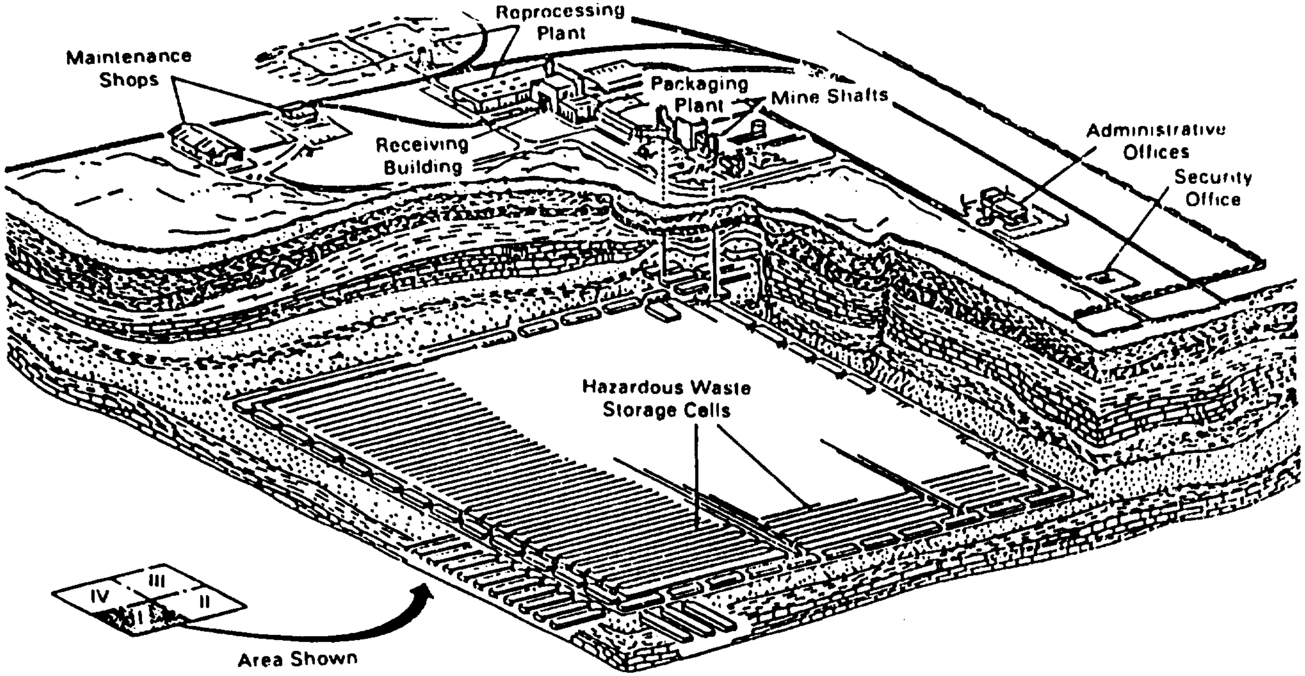
Dust Control Plan. Formation of a dust control plan is an integral part of site cleanup planning. If the dust control plan is not formulated before cleanup commences, but included as an afterthought, it is possible that dust control measures will:

- o Not be performed regularly
- o Not be adequately funded
- o Be performed in a less effective, begrudging manner by employees given the added responsibilities
- o Lack the necessary physical components (for example, the addition of aggregate to unpaved roads that pass through the contaminated area, mud carrout washstands, enclosure fencing for exposed areas, and so on)
- o Not be adequately monitored by appropriate recordkeeping or ambient monitoring

The following tasks should be completed during the formulation of a dust control plan:

- o Identification of dust sources
- o Identification of control measures
- o Development of implementation plan
- o Development of inspection, recordkeeping, and monitoring

Figure 20. Conceptual view of a mine storage facility.



programs

- Allocation of sufficient resources

These dust sources include:

- Vehicle-related
  - Paved roads
  - Unpaved roads
  - Road shoulders along paved/unpaved roads
  - Mud carryout
  - Truck spillage
- From movement of feedstock or contaminated soil/waste
  - Bulldozing
  - Loading onto trucks--travel area, dump
  - Unloading from trucks
  - Grinding or milling operations (phosphate rock)
  - Storage or bagging operations (phosphate rock, urea and ammonium nitrate prills, and GTSP)
- Wind erosion-related--short- and long-term, temporary
  - Storage piles (gypsum tailings) and fugitive dust

Fugitive dust can occur anywhere dusty waste is dumped for disposal. This includes overburden piles, mining spoils, tailings, fly ash, bottom ash, catch from air pollution control equipment, process overload discharges, building demolition wastes, contaminated products, byproducts, and so on. Like open storage, emissions originate from an activity comparable to loading out of the storage pile. However, there may be emissions from transporting the waste material on-site (if it is dry when produced as it indeed is in the Homs area) or from a reclamation process such as landfill covering associated with the waste disposal operation. If the surface of the waste material does not include a compound that provides cementation upon weathering, or if the surface is not compacted, or if an area of very little rainfall (such as the Homs area), wind erosion of fines can occur at wind speeds greater than about 5.3 m/sec. Table 23 lists control techniques for waste disposal sites.

Table 23. Control Technology and Applications for Waste Disposal Sites.

Emmision Points	Control Technique	Efficiency
Handling	Keep material wet	100 %
	Cover or enclose hauling	No estimate
	Minimize free fall of material	No estimate
Dumping	Spray bar at dump area	50 %
	Minimal free fall of material	No estimate
	Semi-enclose bin	No estimate
Wind erosion	Cover with dirt or stable material	100 %
	Chemically stabilize	80 %
	Revegetate	25-100%
	Rapidly reclaim newly filled areas	No estimate
Grading	Water	50 %

Calcium Fluoride Disposal in Gypsum Ponds. Any solid waste generated by scrubbing fluorides would be in the form of CaF_2 or similar precipitates in gypsum ponds. The quantity of precipitate formed is considered negligible compared to the amount of gypsum generated during the production of WPPA, the requisite intermediate for TSP. An example of the relative quantities of each of the solids produced in normal processing with scrubbers that meet emission control guidelines for a 500 T/d P_2O_5 WPPA plant is presented as follows:

Assumptions:

- 2921 kg phosphate rock = 1 T P_2O_5
- phosphate rock is 35 weight % Ca
- uncontrolled emissions of 26.4 kg F^-/hr are reduced to 0.19 kg F^-/hr by a scrubber
- all of the F^- absorbed by the scrubber precipitates in the gypsum pond as CaF_2
- the plant capacity is 500 T/d P_2O_5

$$3\ Ca_{10}(PO_4)_6F_2 + 30\ H_2SO_4 + SiO_2 + 58\ H_2O \longrightarrow$$
$$30\ CaSO_4 \cdot 2H_2O + 18\ H_3PO_4 + H_2SiF_6$$

This reaction implies that: 40 kg Ca = 172 kg gypsum.

$$\text{Gypsum produced} = \frac{500 \times 2921 \times 0.35 \times 172}{24 \times 40} = 91{,}600 \text{ kg/h}$$

$$F^{-} \text{ absorbed in the scrubber} = 26.2 - 0.19 = 26.2 \text{ kg/h}$$

$$Ca^{++} + 2F^{-} \longrightarrow CaF_2$$

$$CaF_2 = 26.2 \times \frac{78}{38} = 53.8 \text{ kg/h}$$

$$\% \text{ increase in solids} = \frac{53.8 \times 100}{91{,}600} = 0.064$$

This example illustrates that the increase in solids production due only to scrubbing F^{-} even stoichiometrically is negligible (0.06 %). The disposal of the large volume of gypsum is by depositing in mined-out areas, and by lagooning, followed by drying and piling. Such piles are as much as 30 meters above grade in some areas.

Site Characterization. A complete site characterization would include mineral analysis, particle size distribution, radionuclide contaminant distribution on various size fractions, soil texture and permeability, moisture content, and so forth. A list of some more important site and waste characteristics that may affect applicability and effectiveness of various control technologies can be found in Table 24.

IV. SOCIO-ECONOMIC ENVIRONMENTAL IMPACT ASSESSMENT OF CURRENT SITUATION

A. Effects of Fluorides on Human Health, Animals, Vegetation, and Materials of Construction

Human Health Effects. The daily intake of fluoride inhaled from the ambient air is only a few hundredths of a milligram--a very small fraction of the total intake for the average person. If a person is exposed to ambient air containing about 8 µg of fluoride per cubic meter, which is the maximum average concentration that is projected in the vicinity of a fertilizer facility with only mediocre control equipment, his total daily intake from this source is calculated to be about 150 µg. This is very low compared with the estimated daily intake of about 1,200 µg from food, water, and other sources for the average person.

There is evidence that airborne fluoride concentrations that produce no plant injury contribute quantities of fluoride that are negligible in terms of possible adverse effects on human health and offer a satisfactory margin of protection for people.

Gaseous HF is absorbed from the respiratory tract and through the skin. Fluoride retained in the body is found almost exclusively in the bones and teeth. Under normal conditions, atmospheric fluoride represents only a small portion of the body fluoride burden. However, these conditions may not exist at the GFC complex.

Many carefully conducted studies were reviewed by the American National Academy of Sciences, which were of human populations living in the vicinity of large stationary sources of fluoride emissions. Even in situations where poisoning of grazing animals was present, no human illness due to fluoride poisoning has been found. In some of these areas, much of the food used by the people was locally produced. Selection, processing, and cooking of vegetables, grains, and fruits gives a much lower fluoride intake in human diets than in that of animals grazing on contaminated pasture.

In poisoned animals, fluorine levels are several thousand times normal in bone, and barely twice normal in milk or meat. Calves and lambs nursing from poisoned mothers do not have fluorosis. They do not develop poisoning until they begin to graze. Meat, milk, and eggs from local animals contain slightly more fluoride than the same foods from poisoned animals. This is due to the fact that fluorine is deposited in the bones almost entirely.

<u>Mammalian Health Effects</u>. In areas where fluoride air pollution is a problem, high-fluoride-content vegetation is the major source of fluoride intake by livestock. Inhalation contributes only a negligible amount to the total fluorides intake of such animals. The available evidence indicates that dairy cattle are the domestic animals most sensitive to fluorides, and protection

Table 24. Site and Waste Characteristics that Impact Remedial Technologies.

Site Characteristics

Site volume
Site area
Site configuration
Disposal methods
Climate
  - Precipitation
  - Temperature
  - Evaporation
Soil texture & permeability
Soil moisture
Slope
Drainage
Vegetation
Depth to bedrock
Depth to aquicludes
Degree of contamination
Cleanup requirements
Direction and rate of groundwater flow
Receptors
Drinking water wells
Surface waters
Ecological areas
Existing land use
Depths to groundwater or plume

Waste Characteristics

Quantity
Chemical composition
Mineral composition
Acute toxicity
Persistence
Biodegradability
Total radioactivity
Radioisotopes and concentration
Ignitability
Reactivity/corrosiveness
Treatability
Thermal properties
Infectiousness
Solubility
Volatility
Density
Partition coefficient
Safe levels in the environment
Compatilibity with other chemicals
Particle size distribution
Radioactivity distribution with particle size

Few instances of health effects in people have been attributed to community airborne fluoride, and they occurred in investigations of the health of persons living in the immediate vicinity of fluoride-emitting industries. The only effects consistently observed are decreased tooth decay and slight mottling of tooth enamel when compared to control community observations. Crippling fluorosis resulting from industrial exposure to fluoride seldom occurs today, owing to the establishment of and adherence to threshold limits for exposure of workers to fluoride. Even persons occupationally exposed to airborne fluoride do not usually come into contact with fluoride concentrations exceeding the recommended industrial threshold limit values (TLV). The current TLV for HF is 3 ppm, whereas that for particulate F^- is 2.5 mg/m^3 expressed as elemental fluorine (F).

of dairy cattle from adverse effects will protect other classes of livestock.

Ingestion of fluoride from hay and forage causes bone lesions, lameness, and impairment of appetite that can result in decreased weight gain or diminished milk yield. It can also affect developing teeth in young animals, causing more or less severe abnormalities in permanent teeth.

Experiments have indicated that long-term ingestion of 40 ppm or more of fluoride in the ration of dairy cattle will produce a significant incidence of lameness, bone lesions, and dental fluorosis, along with an effect on growth and milk production. Continual ingestion of a ration containing less than 40 ppm will give discernable, but nondamaging effects. However, full protection requires that a time limit be placed on the period during which high intakes can be tolerated.

It has been suggested that dairy cattle can tolerate the ingestion of forage that averages 40 ppm of fluoride for a year, 60 ppm for up to two months, and 80 ppm for up to one month. The usual food supplements are low in fluoride and will reduce the fluoride concentration of the total ration to the extent that they are fed.

Fluoride-containing dusts can be noninjurious to vegetation, but contain hazardous amounts of fluoride in terms of forage for farm animals. Phosphate rock is an example of a dust that seemingly has not injured plants, but is injurious to farm animals. This fact was made evident forty years ago when an attempt was made to feed phosphate rock as a dietary supplement source of calcium and phosphate. Fluoride injury quickly became apparent. Phosphate rock is used for this purpose today, but only after defluorinating by heat treatment. Phosphate rock typically contains up to 4 weight percent fluorine.

Vegetative Effects. It was previously stated that atmospheric fluorides normally are not a direct problem to people or animals but that animals could be seriously harmed by ingestion of fluoride from forage. Indeed, the more important aspect of fluoride in the ambient air is its effect on vegetation and its accumulation in forage that leads to harmful effects in cattle and other animals. The hazard to these receptors is limited to particular areas: industrial sources having poorly controlled fluoride emissions and farms located in close proximity to facilities emitting fluorides.

Exposure of plants to atmospheric fluorides can result in accumulation, foliar lesions, and alteration in plant development, growth, and yield. According to their response to fluorides, plants may be classed as sensitive, intermediate, and resistant. Sensitive plants include several conifers, several fruits and berries, and some grasses such as sweet corn and sorghum. Resistant plants include several deciduous trees and numerous vegetable and field crops. Most forage crops are tolerant or only moderately susceptible. In addition to differences among species and varieties, the duration of exposure, stage of development and rate of growth, and the environmental conditions and agricultural practices are important factors in determining the susceptibility of plants to fluorides.

The average concentration of fluoride in or on foliage that appears to be important for animals is 40 ppm. The available data suggest that a threshold for significant foliar necrosis on sensitive species, or an accumulation of fluoride in forage of more than 40 ppm would result from exposure to a 30-day average concentration of gaseous fluoride of about 0.5 $\mu g/m^3$.

Examples of plant fluoride exposures that relate to leaf damage and crop reduction are shown in Table 25. As shown, all varieties of corn and tomatoes are particularly susceptible to damage by fluoride ambient air concentrations projected in the immediate vicinity of fertilizer facilities.

Table 25 . EXAMPLES OF HF CONCENTRATIONS AND EXPOSURE DURATIONS REPORTED TO CAUSE LEAF DAMAGE AND POTENTIAL REDUCTION IN CROP VALUES

Plant	Concentration and Time*	
	Most sensitive varieties -	most resistant varieties
Sorghum	0.7 ppb (0.32 $\mu g/m^3$) for 15 days -	15 ppb (6.9 $\mu g/m^3$) for 3 days
Corn	2 ppb (0.92 $\mu g/m^3$) for 10 days -	800 ppb (366 $\mu g/m^3$) for 4 hrs.
Tomato	10 ppb (4.6 $\mu g/m^3$ for 100 days -	700 ppb (321 $\mu g/m^3$) for 6 days
Alfalfa	100 ppb (45.8 $\mu g/m^3$) for 120 days -	700 ppb (321 $\mu g/m^3$) for 10 days

*Concentrations are expressed in terms of parts per billion (ppb) with the equivalent concentration in micrograms per cubic meter ($\mu g/m^3$) given in parenthesis.

(ref. EPA-450/2-77-005)

Effects on Materials of Construction and Structures. It is well known that glass and high-silica materials are etched by exposure to volatile fluorides such as HF and SiF_4. Some experiments have been performed where panes of glass were fumigated with HF in chambers. Definite etching resulted from nine hours exposure at a level of 590 ppb (270 $\mu g/m^3$). Pronounced etching resulted from 14.5 hours exposure at 790 ppb (362 $\mu g/m^3$). Such levels would, of course, cause extensive damage to many species of vegetation. However, *ambient concentrations of this magnitude are improbable provided that a fertilizer facility properly maintains and operates some type of effective control equipment for abating fluoride emissions*.

At the relatively low gaseous concentrations of fluorides in emissions from industrial processes, 1000 ppm or less, the damage caused by fluorides is probably limited mostly to glass and brick. Occasionally, damage to the interior brick lining of a stack has been attributed to fluorides.

Considerable experience is available on corrosion in WPPA plants, where the presence of fluoride increases the corrosive effects of H_3PO_4. This experience applies to the liquid phase; the effects of fluoride air emissions need more study. Entrained, crude H_3PO_4 will corrode structural steel and other non-resistant materials that it settles on. The corrosive effects of "fumes" from the digestion of phosphate rock have been acknowledged and good design and maintenance practices for plant structural steel are available. More information is needed about effects of gaseous fluorides in low concentration outside of the plant. It is usually difficult to separate the corrosive effects of airborne fluorides from those of other local and background pollutants.

B. Impacts of Other Parameters of Concern--Suspended Solids, Phosphorus, Vanadium and Cadmium

Suspended Solids. Suspended solids include both organic and inorganic materials. Inorganic components include sand, silt, and clay. The organic fraction includes oil and grease, tar, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a conglomeration of both organic and inorganic solids. They adversely affect fishing areas by covering the bottom of the river or lake with a blanket of sludge that destroys the fish-food bottom fauna or the spawning ground of some fish. Deposits containing organic fractions may also deplete bottom dissolved oxygen supplies and produce H_2S, CO_2, CH_4, mercaptans, and other noxious gases through anaerobiosis within the benthos.

Solids may be suspended in water for a time and then settle to the bed of the river or lake. These settleable solids discharged with man's wastes may be inert, refractory, slowly biodegradable, or rapidly decomposible substances. While in suspension, they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Phosphorus. During the past 40 years, a formidable case has developed for the theory that increasing, standing crops of aquatic plant growths, which often interfere with water uses and are nuisances to man, frequently are caused by increasing supplies of phosphorus. Such phenomena are associated with a condition of accelerated eutrophication or aging of waters. It is generally recognized that phosphorus is not the sole cause of eutrophication, but there is ample evidence to substantiate that it is frequently the key element of all the elements required by fresh water plants and is generally present in the least quantity relative to need. Therefore, an increase in phosphorus allows use of other, already present, nutrients for plant growth and sustenance. For this reason, phosphorus is usually considered as a "limiting factor."

When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities become immedately apparent. Dense populations of lake weeds make swimming dangerous. Boating and fishing (pleasure and commercial) may be eliminated or severely limited because of the mass of vegetation that serves as a physical impediment to those activities. Plant populations have been associated with stunted fish populations and with reduced fishing catches and production. Plant nuisances, such as blue-green algae, emit vile stenches, impart tastes and odors to water supplies (including irrigation water), reduce the efficiency of industrial and municipal water treatment, impair aesthetics, reduce or restrict resort commerce, cause skin rashes to man during and after water contact, and serve as a desired substrate and breeding environment for flies.

Vanadium. Metallic vanadium does not occur freely in nature, but minerals containing vanadium are widespread. Vanadium is found in many soils and occurs in vegetation grown in them. Vanadium adversely affects some plants in concentrations as low as 10 mg/l. Vanadium as calcium vanadate can inhibit the growth of chicks, and, in combination with selenium, increases mortality in rats. Vanadium appears to inhibit the synthesis of cholesterol and accelerate its metabolism in rabbits.

Vanadium causes death to fish at low concentrations. The amount needed for lethality depends on the alkalinity of the water and the specific vanadium compound present. The common bluegill can be killed by about 6 mg/l in "soft" water and by 55 mg/l in hard water when the vanadium is expressed as vanadryl sulfate. Other fish are similarly affected.

Cadmium. Cadmium in drinking water is extremely hazardous to humans, and conventional treatment as practiced in many places is ineffective at removing it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 µg/day of cadmium.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious, progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds that might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms as well.

Cadmium acts synergistically with other metals and copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissue and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

The major source of cadmium at GFC appears to be from GTSP production processes with up to 500 mg/l found (in a 1982 water quality survey report) in both water treatment sludge and in gypsum pond tainings.

C. Impacts of Acidic Deposition

Within the last half-century there has been demonstrable acidification of some lakes and streams in North America and Eastern and Western Europe. This acidification is generally attributed to deposition of acidic sulfur and nitrogen materials derived from, in part, the burning of fossil fuels. The cause and effect relationships of acidification are not yet well understood and continue to be debated. Some scientists believe that what has been attributed solely to acidic deposition from power plant emissions is actually a combination of anthropogenic and natural processes, including acid mine drainage.

The current extent and magnitude of acidifying chemical changes in surface waters that can be attributed to atmospheric deposition are difficult to determine. Regional acidic deposition of anthropogenic origin probably began before the turn of the century and reached a peak in the early 1970s. No historical records exist of changes in atmospheric deposition, emissions of acidic precursors, or changes in surface water chemistry over the past 100 years, and relationships can only be inferred.

Recent regional surveys of lake and stream chemistry in the United States have identified water bodies potentially sensitive to acidic deposition; comparable studies and surveys are underway in Canada.

Because quantitative predictions concerning the responses of the acidification of surface waters and the loss of biological resources to acidic deposition on a national or continental scale cannot be made, impacts on aquatic biota are uncertain. Experimental studies suggest that the biological effects of long-term stress on lake ecosystems could contribute substantially to decreases in biological productivity of lakes in areas receiving acidic deposition. These effects could be disproportionate because of the nonlinearity of observed responses.

Reductions in SO_2 and NO_x emissions could contribute to an amelioration of current impacts of acidic deposition on surface waters. Recovery of water quality as emissions decline could result from both natural and human introduction of substances that neutralize acidity or increase the rate of production of acid neutralizing capacity (ANC). Because acidity reflects the balance between a watershed's production of natural ANC through weathering of rocks and soils and the input of acid-producing materials, a reduction in atmospheric deposition could alter the balance toward less acid conditions in many waters. In view of the uncertainties in directly relating changes in emissions of SO_2 and NO_x to changes in chemistry of surface waters, definite predictions cannot be made about any expected changes in water quality. Based on current scientific information, however, it can reasonably be assumed that the regional changes in water quality impacts would generally parallel the changes in SO_2 and NO_x emissions. Current research indicates further that aquatic systems could recover from the effects of acidic deposition after emissions of SO_2 and NO_x have been reduced. Uncertainties exist, however, about the rate and extent of recovery and whether recovery would result in the reestablishment of the same biological community that existed prior to acidification. Some studies indicate that the rate of recovery of biotic communities is slow.

Possible effects of acidic deposition on terrestrial ecosystems are also a concern. Current acidic deposition levels have been associated, in part, with the decline of forest productivity, especially at higher elevations in mountainous areas, changes in species composition of wetlands, and effects of habitat loss and food chain modifications on wildlife in some countries, and have been postulated to impact these resources in others. Reductions in crop yields have been related to ozone (O_3) for some crop species. Potential impacts on terrestrial ecological resources are primarily related to the continued exposure and possible long-term effects from acidic deposition. Increased SO_2 and NO_x emissions from 1989 to 2010 could contribute to greater impacts on terrestrial ecosystems, including forest damage, reduction in crop yields, and increased input of sulfur to wetlands. The increase in NO_x emissions could substantially impact growth and yields of sensitive agricultural species and enhance the formation of O_3. Reduced emissions of SO_2 and NO_x by the year 2010 could contribute to a retardation of the degradation of terrestrial resources and to improvement of the status of damaged ecosystems. The agricultural area between the power plant/GFC complex and Kattinah Lake and Homs would benefit most from SO_2 and NO_x emission reductions.

V. LATEST METHODS OF ENVIRONMENTAL IMPACT ASSESSMENT

Phosphate Industry

Environmental Impact Statement Outline

Section

1 Public policy issues and regulatory authorities bearing on the proposed action
  - A. Public policy
  - B. Public participation
  - C. Regulatory authorities

2 Proposed action
  - A. New sources
    - 1. Mining and beneficiation requirements
    - 2. Chemical processing requirements
    - 3. Additional considerations
    - 4. Relationship between areawide EIS and site-specific EIS
  - B. Existing sources
    - 1. Process modifications
    - 2. Operations and maintenance

3 Summary of primary impacts of the proposed action
  - A. Introduction
  - B. Natural environment
    - 1. Atmosphere or air
    - 2. Land
    - 3. Water
  - C. Man-made environment
    - 1. Land use
    - 2. Archeological, cultural, historical and recreational sites
    - 3. Demography, economics and cultural resources
    - 4. Resource use

4 Summary of secondary impacts of the proposed action
  - A. Natural environment
    - 1. Land
    - 2. Water
  - B. Man-made environment

5 Available minimizing and mitigative measures for the unavoidable adverse impacts
  A. Atmosphere or air
  B. Land
  C. Water
    1. Spills
    2. Dam breaks, etc. (from gypsum ponds)
  D. Recommended surveillance program
  E. General administration
6 Short-term use versus long-term productivity
7 Irreversible and irretrievable commitments of resources
8 Research needs
9 Cited references
  Illustrations
  Tables

New Sources of the Proposed Action

A.1. Mining and beneficiation requirements

- Eliminate the rock-drying operation at beneficiation plants and transport wet (6-20 % moisture) rock to chemical plants. Only rock to be used in TSP would be dried and this would be at the chemical processing plant or at driers designed for the purpose.
- Eliminate conventional, aboveground slime-disposal areas. Establish a method whereby the slimes (or slimes/tailings mixture) would be used for reclamation or some other purpose. (The need for an initial aboveground storage area is recognized as is the need for small retaining dikes around certain areas reclaimed with a slimes/tailings mixture.) If the percentage of waste clay at a mine exceeds the proportionate amount that can be utilized, the incremental amounts beyond that which can be handled by new slime-dewatering methods may be placed in a holding pond for reclamation after adequate settling.

- Provide storage that allows recirculation of water recovered from slimes. The designed storage capacity should allow for capture of 100 percent of water recovered from slimes for reuse.
- Use connector wells for dewatering the shallow groundwater from the water-table aquifer before mining, while replenishing a portion of the water pumped for purposes of transportation and beneficiation. Note following precautions: Maximum utilization of water obtained from dewatering; monitoring by industry to assure that the drained water meets recommended drinking water criteria chemically, bacteriologically, and radiologically at all times; and assurance that wells will be adequately cemented and grouted before being abandoned.
- Address radiation levels projected by mining and reclamation plans for new-source mines based on test borings of material to be encountered. The EIS should also develop a reclamation plan that considers radiation of spoils material and reduces as much as possible the amount of radionuclide-bearing material left within 3-4 feet (one meter) of the surface.
- Meet local requirements and include in the site-specific EIS an inventory of types of wildlife habitat in the area to be mined and the area immediately surrounding it. The plan will take into account the protection and restoration of habitat so selected species of wildlife will be adequately protected during mining and reclamation.
- Maintain and protect wetlands within and contiguous to rivers and streams having an average flow exceeding 5 ft^3/sec (0.2 m^3/sec).
- Make efforts to preserve archeological or historical sites through avoidance of (or mitigate by salvage excavation) any sites deemed significant by local or regional authorities.

A.2. Chemical processing requirements

- Attempt to attain air quality performance standards and design surge capacity for process water systems.
- Line gypsum ponds with an impervious material unless it can be demonstrated in the site-specific EIS that such lining is unnecessary in protecting groundwater from chemical and radiological contamination.
- Recirculate process and non-process waters. The non-process system should have the same design surge capacity as required in the standards of performance for process water systems.
- Provide for recovery of fluorides from phosphoric acid evaporators unless it is determined that market conditions are such that the cost of operation (not including amortization of initial capital cost) of the recovery process exceeds the market value of the product.
- Encourage recovery of uranium based on economic feasibility data to be included in the site-specific EIS.

A.3. Additional considerations

- Following is a list of concentrations recommended performance standards and recommended effluent concentrations on which treatment and control systems designed for new-source chemical plants should be based:

Recommended Maximum Concentrations

	24-hr max	30-day average
P	30 mg/1	10 mg/1
F	30 mg/1	10 mg/1
TSS	60 mg/1	20 mg/1
Ra-226	9 pCi/1	4 pCi/1
pH	6.0-9.5	6.0-9.5

pCi/l = picocurie per liter

Standards of Performance

	24-hr max	30-day average
P	105 mg/1	35 mg/1
F	75 mg/1	25 mg/1

Based on the conversion factor that an individual will be exposed to 1.85 µroentgens per hour of gamma radiation for each picocurie per gram of radium-226 radioactivity concentration of a surface, the maximum annual dose equivalent for continuous occupancy in the mining pit (an absurd situation) would be less than the guide for the general population. Occupational guidelines state that employees should not receive a whole-body exposure (external exposure from gamma radiation) of more than 5 rem (5000 millirem) per year or lung exposure (inhaling airborne radionuclides in the form of dust) of more than 15 rem (15,000 millirem) per year. Guidelines for the general population are one-tenth of these values.

Since mining exposes bedclays and residue matrix material in areas where the surface was previously native soil, the potential is to increase the "surface" radium-226 radioactivity concentration from 1.5 pCi/g to approximately 50 pCi/g. This adverse effect is offset somewhat by backfilling the mining cuts with waste and tailings (7.5 pCi/g) and overburden (10 pCi/g excluding leach-zone or vadose material). Areas of cuts dedicated to waste clay-slime impoundments are expected to exhibit very low background radiation, while slime particles (45 pCi/g) are covered with decant waters (1-2 pCi/l); however, as these areas dewater, background radium-226 concentrations in the surface material should approach the level given for the slime particles.

Localized increases in radiation levels may result from implementation of uranium recovery plants (modules). The levels associated with this process should be well within guidelines for workers and, with implementation of prudent protective measures, well within guidelines established for the general public.

Reduction in radiation levels will occur as dry-rock grinding is replaced by wet-rock grinding and driers are eliminated, thus lowering fugitive dust levels and escaping radionuclides, and also result in lower radiation levels in the immediate vicinity of the grinders and the eliminated driers. Based on data gathered at a Florida drier processing phosphate rock, emissions of 64.5 T/yr of particulates contained 24.5×10^8 pCi/yr of radium-226; the maximum potential lung dose outside the plant proper (that is, 400 meters from the drier) was 48 millirems per year.

EPA recommended limits on concentrations of radioactivity in drinking water are 5 pCi/l for radium-226 and 15 pCi/l for gross alpha-particle activity; 9 pCi/l for radium-226 as the effluent guideline for the phosphate industry (see two pages previous). Radon-222 is a gaseous isotope, reflecting emission of radioactivity from the soil into the air.

VI. CONCLUSIONS [11/]

From the information gathered, through investigation of the CAN, Ammonia/Urea, WPPA and GTSP production facilities and their respective wastewater treatment plants, together with interviews of the technical staff within each unit, and review of the pertinent literature on air emissions, wastewater discharges, and hazardous wastes generated from fertilizer manufacturing establishments, the following *conclusions can be made:*

- Many of the environmental problems associated with the GFC fertilizer facility stem from both feedstock and product losses. Examples include phosphate rock dust, prill tower emissions of ammonium nitrate and urea, dolomite and sulfur dust and particulates, nitric acid process tail gas and vents, ammonia and sulfuric acid fugitive emissions.
- Major facility structure degradation and environmental deterioration are being caused by acidic deposition from stack emissions of NO, NO_2, N_2O_4, SO_2, SO_3, and acid mists from nitric, sulfuric and WPPA manufacture. Downwash of the latter acid gases on stacks and nearby metal equipment is causing severe corrosion in some areas.
- Exposure to potentially harmful radioactive materials such as radium and radon in phosphate rock storage and milling areas exists and may cause detrimental health effects to workers.
- With the closure of the aluminum fluoride plant that

recovered fluosilicic acid and the fact that the phosphate rock feedstock from the Khnefis mine contains 3 % fluorine, uncontrolled fluoride emissions remain a serious problem from the human health, animal and vegetative, and material of construction perspective.

- Biuret content of prilled urea product exceeds recommended maximum allowable concentration of 1 %. Biuret possesses herbicidal properties and product quality control must be maintained.
- The oil and grease separator unit in the ammonia/urea processing area is not functioning properly, if at all. It is causing major difficulties with the design function of the cooling tower; it must be repaired and placed back into service.
- The wastewater produced from the ammonia/urea processes contains unacceptably high concentrations of NH_3-N and urea for effective treatment by the biological and ion exchange treatment systems.[12]
- Pollutional discharges (wastewater and sludges) from the GFC complex to Lake Kattinah and the Assi River far exceed the assimilative capacities of either water body as evidenced by the heavy production of undesirable aquatic organisms, including blue-green algae. The result of this pollution is algal contamination of agricultural irrigation water and lake eutrophication.
- Gypsum tailings and pond water contain both large quantities of fluorides that are currently not being recovered or controlled, are acidic, and contain radionuclides of unknown concentration.
- Hazardous wastes produced by the GFC manufacturing processes include gypsum tailings, zinc sulfide from natural gas desulfurization, sulfur fines/sludge/filter cake from sulfuric acid production, and spent catalysts such as vanadium pentoxide.

In response to the review comments, the expert made additional equipment recommendations and comments.[13]

ANNEX I

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ANNEX II

Recommended Training

The most important, positive step to ensure proper and effective environmental control at any chemical manufacturing facility is the presence of a skillfully trained technical management staff. Oftentimes, in developing nations, the intent is there to implement recommendations of the UNIDO expert, however, prevailing economic conditions may restructure priorities. In this respect, I have recommended an educational course of action for the General Fertilizer Company in addition to both specific and general recommendations made earlier in this report.

All candidates, with the exception of one--Mr. M. Alanssary--possess a rudimentary knowledge of the English language, but, with perserverence and application, each should be capable of dealing with the coursewook. Mr. Alanssary, however, not only has mastered the English language, but continues to challenge himself by writing his GFC technical log both in English and in Arabic. He was one of the few students who obtained a post-graduate diploma in Environmental Studies and Technology at Delft, Holland, in 1987. He has recently been elevated to the position within GFC of Head, Department for Environmental and Water/Wastewater Affairs. I not only fully support his participation in the recommended UNIDO-sponsored "training opportunities for industrial development" courses, but strongly recommend that he be actively considered for a UNIDO fellowship in environmental studies.

The following sections contain: (a) a listing of candidates and the recommended educational courses (selected from the "green" UNIDO training guide); and (b) the candidates' names, degrees, locations/dates, and experiences. Annex III contains the list of UNIDO-sponsored training courses, a description of the courses/curricula.

Course Title/Subject Area	Location	Selectee
Ammonia/Urea	Linz, Austria	M. Mandou
Ammonia	ditto	M. Alanssary
Ammonium Nitrate	ditto	B. Al-Salim
Nitric Acid	ditto	B. Al-Salim
Urea	ditto	M. Alanssary
Materials Testing/Chemical Plants	ditto	M. Alanssary
Fertilizer Industry	UK	M. Alanssary
Fertilizer Industry Production Technology	Sao Paulo, Brazil	A. Alsibai
Non-Waste Technology & Environmental Control	Prague, Czech.	S. Kalo
Electronic Devices and Process Controls	UK	M. Lababidi
Environmental Impact Statements	Washington, DC	M. Alanssary
Environmental Protection; Energy Management	Linz, Austria	M. Alanssary
Water Supply & Sewerage	Budapest, Hung.	F. Shullar

Name	Degree	Place and Date	Experience
			Dept. 1 year as Head, Pollution Control Dept.
Badr Al Salim	Chemical Engr.	Homs, 1980	3 years at CAN Dept. 1 year at Pollution Control Dept. 2 years at Beet Sugar factory. 2 years at Yeast Dept.
M. N. Lababidi	Chemistry	Damascus, 1965	8 years in Food Industries. 10 years at GFC. 1 year, international studies in Environmental Science and Technology, Delft, Holland.
Man Mandou	Chemical Engr.	Homs, 1981	7 years at Urea Production Dept. 1 year at Pollution Control Dept.
Fehmi Shullar	Chemical Engr.	Homs, 1979	5 years in Suga industry. 3 years in TSP Dept. 2 years in Pollution Control Dept.

Name	Degree	Place and Date	Experience
Ammar Alsibai	Chemistry	Damascus, 1975	5 years lecturer at the SPECIALIZED intermediate institutes. 2 years at PHOSPHORIC ACID department. 4 years as Head, Water and Wastewater Treatment Dept. 2 years, Director, Production at GFC.
Marwan Alanssary	Chemical Engr. Post Graduate Diploma in Envir. Stud. & Technology	Homs, 1979 Delft, Holland, 1987	2 years as SHIFT ENGINEER, Phosphoric Acid Dept. 5 years as TECHNOLOGICAL ENGR. at Water and Wastewater Dept. 1 year, international studies in Environmental Science and Technology, Delft, Holland. 2 years in Pollution Control Dept. Recently, will head, Studies Dept. for Environmental and Water-Wastewater Affairs.
Suleman Kalo	Chemical Engr.	Homs, 1980	4 years at Homs refinery. 1 year at CAN Dept. 3 years as Head, Bio-Chemical

ANNEX III

Course descriptions/curricula obtained from UNIDO "1989 Guide to Training Opportunities for Industrial Development, 17th Issue"--the "green" book.

Ammonia-urea (NPK) plants

General description: Quality control measures in ammonia-urea plants. *Commencing date:* Throughout the year except in July and August. *Duration:* 4-6 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week.

Host institution: Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Management and production in ammonia plants

General description: Organization of ammonia plants; natural gas supply; desulphurization; steam reforming; Benfield system; high pressure section; synthesis loop; trip system of single train plant; revamping of NH_3 converter; start-up and shut-down system; Argon and CO_2 liquifaction plant; computer process control system; study of diverse P and I diagrams; pilot burner and auxiliary boiler; monitoring and control system of compressors and turbines; analytical control of process steps; control loops; co-operation with technical departments; inspection and revision intervals; predictive and preventive maintenance system; planning of overhaul time; data collecting and monitoring. *Commencing date:* Throughout the year except in July and August. *Duration:* 6-8 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week. $1700/wk

Host institution: Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Management and production in ammonium nitrate plants

General description: Process steps; neutralization of ammonia with nitric acid; prilling and granulation techniques; study of P & I diagrams; supply of utilities; initial signal and shut-down systems; process control system; start-up and shut-down procedures; off-gas treatment. *Commencing date:* Throughout the year except in July and August. *Duration:* 4 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week.

Host institution: Chemserv Industrie GmbH
St. Peterstrasse 25
4021 Linz, Austria

Management and production in nitric acid plants

General description: Organization of nitric acid plants; ammonia evaporation and combustion; nitrous gases compression and absorption; cooling of absorption tower; start-up and shut-down procedures. *Commencing date:* Throughout the year except in July and August. *Duration:* 4 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week.

Host institution:
Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Management and production in urea plants

General description: Organization of urea plants; modification of urea prills; corrosion problems and other problems faced in urea plants; data collecting and monitoring. *Commencing date:* Throughout the year except in July and August. *Duration:* 4 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week.

Host institution:
Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Material testing, corrosion problems, inspecting and overhauling chemical plants

General description: Material testing; metallography; laboratory; inspection and revision. *Commencing date:* Throughout the year except in July and August. *Duration:* 4-6 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* S 24,000 per week.

Host institution:
Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Fertilizer industry

General description: Production planning and plant management. Latest techniques of process controls, ammonia synthesis, nitric acid and ammonium nitrate technology; instrumentation technology; pollution control, water preparation; health and safety maintenance of plant. *Commencing date:* To be arranged. *Duration:* 3 months. *Qualifications:* Professional qualifications. Good English. *Last date for receipt of applications:* 1 month before commencing date. *Fee:* To be arranged.

Host institution:
Chattaway (UK) Training Services
Pool Chambers
26 Dam Street
Lichfield, Staffordshire WS13 6AA, United Kingdom

Fertilizer production technology

General description: Structure of fertilizer industry; nitrogen fertilizers; phosphate fertilizers; potash fertilizers; compound fertilizers; organic and organic mineral fertilizers; secondary and micronutrients; physical properties of fertilizers; environmental factors on fertilizers production. *Commencing date:* 8 October 1990. *Duration:* 5 days. *Qualifications:* Chemists, engineers, economists. English, Portuguese. *Last date for receipt of applications:* —. *Fee:* $US 500.

Host institution:
Centro de Estudos de Fertilizantes (CEFER)
Instituto de Pesquisas Tecnológicas do Estado de São Paulo
SA (IPT)
C.P. 7141
Cidade Universitária
05508 São Paulo, São Paulo, Brazil

Non-waste technologies and environmental control

General description: Influence of industrial technologies on environment; industrial wastes and waste recycling technologies; secondary raw materials and energy recovery; environmental management; low-waste and non-waste technologies; treatment of toxic wastes; municipal solid wastes processing; information and control systems for environment; advanced technology development trends. *Commencing date:* October 1990. *Duration:* 2 weeks. *Qualifications:* Industrial, environment or chemical engineers; at least 3 years of experience in environmental control. English. *Last date for receipt of applications:* 30 June 1990. *Fee:* —.

Host institution:
UNIDO
Czechoslovakia Joint Programme for Co-operation
Metallic Industries
INORGA Institute
Letenská 17
118 06 Prague 1, Czechoslovakia

Electronic devices and process control

General description: Short courses on: fundamentals of electronic measuring devices; basic electronics in instrumentation; introduction to process computers; process measurement technology; process control technology; industrial boiler control systems; fundamentals of mechanical and pneumatic instrumentation. *Commencing date:* To be arranged. *Duration:* 1-2 weeks. *Qualifications:* Instrument engineers and senior technicians. English. *Last date for receipt of applications:* 4 weeks before commencing date. *Fee:* £350-£500.

Host institution:
Foxboro Great Britain Ltd.
Redhill, Surrey RH1 2HL, United Kingdom

Environmental impact analysis

General description: Topics discussed include: designing Environmental Impact Analysis (EIA); making EIA cost-effective; simplifying assessment and evaluation methodologies; implementing EIA. *Commencing date:* 1 May 1989. *Duration:* 2 weeks. *Qualifications:* Bachelor's degree or equivalent. English. *Last date for receipt of applications:* 1 month before commencing date. *Fee:* $US 1,500.

Host institution:
International Institute for Development
Graduate School, USDA
600 Maryland Avenue, S.W., Suite 134
Washington, DC 20024, United States of America

Environmental protection, energy management and optimization

General description: Energy control; single train unit (NH_3); gas compression; urea plant; environmental protection, safety aspects; air pollution; water pollution; waste water control and purification; fire brigade; alarm system; storage of combustible and inflammable material; use of solvents. *Commencing date:* Throughout the year except in July and August. *Duration:* 6 weeks. *Qualifications:* Professional qualifications. English. *Last date for receipt of applications:* To be arranged. *Fee:* $ 24,000 per week.

Host institution:
Chemserv Consulting GmbH
St. Peterstrasse 25
4021 Linz, Austria

Water supply and sewerage

General description: Water supply and sewerage in water management; hydrology and hydraulics; control of water quality; access to underground waters; the technologies of well boring; water purification; arrangement of power rooms in waterworks, their operation; operation of water distributing networks; automation of waterworks; desinfection and its methods; industrial water supply; pumps and compressors, their operation and maintenance. *Commencing date:* To be arranged. *Duration:* 6 months. *Qualifications:* Medium-level qualifications. English, Arabic or to be arranged. *Last date for receipt of applications:* To be arranged. *Fee:* To be arranged.

Host institution:
International Training Centre, Vép
in collaboration with
Organization for International Technical and Scientific Co-operation (TESCO)
Rosenberg hsp. utca 21
1051 Budapest, Hungary

ANNEX IV

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General Interest

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NOTES

1/ Actual production figures were not made available to the expert for comment, although, on several occasions, the request was made. The expert's opinion is that such figures were not really available and were not purposefully withheld. However, noting that fact that it was a rare occasion when the complex was fully operative and the fact that the General Establishment of Chemical Industries (GECI) admits to "low capacity utilization, high losses, high energy consumption and low quality products, ... reaching in certain cases to 33% of the nominal production capacity," it is probably reasonable to assume this figure as a good "guesstimate" of current production capacity in lieu of a completely unsubstantiated estimate.

2/ During the inspection tour of the seven production units employed at GFC, namely, nitric acid, ammonium nitrate (and CAN), ammonia, urea, sulfuric acid, phosphoric acid (WPPA), and triple superphosphate (GTSP), there were so many notable fugitive emission sources that were redundant that the expert decided that a grouping of sources would prove more beneficial with a thorough explanation of generic sources identification (see Fugitive Emissions Control section, pp. 54/56), followed by listings of technology methods for control of inorganic vapors (see Table 12, p. 55) and organic vapors emitted from pumps, valves, pipes, compressors, and connections (s Table 13, p. 57).

3/

Table 1 would gain more usefulness if actual emission rates (measured) from GFC unit processes were convertible to the same unit system displayed in the table. However, two major problems exist here: (1) As explained in the new Preface, there are an absolute paucity of <u>measured</u> emissions data (in most cases, there are no data), and (2) the existing emissions data is probably no more accurate than $\pm$ 100%. To give an impression of how serious the uncontrolled emissions problem is, consider the following:

- Total NO_x ($NO + NO_2$)(Figure 2, p. 15) tail gas concentration = 0.17% or 1700 ppm (sample taken 22 June 1989), compared to the Air Quality Primary Standard for NO_2 (from Table 1, p. 17), annual arithmetic mean, of 0.05 ppm. This amounts to an uncontrolled emission in the nitric acid process unit of 34,000 times that permitted.

- SO_x (SO_2 + SO_3)(Figure 6, p. 33) emission concentration = 0.053% or 530 ppm, compared to the Air Quality Primary Standard for SO_2 (from Table 1, p. 17), annual arithmetic mean, of 0.03 ppm or for 24-hours, 0.14 ppm. This amounts to an uncontrolled emission in the sulfuric acid process unit of 17,700 (for annual arithmetic mean) or 13,250 (for 24-hour period) times that permitted.

In other words, if one assumed the two measurements were reasonably accurate, then the levels of these two criteria pollutant emissions alone are sufficient cause for alarm, based on the health issue alone, not to mention acidic deposition and its inherent environmental effects.

4/ Using data on ammonium nitrate (AN) provided by the Head, AN Pollution Control Unit, AN particulate emissions amounted to:

Mixer	0.035	T/hr
Drier	0.112	"
Cooker	0.030	"
Bagging	0.036	"
Total	0.213	T/hr

The prill tower (with a 10 meter diameter and cover and 300,000 Nm^3/hr air upflow) emissions are estimated to be 150% of the sum of the listed four sources or 0.3 T/hr of AN. Hence, the total uncontrolled AN particulate emissions sum to 0.5 T/hr. Plotting data from Table 3 (p. 22) and using the design capacity of 480 T/d for the AN production, one obtains an AN emission rate of 13.5 kg/hr. AN emissions from individual sources have been found to range from 0.03 to 147.2 kg/T of AN produced for the granulation technique; however, limits on particulate emissions from AN facilities are usually based on the facility's production rate, which would be 0.675 kg/T of AN. In the case of the CAN unit at GFC, the AN emission rate is 0.5 T/hr or 500 kg/hr, which calculates to 25 kg/T of AN produced, significantly higher than 0.675 kg/T and indicative of a major product loss to the atmosphere.

5/ No recorded information available regarding quality/quantity of process condensate, steam, or emissions. Only information available regarding effluent or wastewater was indirect from the wastewater treatment plant supervisor, who stated that the combined wastewaters from the ammonia and urea units was of low volumetric rate, 20 m^3/h, and high strength, up to 1,000 mg/l NH_3 and 16,000 mg/l urea (the latter represents a major product loss of urea if not an aberration). Additional indirect information comes from the Hungarian engineer from the Central Research Institute for Chemistry in Budapest, who was conducting cooling tower corrosion inhibitors and algicides testing: Ammonia unit rarely up for two consecutive days. Pumps all leaking; no spares that are operable; corrosion evident. Those pumps disassembled showed excessive corrosion, impeller erosion/pitting, very little if any preventative maintenance. On one accasion, the engineer asked a GFC engineer what the delta-T was across the high pressure heat exchange unit, and the GFC engineer replied it was 0.5 °C, but did not comprehend that there was no heat exchange with a delta-T equal to 0.5 °C. Disassembly of the heat exchanger showed that four tubes has literally exploded because the low pressure side was plugged with globs of oil & grease, which had not been removed from the cooling water because the oil & grease separation unit has not been operable for two years. The Hungarian engineer thought that the GFC engineers simply had little motivation to report obvious problems, correct such problems or were aware of the seriousness of such problems. Regarding corrections to these and similar problems, see Specific Recommendations 10, 11, 12, and 14 and General Recommendations 1, 2, 3, and 7.

6/ The condensed, unreacted steam from the ammonia unit is recycled and reused, but a blowdown (estimated at less than 25% of total) is pumped to the ammonia-urea wastewater treatment plant. Since the installed biological treatment is not functional, that is, the nitrification/denitrification treatment unit (see pp. 77-79 on operational requirements for such a facility), this blowdown is treated in the ion exchange train, which comprises solids removal through clarification-sedimentation, followed by diatomaceous earth polishing to remove fine solids, followed by a sequence of cation-anion-mixed bed ion exchange, whereupon the deionized water is recycled to the ammonia unit condensers/boilers as makeup.

7/ Prill tower losses observed were high--no measurements. The emission data shown in the Figure were not measured, but represent design figures. But, based on the prill tower urea particulate emission (design) of 0.54 T urea/d and assuming full production of 1050 T urea per day, one can calculate an emission factor of 0.514 kg/T of urea product for this size of production unit, which is 20% higher than the allowable particulate emission factors by plant size shown in Table 6, p. 31 (which is about 0.40) and this is based on design. (See also Table 11, p. 55, for emissions control effectiveness.)

8/ ________________. The two scrubbers used in conjunction with the granulator and drier particulate emissions were inoperable and appeared not to have utilized for some time. Only one of three batch reactors were in operation. The TSP reactor scrubber, although in the operating mode, did not appear to be removing effectively any particulates or emissions--it was noisy and was covered with thick layers of TSP particulates and dustand was overdue for badly needed maintenance and repair. As to the scrubber type, it was impossible to determine because of the dust and clutter. Figure 8 demonstrates that, at least when measurements of TSP dust and SiF_4 were made, each was excessive.

9/ The methods listed in this section are reflected in the recommendations, as follows:

	Recommendation
Fluoride Emissions/Control Techniques	S6, S9
Process Changes--Wet-Rock Grinding	S7
Process Changes--Simplot Limestone	S9
Process Changes--Hemihydrate	S9
Fabric Filters for AN and Urea	S3
Wet Scrubbing--Wetted Fibrous Filters	S1, S2, S3
Fugitive Emissions Control	S4
Storage Piles--Wind Erosion/Dust Control	S5
Acid Gases Reduction	S1, S2, S15

10/ All three raw water treatment facilities at GFC appear to be state-of-the-art, including the biotreatment unit for ammonia-urea-domestic wastewater (although the Roumanian operators manual contains some contradictory instructions and procedures). The problem involves lack of routine maintenance, spare parts, motivation of operators and engineers, and just plian good housekeeping. Staff must be apprised of current methods of sampling, sample preservation, the differences between grab and compositie samples, quality assurance/quality control, standard methods of analysis; the support laboratories must have some reasonably contemporary equipment, and must be properly trained and routinely certified; and finally shift engineers must keep staff motivated. The ultimate responsibility for this motivation is the senior staff and the policies it pursues (see General Recommendations G1, G2, G3, and G5).

11/ Cross-reference between Conclusions and Recommendations:

Conclusions, subject	Counterpart Recommendations
Feedstock and product losses	(See S1, S2, S3, S4, S7, S15, G1)
Acidic deposition	(See S1, S2, S6, S14, S15)
Radioactivity	(See S6, S7, S9, S14, S15, G7)
Fluoride emissions	(See S5, S6, S7, S9, S13, S14, G1, G6, G7)
Biuret in urea	(See S8)
Oil & grease	(See S10)
Biotreatment plant	(See S12)
Wastewater influent	(See S11, S12, G2, G3, G5)
Wastewater treatment sludges	(See S11)
Gypsum tailings	(See S6, G6)
Hazardous wastes	(See S5, G1)

12/ Currently, the biotreatment unit is shut down because it is unable to process low volume, high strength wastewater from the ammonia-urea process units. Pages 77-79 are an attempt to indicate to the reader the chemistry, biochemistry and other information needed in order to operate such a unit properly. GFC has the pilot plant data somewhere; it merely needs to be read, interpreted, and utilized properly by trained operators and engineers. The expert did not come away with the impression that there was any coordinated or communicative effort between production engineering and wastewater treatment staffs.

13/ Equipment Recommendations. I strongly urge UNIDO to provide funding to purchase the following items for GFC (from the ~$ 7K budget):

- Geiger-Muller counter, portable--to conduct a survey of potential radioactively contaminated "hot spots" in and around the phosphate rock storage and grinding operations, within the WPPA and GTSP process units, and in the vicinity of the gypsum pond/spoils area near Lake Kattinah and the currently employed disposal site 40 km south near the Damascus highway.
- Rad safety badges (total-body-count types) for personnel--these can be worn attached to the trousers, collected and monitored or "read" monthly to record any high levels of human exposure.
- pH meter, portable, battery-operated (with spare batteries) for instantaneous pH readings (also need standard pH buffer solutions--pH 4, 7, 11, e.g.) for daily calibration.
- Specific ion electrodes for special cations/anions (can be used in conjunction with the pH meter)--for PO_4^{-3}, F^-, Cd^{+2}, $SO_4^{=}$, Cl^-.

Additional Commentary

This expert strongly believes that a SAR UNIDO experts briefing/debriefing symposium should be held (with at least one-half of the total membership present) in order to discuss the pros and cons of the umbrella project, the good and the bad experiences of each expert, benefits of the UNIDO program, report preparation, and finally go through an exercise known as "brainstorming" or how to improve the current process. The site, of course, should be at UNIDO headquarters in Vienna and should occur prior to termination of the assistance project with the SAR.

Additionally, training of SAR counterpart personnel utilizing UNIDO-sponsored special cources relative to the fertilizer production and other specials areas of concern, followed by actual on-site manufacturing facility exposure and experience, and finally attendance at international coferences, meetings, and symposia should be rountine.

AVERAGE DAILY EFFLUENT FLOW RATE OF 8 m^3/h — DOMESTIC WATER TREATMENT

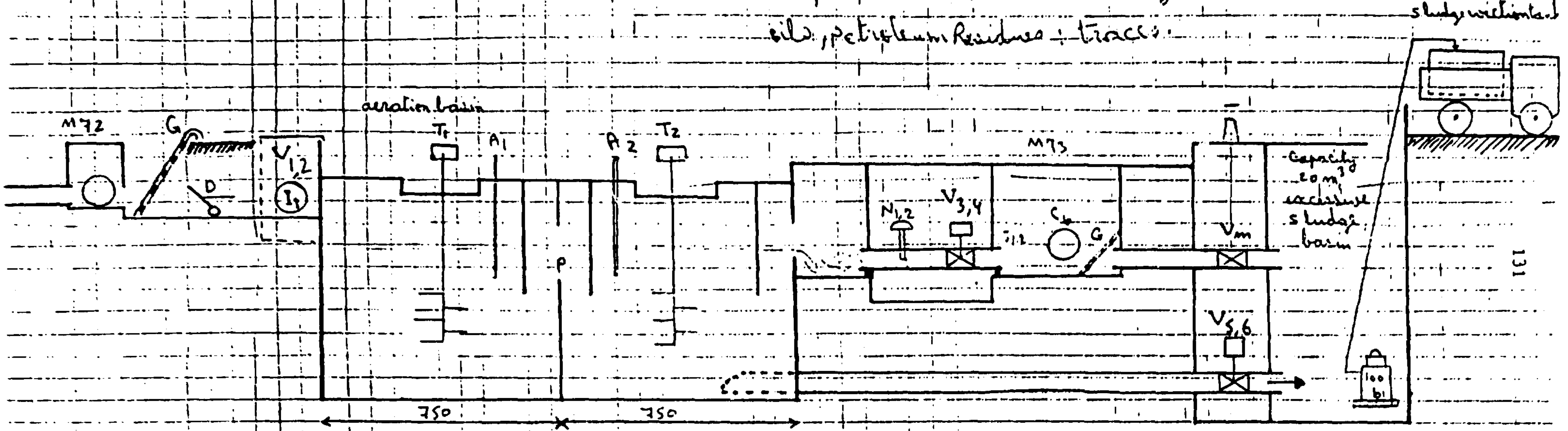
in fluent CHARACTERISTICS at the station ~~outlet~~ inlet : PH = 6.5 - 8.5 — BOD_5 = 400 mg/L

Suspended matters = 350 mg/L

TREATED WATER CHARACTERISTICS : PH = 6.5 - 8.5 — BOD_5 = 20 - 30 mg/L

Suspended matters 25 - 50 mg/L

oils, petroleum Residues : traces.



Major Pollutants of Concern Versus Unit Process/Source

	NO_x	SO_x	Particulates	Radioactivity	Fluoride	Phosphorus	Wastewater	Hazardous Waste	
HNO_3	X						X		
CAN			X				X		
NH_3	X	low					X	X	
Urea			X				X		
H_2SO_4		X					X	X	
H_3PO_4			X	X	X	X	X	X	
GTSP		X	X	X	X	X	X	X	
Phos Rock		X	X	X	X	X			
Power Plant	X	X	X				X	X	