INDUSTRIAL HYGIENE CHARACTERIZATION OF THE PHOSPHATE FERTILIZER INDUSTRY

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DISCLAIMER

ABSTRACT

The National Institute for Occupational Safety and Health (NIOSH) performed in-depth industrial hygiene surveys at five locations to characterize occupational health hazards in the phosphate fertilizer industry. Four fertilizer plants (plants A-D) and one phosphate ore mining and beneficiation facility (plant E) were selected. Measurements were conducted for floride, sulfuric acid, phosphoric acid, cadmium, chromium, uranium, vanadium, arsenic, respirable free silica, and respirable quartz. All results for all locations were below applicable OSHA standards except for fluoride (3.39 mg/m^3) at plant C and for arsenic (.08 mg/m^3) vanadium (.08 mg/m^3) and respirable silica (0.195 mg/m^3) at plant D. Area samples at the beneficiation operation revealed levels above the applicable OSHA standards for uranium (.228 mg/m^3). Arsenic levels (.003 mg/m^3) at this location exceeded the NIOSH recommended standard, while the respirable silica (.07 mg/m^3) and respirable dust (1.62 mg/m^3) exceeded both OSHA standards and NIOSH recommended standards. Chromium levels at Plants A-E exceeded NIOSH recommended levels for carcingoenic chromium (VI), however, the oxidation state of these samples was not determined and an assessment of levels of Chromium VI cannot be made at this time. This report includes recommendations for further sampling for Chromium (IV) as well as the establishment and enforcement of an agressive personal protective equipment program for all workers.

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INTRODUCTION

In early 1974, it was reported to the National Institute for Occupational Safety and Health (NIOSH) that three cases of lung cancer had been found in workers at a phosphate fertilizer plant in central Florida. The three cases were alleged non-smokers, who had held the same job for approximately the same period of time. The three men periodically entered reactor vessels to clean out the calcium sulfate ($CaSO_4$) precipitate which is a by-product of phosphoric acid production.

Plant selection for the study of the phosphate fertilizer industry concentrated on those facilities located near the central Florida phosphate fields where the health problem had been reported. One Western phosphate operation was chosen to explore differences due to geographical location. The primary operation studied was the production of phosphoric acid from phosphate rock and sulfuric acid. Other processes investigated at the chemical facilities included the production and ammoniation of superphosphates. Also, one mining operation and associated beneficiation facility was studied to explore exposures in the mining phase of the industry and to obtain data for comparison with processing plant data.

The particular task of most concern in the fertilizer plants was the attack vessel (reactor) cleaning operation. Reactor cleaning is performed by workers who enter the reactor to chip away the gypsum deposited on the agitator and side walls using manual and pneumatic equipment. The gypsum is removed, loaded into a bucket, and hoisted out of the reactor. The cleaning procedure is usually performed on an annual basis, requiring three to five days to complete.

This report presents the results of sampling activity at the selected locations. At four processing plants, personal and general area samples were collected and analyzed for phosphoric acid mist, sulfuric acid mist, particulate and gaseous fluoride, cadmium, chromium, vanadium, uranium, arsenic, respirable silica, and respirable dust during the reactor cleaning operations. Radon gas and beta radiation levels were measured at one reactor, and radon daughter samples were collected at two other reactors. Noise levels were measured at one reactor.

At the one beneficiation facility surveyed, personal and general area samples were collected and analyzed for fluoride, cadmium, chromium, vanadium, uranium, arsenic, respirable silica, and respirable dust. Radon daughter levels were also measured.

Description of Processes

Mining

The sources of phosphate for the Florida phosphate fertilizer industry are the hard rock phosphates located on the west side of Florida (extending from Suwannee and Columbia counties in the north to Hernando county in the south), and the land-pebble phosphates found in Manatee, Hardee, Hillsborough, and Polk counties. Hard rock phosphates are strip mined and the ore is transported by side dump cars to a central beneficiation plant. Land-pebble phosphate ore is strip mined and stacked in a suction well or sluice pit, where it is slurried with high pressure water. It is pumped to a beneficiation plant in its matrix of clay slimes and silica sand.

Western phosphate rock is found in portions of Idaho, Montana, Nevada, Utah, and Wyoming, with high-grade ore located primarily in southeastern Idaho. Western phosphates are mined by surface stripping where possible, or by underground mining. There are also deposits of phosphate-bearing ore in North Carolina, Kentucky, Arkansas, and Virginia. Except for North Carolina, these deposits are generally low-grade ore and are difficult to mine.

Beneficiation

Beneficiation is a process of separating phosphate ore from its clay and sand matrix, and then concentrating the fines which contain phosphate. Beneficiation is accomplished by the use of hammer mills, vibrating screens, dewatering, and concentration and flotation devices, resulting in the following products: coarse rock, regular rock, and concentrated fines. The coarse rock is usually sold or reserved for high grade use, while the regular rock and concentrate are used for fertilizer manufacture. The fertilizer industry uses 85 to 90% of all phosphate shipments from the Florida fields.

Phosphoric Acid Production

The wet process production method was used at all facilities studied; over 75% of the phosphoric acid manufactured in the United States is produced by this method. The wet process consists of digestion of phosphate ore with strong acid (usually sulfuric acid) to convert the phosphate from practically insoluble forms to water soluble forms. The production of phosphoric acid is the initial step in the manufacture of phosphate fertilizers (see Figure 1, Appendix B).

The term "phosphoric acid," as used in the fertilizer industry, refers to phosphorous pentoxide (P_2O_5). In chemical manufacturing, orthophosphoric acid (H_3PO_4) is commonly known as phosphoric acid. The strengths of orthophosphoric acid, phosphate rock, and phosphate fertilizers are usually expressed in terms of phosphoric acid (P_2O_5). The availability of phosphates in fertilizer is designated by the American Association of Official Agricultural Chemists as the amount of phosphate soluble in a neutral ammonium citrate solution (1).

The principal mineral constituent of phosphate ore is fluorapatite, $Ca_5(PO_4)_3$ (OH, F, Cl). The ore is a complex mixture of compounds, including a variety of compounds of calcium, phosphorous, fluorine, chlorine, iron, aluminum, silicon, arsenic, chromium, vanadium, and uranium. The wet process method consists of decomposition of the phosphate ore with sulfuric acid in a reactor vessel to convert the calcium phosphate constituent to orthophosphoric acid and calcium sulfate.

The chemical reactions which take place can be symbolized by the following series of equations:

(1) $Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$

This is the primary reaction, converting the calcium phosphate to orthophosphoric acid and calcium sulfate

(2) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

The calcium fluoride constituent of the ore is converted to calcium sulfate and hydrogen fluoride

(3) $CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF$

Calcium fluoride also reacts with orthophosphoric acid to form monocalcium orthophosphate and hydrogen fluoride

(4) $6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$

Hydrogen fluoride combines with silica to produce fluosilicic acid and water

(5) H_2SiF_6 + heat and/or acid $\rightarrow SiF_4 + 2HF$

In the presence of heat and/or acid, fluosilicic acid decomposes to tetrafluorosilane and hydrogen fluoride

(6) $3\ SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$

Tetrafluorosilane reacts with water to regenerate fluosilicic acid and silica

(7) Fe_2O_3 (or Al_2O_3) $+ 2H_3PO_4 \rightarrow 2FePO_4$ (or $AlPO_4$) $+ 3H_2O$

Oxides of iron (or aluminum) are converted to their phosphates

(8) $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

Calcium carbonate reacts with sulfuric acid to form calcium sulfate, carbon dioxide and water

In orthophosphoric acid production by the wet process method, beneficiated phosphate ore and concentrated fines are fed into the reactor vessel, where they are mixed with sulfuric acid and recirculated phosphoric acid slurry (see Figure 2, Appendix B). The process can take place in a series of four or more agitated reactor tanks through which the reaction slurry flows by gravity, or in a single, multicompartment reactor tank. In either case, the contact time between the phosphate ore and sulfuric acid is 4 to 8 hours. The product slurry is split into two streams, one of which is recycled to the reactor tank. The other stream is filtered to remove the crystalline calcium sulfate (gypsum). The product acid from the wet process method is approximately 30% P_2O_5 and is concentrated to 40 to 55% by vacuum concentrators or submerged combustion chambers. The concentrated acids are necessary for use in other manufacturing processes, including fertilizer production.

The primary objective of the reactor is to obtain the maximum extraction of orthophosphoric acid with production of easily filterable calcium sulfate. The calcium sulfate precipitate which deposits on the walls and agitator of the reaction vessel is removed approximately once per year, as previously described.

Phosphate Fertilizer Production

The three major types of phosphate fertilizers are normal superphosphate, triple superphosphate, and ammonium phosphates. Manufacturing processes and characteristics of each type are described below.

The term superphosphate is generally applied to the product obtained when finely ground bone or phosphate rock is treated with sulfuric acid. The reaction process converts insoluble phosphate rock (containing tricalcium phosphate) to a mixture of calcium sulfate and hydrated monocalcium phosphate, $CaH_4(PO_4)_2\ H_2O$. The primary chemical reaction is symbolized by the following equation:

$$CaF_2\ 3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O \rightarrow 3CaH_4(PO_4)_2\ H_2O + 2HF + 7CaSO_4$$

In superphosphate manufacture, the mixture of 65 to 75% sulfuric acid and phosphate rock moves from the mixer (where the reactions begin) to a closed chamber or den where the acidulation of the phosphate rock continues. The material is excavated from the den after 1 to 24 hours, and conveyed to storage piles where it cures and dries for 2 to 4 weeks. After curing, the superphosphate fertilizer is bagged or shipped in bulk. The product typically contains 18 to 20% available P_2O_5 (see Figure 3, Appendix B).

Triple superphosphate is a concentrated fertilizer, containing 44 to 51% available P_2O_5. It is produced by acidulation of phosphate rock with 45 to 55% orthophosphoric acid, as shown in the following reaction:

$$CaF_2\ 3Ca_3(PO_4)_2 + 14\ H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$

The reaction takes place in a granulator where phosphate rock and orthophosphoric acid are mixed and granulated. The product is cooled, screened, and conveyed to bulk storage for 1 to 2 weeks of curing (see Figure 4, Appendix B).

Ammomium phosphate fertilizers are produced by the ammoniation of orthophosphoric acid or superphosphates. The resulting fertilizers supply phosphorous and nitrogen. When orthophosphoric acid is ammoniated, the primary products are monoammonium phosphate, $NH_4H_2PO_4$, and diammonium phosphate, $(NH_4)_2HPO_4$. Ammoniation of superphosphates produces mono-or diammonium phosphate, and di-or tricalcium phosphate, depending upon the reaction conditions. Ammoniation is accomplished by spraying anhydrous ammonia, ammonia solutions, or solutions of urea and ammonium nitrate into the solid phosphate material. After mixing in the ammoniator, the material is dried, cooled, and bagged or shipped in bulk (see Figure 5, Appendix B).

Description of Facilities

Plant A

This plant represented the phosphate fertilizer industry in the western phosphate fields. It was built in 1954 and consists of five main operating units: crushing and grinding, phosphoric acid plant, triple superphosphate unit, diammonium and monoammonium phosphate unit, and storage facilities. There are approximately eighty production workers divided among the three shifts. The major products are phosphoric acid (52% P_2O_5), superphosphoric acid (68% P_2O_5), hydrofluosilicic acid, diammonium phosphate, monoammonium phosphate, and triple superphosphate. The raw materials are phosphate ore, sulfuric acid, and anhydrous ammonia.

Employees are provided with safety glasses and hard hats. The employees are not required to wear safety shoes; however, the company will pay 60% toward the purchase of safety shoes. Respiratory protective equipment consists of NIOSH-approved self-contained breathing apparatus, gas masks, and dust and chemical cartridge half masks. Respirators with appropriate cartridges were used while working inside the reactor vessel during the cleaning operation.

Plant B

This plant began operation in 1964 and consists of six main operating units: crushing & grinding, sulfuric acid plant, phosphoric acid plant, triple superphosphate production facility, mono-ammonium phosphate and diammonium phosphate unit, and storage and drying area. There are 271 persons employed in the production of phosphoric acid (54% P_2O_5), triple superphosphate, and fluosilicic salts and acids.

The plant employs a safety engineer and operates an active safety program. Employees are provided with safety glasses and hard hats and are required to wear safety shoes which are purchased at their expense. Respiratory protective equipment consists of Scott Air Packs, White Cap units, NIOSH-approved half-mask respirators with acid gas cartridges, and disposable dust respirators for nuisance dust.

Plant C

This plant began operating in 1953, and significant modifications have been made every several years, with the latest made in 1975. The facility consists of twelve major operating areas: sulfuric acid plant, phosphoric acid plant, acidulation plant, 3 diammonium phosphate plants, 2 product storage areas, 2 shipping areas, operations and staff offices, and the quality control laboratory. The plant employs approximately 400 persons in the production of diammonium phosphate and dicalcium phosphate. The primary raw materials include ground phosphate rock, liquid sulfur, and anhydrous ammonia.

A safety supervisor is responsible for the safety program and periodic sampling for sulfur dioxide, noise, ammonia, and fluoride. The safety program provides personal protective equipment, safety showers, eye wash fountains, and first aid and job training programs.

Plant D

This plant was opened in 1945 and consists of nine major areas: sulfuric acid plants, wet phosphate rock storage, phosphate rock dryer, phosphate rock grinding, sulfuric acid storage, diammonium and monoammonium phosphate plants, granulated triple super phosphate plants, bulk storage and shipping, and laboratory and main offices.

There are approximately 325 persons employed in the production of granular triple phosphate, diammonium phosphate, monoammonium phosphate, and orthophosphoric acid. The company's raw materials are sulfur, phosphate rock, and anhydrous ammonia.

A full-time safety supervisor directs the use of safety equipment (clothing, glasses, shoes, and respirators) and directs the maintenance of safety showers and eye baths. The environmental engineering staff periodically samples for sulfur dioxide, particulate, and fluoride emissions, and collects vegetation samples for analysis of possible fluoride contamination.

Plant E

This plant is representative of mining and beneficiation operations in Florida. It was opened in 1948 and has been continuously updated. The beneficiation plant consists of seven major buildings: washing, screening and floatation; drying and grinding; maintenance and warehouse; process engineering, research and development, and environmental services; quality control; administrative operations; and fabrication and tractor shop. There are a total of 1620 employees in the mining area and beneficiation facility. The ore mined generally is 64 to 78 bone phosphate of lime (BPL) from phosphate rock. Bone phosphate of lime is an expression for the percentage of tricalcium phosphate in the ore.

A safety supervisor and an assistant carry out the safety program with the assistance of representatives from the production areas. The industrial hygiene program is conducted by the environmental engineering staff, who do periodic sampling for sulfur dioxide, fluoride and particulates. In addition, film badges are located throughout the plant to assess radiation levels.

Description of Survey Methods

Phosphoric Acid

Phosphoric acid mist samples were collected at a flow rate of 2.0 liters per minute (lpm) by a MSA Model G sampling pump using 37-mm AA Millipore filters, 0.8-μm pore size, as a collection media. The sampling duration varied from 4 to 8 hours. The phosphoric acid was analyzed using a heteropolyblue colorimetric method, NIOSH Method No. S333 (8).

Sulfuric Acid

Sulfuric acid mist samples were collected in the same manner as phosphoric acid mist. Analysis was performed by titration with barium perchlorate, NIOSH Method No. S174 (8).

Fluoride

Total fluoride samples were collected with a midget impinger containing 10 ml of 1 molar sodium acetate and a MSA Model G pump operated at a flow rate of 2.0 lpm. Particulate fluoride samples were collected on a 37-mm, 0.8-μm Millipore filter using Model G pumps as previously described. Gaseous fluoride was determined by sampling with an impinger (as described for total fluoride) preceded by a membrane filter. Analysis was performed by specific ion electrode, NIOSH Methods P&CAM 117 and 212 (8).

Heavy Metals

Heavy metals were collected at a flow rate of 2.0 lpm by a MSA Model G sampling pump using 37-mm, AA Millipore filter, 0.8-μm pore size, as a collection media. The sampling duration varied from 4 to 8 hours. The analysis was done using atomic absorption spectroscopy, NIOSH Method No. P&CAM 173 (8).

Uranium

Uranium particulate was collected on glass fiber filters for at least 4 hours using a high volume sampler at a flow rate of 45 lpm. Samples were analyzed by the Dibenzoylmethane method. This method is a slightly modified version of a procedure developed by

Western Nuclear, Inc. This procedure is based upon a method developed by Francois, and published in Analytical Chemistry, 30, 50 (1958). The method is best suited to the determination of U_3O_8 in the range of 0.002 to 1 percent.

Respirable Dust and Free Silica

Respirable dust samples were collected at a flow rate of 1.7 lpm using 37-mm PVC filters (5.0-µm pore size) attached to 10-mm nylon cyclones and MSA Model G pumps. Samples were collected for approximately 8-hour periods. NIOSH Method No. P&CAM 109 was used to determine the percentage of free silica (quartz, cristobalite and tridymite) on each filter, and the total mass of particulate on each filter was determined gravimetrically (8).

Radon and Radon Daughters

Initially, radon gas samples were collected in 1-liter evacuated flasks. Air was drawn through the flask for 5 minutes to make certain no residual air remained in the flask. The samples were sent to the EPA Regional Health Unit in Las Vegas, Nevada for analysis.

Later in the study, radon daughters levels were determined by collection of an air sample at the rate of 10.8 lpm for 5 minutes through a glass fiber filter. After waiting 40-90 minutes the alpha radiation present was measured using an alpha-scintillation detector and counter.

Noise

Noise levels were measured on the A-weighted scale using a General Radio Model 1565-B sound level meter.

Criteria For Evaluations

The current Occupational Safety and Health Administration (OSHA) permissible concentrations (2), NIOSH-recommended exposure limits (3), and American Conference of Governmental Industrial Hygienists Threshold Limit Values (TLVs) (4) for materials of interest in this study are presented in Table 1.

Table 1
Criteria for Evaluation of Exposure

Substance	OSHA Standard	NIOSH Exposure Limit	ACGIH - TLV (1980)
	All concentrations in mg/m^3 unless otherwise noted		
Fluoride (F)	2.5	2.5	2.5
Sulfuric Acid (H_2SO_4)	1.0	1.0	1.0
Phosphoric Acid (H_3PO_4)	1.0		1.0
Cadmium (Cd)	0.2 (dust)	0.04	0.05
Chromium (Cr)		Note 1	
soluble salts	0.5		0.5
metal, insoluble salts	1.0		0.05
Uranium (U)			0.2 (all natural compounds)
soluble cpds	0.05		
insoluble cpds	0.25		
Vanadium (V)		1.0	
V_2O_5 dust	0.5	0.05 (ceiling)[2]	0.05[3]
Arsenic (As)	0.01	0.002 (ceiling)	0.5
Respirable Free Silica		0.05	
Respirable Quartz	$10/\%SiO_2+2$		

Notes
1. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: they are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than chromium (VI). NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to 0.001 mg/M^3 and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to 0.025 Cr (VI) mg/M^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.05 Cr (VI) mg/M^3 averaged over a 15- minute period. It is recommended further that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromium (VI) and Chromic Acid should be consulted for more detailed information (9,10).
2. The NIOSH recommended exposure limit cited includes all chemically combined forms of vanadium except alloys, intermetallics, and vanadium carbide.
3. Intended change, 1980.

Survey Results

Plant A

During the reactor cleaning operation, analysis of personal samples revealed an average of 0.01 mg/m^3 of sulfuric acid and 0.05 mg/m^3 orthophosphoric acid. In addition, general area samples were analyzed for fluoride, cadmium, chromium, and uranium yielding average levels of 0.05, 0.003, 0.001, 0.01 mg/m^3 respectively. Levels of beta radiation were measured and radon gas samples were collected above the reactor at initial opening, during the cleaning operation, and after the reactor vessel had been cleaned and averaged 0.41 pC/l and 100 mR/hr.

Plant B

Personal samples for cadmium (0.001 mg/m^3), chromium (0.001 mg/m^3), vanadium (0.009 mg/m^3), sulfuric acid (0.07 mg/m^3), and orthophosphoric acid (H_3PO_4) (0.254 mg/m^3) were collected during the reactor cleaning procedure. General area samples were collected during reactor cleaning for particulate (0.126 mg/m^3) and gaseous fluoride (0.183 mg/m^3). The results of all samples analyzed were below the current recommended and legal standards (Table 1). Table 3 indicates the range of contaminant levels measured.

Plant C

During the cleaning of the phosphoric acid reactor vessel at Plant C, personal samples were collected for cadmium (0.002 mg/m^3), chromium (0.002 mg/m^3), vanadium (0.01 mg/m^3), arsenic (0.001 mg/m^3), uranium (0.01 mg/m^3), sulfuric acid (0.11 mg/m^3), and orthophosphoric acid (0.025 mg/m^3).

In addition, general area samples were collected for fluoride (3.34 mg/m^3), and radon daughters (0 to 25 counts per minute). Noise levels were measured in the general work area and at the top of the reactor loading platform during reactor cleaning and ranged from 85-98 dBA.

Sample results were below currently recommended levels, with the exception of two fluoride levels which exceeded the NIOSH and OSHA standard (Table 1). Sampling results are summarized in Table 4.

Plant D

Personal samples were collected during the reactor vessel cleaning operation at Plant D and analyzed for orthophosphoric acid (0.75 mg/m^3), sulfuric acid (0.57 mg/m^3), arsenic (0.08 mg/m^3), cadmium (0.003 mg/m^3), chromium (0.003 mg/m^3), vanadium (0.08 mg/m^3), respirable silica (0.195 mg/m^3), and respirable dust (0.38 mg/m^3). In addition, bulk samples of process sludge, gypsum cake, orthophosphoric acid, and phosphate rock were analyzed for uranium content. Results of the bulk sample analysis are presented in Table VIII, Appendix A.

Table 2

Plant A
Environmental Data - Personal and Area Samples
mg/m^3 Except as Noted

	Number of Samples	Range	Average
Fluoride	6	0.03 - 0.07	0.05
Sulfuric Acid	12	0.1	0.1
Phosphoric Acid	8	0.02 - 0.08	0.05
Cadmium	5	0.003	0.003
Chromium (total)	5	0.001 - 0.002	0.001
Uranium	5	0.01 - 0.01	0.01

Radon and Beta Radiation Sample Results

	Number of Samples	Range	Average
Radon (gas)	3	0.27 - 0.56 pC/l*	0.41 pC/l
Beta Radiation (continuous monitor)		75 - 125 mR/hr**	

* picocuries per liter
** milliroentgens per hour

Table 3

Plant B
Environmental Data - Personal and Area Samples
mg/m^3

	Number of Samples	Range	Average
Fluoride (particulate)	7	0.071 - 0.189	0.126
Fluoride (gaseous)	7	0.068 - 0.676	0.183
Cadmium	8	0.001	0.001
Chromium (total)	8	0.001 - 0.003	0.001
Vanadium	8	0.009	0.009
Sulfuric Acid	8	0.07	0.07
Phosphoric Acid	9	0.005 - 2.118	0.254

Table 4

Plant C
Environmental Data - Personal and Area Samples
mg/m^3

	Number of Samples	Range	Average
Fluoride	7	0.02 - 13.24	3.39
Sulfuric Acid	8	0.013- 0.22	0.11
Phosphoric Acid	8	0.03 - 0.52	0.25
Cadmium	11	0.002	0.002
Chromium (total)	11	0.001- 0.02	0.002
Uranium	2	0.005- 0.014	0.010
Vanadium	11	0.01	0.01
Arsenic	4	0.001	0.001

Radon Daughter Sample Results

Number of Samples	Counts per minute (range)	Working Level* (range)
7	0 - 25	0.00 - 0.02

* Working Level is defined as any combination of short-lived radon-222 daughters, polonium-218, lead-214, bismuth-214, and polonium-214, in one liter of air, without regard to the degree of equilibrium, that will result in the ultimate emmission of 1.3×10^5 MeV of alpha particle energy (11).

All airborne concentrations were below the legal limits established by OSHA with the exception of one sulfuric acid sample and one fluoride sample. These two results deviate widely from the other sample results and their validity is questionable. Table 5 indicates the range of contaminant levels measured.

Personal samples analyzed for arsenic, vanadium, and respirable silica exceeded the current NIOSH recommended standards. No measurable levels of radon daughters were observed.

Plant E

Personal and general area samples were collected at the grinder, ball mill, dryer, sizing screens, and car loading stations in this beneficiation plant. Personal samples were analyzed for cadmium (0.003 mg/m^3), chromium (0.008 mg/m^3), vanadium (0.019 mg/m^3), arsenic (0.003 mg/m^3), fluoride (0.57 mg/m^3), respirable silica (0.07 mg/m^3), and respirable dust (01.62 mg/m^3). General area samples were analyzed for cadmium, chromium, vanadium, uranium, arsenic, and radon daughters.

OSHA standards for respirable dust containing quartz and NIOSH standards for respirable free silica were exceeded in personal samples collected at the ground loader and dry rock distributor. OSHA standards for uranium were exceeded in general area samples collected in the vicinity of the ball mill. The NIOSH-recommended standard for arsenic was exceeded in a general area sample collected in the vicinity of the ball mill. No measurable levels of radon daughters were observed. The range of sample results is shown in Table 6.

Discussion of Results

Reactor Cleaning

Personal and area samples collected during reactor cleaning and associated operations at Plants A and B showed that levels of airborne contaminants were below recommended and legal standards. Airborne fluoride concentrations in the area of reactor cleaning at Plant C exceeded OSHA standards as well as NIOSH recommended levels. All other levels of airborne contaminants were below recommended and legal standards. At Plant D, personal samples collected during reactor and flash cooler cleaning showed exposures exceeding the NIOSH recommended standards for arsenic, vanadium, and respirable silica. All other sample results were below recommended and legal standards.

Of the contaminants which were observed to exceed NIOSH-recommended exposure limits, arsenic and respirable silica have been associated with diseases of the respiratory tract. The exposure limit for respirable silica was established to protect against development of acute and chronic fibrogenic disease (silicosis) or functional incapacities arising from inhalation of free silica (5). The exposure limit for

Table 5

Plant D
Environmental Data - Personal and Area Samples
mg/m^3

	Number of Samples	Range	Average
Fluoride (particulate)	6	0.05 - 0.84	0.20
Fluoride (gaseous)	4	0.04 - 8.02	2.10
Sulfuric Acid	11	0.16 - 3.31	0.57
Phosphoric Acid	9	0.018- 0.129	0.075
Cadmium	9	0.002- 0.004	0.003
Chromium (total)	9	0.002- 0.004	0.003
Uranium	2	0.004	0.004
Vanadium	18	0.03 - 0.39	0.08
Respirable Free Silica	3	0.015- 0.51	0.195
Respirable Dust	3	0.17 - 0.55	0.38
Arsenic	10	0.06 - 0.10	0.08

Table 6

Plant E
Environmental Data - Personal and Area Samples
mg/m^3

	Number of Samples	Range	Average
Fluoride	6	0.21 - 0.88	0.57
Cadmium	10	0.001- 0.05	0.003
Chromium (total)	10	0.001- 0.05	0.008
Uranium	3	0.022- 0.514	0.228
Vanadium	10	0.008- 0.05	0.019
Arsenic	3	0.001- 0.005	0.003
Respirable Free Silica	3	0.04 - 0.09	0.07
Respirable Dust	3	0.45 - 3.63	1.62

arsenic was established to protect against the noncarcinogenic effects of inorganic arsenicals such as skin disorders, and carcinogenic effects on the lungs and lymphatic system (6). The observed arsenic levels in personal samples collected during reactor cleaning at Plant D indicated that workers engaged in this operation were exposed to hazardous levels of airborne arsenic.

Beneficiation

General area samples collected at the ball mill of the beneficiation plant (Plant E) exceeded OSHA standards for uranium. General area samples from the ball mill and sizing screens at Plant E exceeded NIOSH-recommended exposure levels for arsenic. Workers at the ground loader and dry rock distributor of Plant E were exposed to levels of respirable silica and respirable dust (containing quartz) which exceeded OSHA and NIOSH standards.

Exposure to Chromium

At the four plants where reactor cleaning and associated maintenance activities were studied, and at the beneficiation facility, observed levels of airborne chromium ranged from less than 0.001 to 0.05 mg/m^3. The samples collected for chromium were analyzed by NIOSH Methods P&CAM 173 and P&CAM 152 (7), atomic absorption methods which do not distinguish between the various oxidation states or valences of chromium. The results of analyses performed by these methods reflect the total amount of chromium present, regardless of form. The presence of potentially hazardous airborne chromium (VI) levels during reactor cleaning and beneficiation has not been documented, nor can it be ruled out. NIOSH has recommended to the study facilities that further sampling be performed to thoroughly characterize exposures to chromium in the phosphate fertilizer industry.

Exposure to Radiation

Radon daughter levels were measured at the beneficiation plant and two fertilizer production facilities. Of 19 samples analyzed, 2 samples showed detectable levels of radon daughters (0.02 working level). At Plant A, the beta radiation levels measured by a scintillation counter ranged from less than 75 to 125 milliroentgens per hour. The U.S. Environmental Protection Agency (EPA) Office of Radiation Programs has also conducted surveys in the phosphate fertilizer industry to evaluate external gamma radiation doses and lung doses due to inhalation of radioactive particulates of uranium, thorium, and radium, and radon gas and its daughters (8). These studies concluded that direct gamma exposures and estimated lung doses were below applicable occupational exposure standards and Radiation Protective Guides for the general population.

RECOMMENDATIONS

The results of this study represent a first effort to characterize potentially hazardous exposures in the phosphate fertilizer industry. Due to analytical problems with the survey, it is not possible to draw meaningful conclusions as a result of the data presented here. This survey has identified potentially hazardous substances and described areas where these substances might be found. Based on this guidance, further research is highly recommended. Further research is recommended in the following areas:

1. Arsenic and respirable silica
2. Chromium

These problem areas should be further documented through additional field studies. In the interim, a meaningful and aggressive program of respiratory protection should be undertaken. As a long range goal, engineering controls should be developed (e.g., ventilation, improved work practices, etc.) to limit exposure of worker to the hazards in this industry.

References

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8. Environmental Protection Agency "Radiation Dose Estimates to Phosphate Industry Personnel", Publication Number EPA-520/5- 76-014 (December 1976).

9. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard: Occupational Exposure to Chromium (VI), DHEW Publication No. (NIOSH) 76-129, Cincinnati, Ohio, U.S. Department of Health, Education and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1975.

10. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard ... Occupational Exposure to Chromic Acid, DHEW Publication No. (NIOSH) 73-11021, Cincinnati, Ohio, U.S. Department of Health, Education and Welfare, Public Health Service, NIOSH, 1973.

11. Occupational Safety and Health Administration, OSHA safety and health standards. 10 CFR Part 20, Appendix B.

Appendix A

Environmental Data

Table 1
Plant A
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3						
		F	H_2SO_4	H_3PO_4	Cd	Cr	U	Ra (pC/l)
Upper Portion of Digester Tank	GA	0.05						
Upper Portion of Digester Tank	GA	0.05						
Upper Portion of Digester Tank	GA	0.07						
Upper Portion of Digester Tank	GA	0.05						
Upper Portion of Digester Tank	GA	0.05						
Upper Portion of Digester Tank	GA	0.03						
Clean-out Digester Tank	BZ		<0.1					
Shoveling Gypsum out of Digester	BZ		<0.1					
Cleaning walls of Digester	BZ		<0.1					
Clean-out Digester	BZ		<0.1					

Table I
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3						
		F	H_2SO_4	H_3PO_4	Cd	Cr	U	Ra (pC/l)
Clean-out Digester	BZ		0.1					
Clean-out Digester	BZ		0.1					
Clean Digester - Assist Crane Operator	BZ		0.1					
General Area	GA		0.1					
Clean-out Digester	BZ		0.1					
Clean-out Digester	BZ		0.1					
Clean-out Digester	BZ		0.1					
Clean-out Digester	BZ		0.1					
General Area	GA			0.08				
General Area	GA			0.02				
General Area	GA			0.03				
Cleaning Walls of Digester	BZ			0.08				
Clean-out Digester	BZ			0.02				
Clean-out Digester	BZ			0.02				

Table I
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3						
		F	H_2SO_4	H_3PO_4	Cd	Cr	U	Ra (pC/1)
General Area	GA			0.04				
General Area	GA			0.07				
General Area	CA				0.003	0.002	0.01	
General Area	GA				0.003	0.001	0.01	
General Area	GA				0.003	0.001	0.01	
General Area	GA				0.003	0.001	0.01	
General Area	GA				0.003	0.001	0.1	
Above Tank Opening								0.39
Inside Tank During Cleaning								0.56
Inside Tank After Cleaning								0.27

GA - General Area Sample
BZ - Breathing Zone (personal) Sample
pc/l - picocuries per liter
mg/m^3 - milligrams per cubic meter

Table II
Plant B
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3						
		F (particulate)	F (gaseous)	H_2SO_4	H_3PO_4	Cd	Cr	V
"C" Agitator	GA			<0.070	0.01			
"C" Agitator	GA			<0.07	0.05			
"E" Agitator	GA			<0.070	0.005	<0.001	<0.001	<0.009
"E" Agitator	GA				<0.005	<0.001	<0.001	<0.009
"F" Agitator	GA			<0.070	0.05	<0.001	<0.001	<0.009
"F" Agitator	GA			<0.070		<0.001	0.003	<0.009
"F" Agitator	GA					<0.001	0.002	<0.009
Center Well	GA	0.071	0.676	<0.070	<0.005	<0.001	<0.001	<0.009
Center Well	GA	0.075	0.100	<0.070	<0.005	<0.001	<0.001	<0.009
Center Well	GA	0.096	0.113		0.05			
Center Well	GA	0.142	0.126					
Center Well	GA	0.170	0.108					
Center Well	GA	0.136	0.091					
Center Well	GA	0.189	0.068					
Laborer	BZ			<0.070	2.118	<0.001	0.002	<0.009

Table III
Plant C
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3							
		F	H_2SO_4	H_3PO_4	Cd	Cr	U	V	As
Phos-Acid Filter Main	BZ		0.013		<0.001	0.02		<0.01	<0.001
Attack Tank Cleaning	BZ			0.03	<0.001	<0.001		<0.01	
Flash Cooler Cleaning	BZ		0.03	0.22	<0.001	<0.001		<0.01	<0.001
Flash Cooler Cleaning	BZ		0.16	0.25	<0.001	<0.001		<0.01	
Flash Cooler Cleaning	BZ			0.23					
DAP #2 Storage	GA				<0.001	<0.001		<0.01	
DAP Storage	GA				<0.001	<0.001		<0.01	<0.001
DAP Cooler	GA				<0.001	<0.001		<0.01	
DAP Cooler	GA				<0.002	<0.002		<0.01	
Attack Tank Cleaning	GA	13.24	0.18		<0.002	<0.002		<0.01	
#2 Phos-Acid Filter	GA		0.03	0.17	<0.001	<0.001		<0.01	
Flash Cooler Cleaning	GA	1.91		0.23	<0.001	<0.001		<0.01	<0.001
Attack Tank #2 Compartment	GA		0.06						
Sulfur Burner #7	GA		0.19						

Table III
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3							
		F	H_2SO_4	H_3PO_4	Cd	Cr	U	V	As
S. Side Adsorbent Tower	GA		0.22						
Flash Cooler #3 Train	GA			0.52					
#2 Phos-Acid Filter	GA			0.32			0.005		
DAP Control Room (1&3)	GA	0.02							
Attack Tank Cleaning	GA	0.27							
Attack Tank Cleaning	GA	0.41							
Attack Tank Cleaning	GA	5.85							
Flash Cooler Cleaning	GA	2.06							
Acid Plant Mixing Area)	GA						0.014		

Table IV
Plant C
Noise Measurement Results

Description of Sampling Area	dB(A) (Average)
General Reactor Area	85-95
Top of Loading Platform	98

Table V.
Plant C
Radon Daughter Sample Results

Description of Sampling Area	Cpm	Working Level
N. Car Unloading	25	0.02
Attack Tank Feed	25	0.02
Attack Tank between #3&4 Compartment	0	0.0
Flash Cooler	0	0.0
Attack Tank #4 Compartment	0	0.0
Storage Bin DAP Truck Unloading #1 Shipyard	0	0.0
Control Room - Rock Unloading	0	0.0

Cpm - counts per minute

Working Level is defined as any combination of short-lived radon-222 daughters, polonium-218, lead-214, bismuth-214, and polonium-214, in one liter of air, without regard to equilibrium, that will result in the ultimate emmission of 1.3×10^5 MeV of alpha particle energy (10 CFR Part 20, Appendix B).

Table VI
Plant D
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3					
		F (particulate)	F (gaseous)	H_2SO_4	H_3PO_4	Cd	Cr
#9 Tank Cleaning	BZ			0.67	0.086	0.004	0.004
#9 Tank Cleaning	BZ			0.64	0.077	0.004	0.004
Flash Cooler Cleaning	BZ			0.19	0.085	0.003	0.003
Flash Cooler Cleaning	BZ				0.080		
#9 Tank Cleaning	BZ			0.19	0.030	0.003	0.003
Clean Duct Work Ground Level	BZ			0.19	0.041		
Flash Cooler Cleaning	BZ			0.28	0.129		
#9 Tank Cleaning	BZ				0.128	0.003	0.003
Flash Cooler & Tank Cleaning	BZ			0.17	0.018	0.002	0.002
#9 Tank Cleaning	BZ			0.32		0.004	0.004
Flash Cooler	GA	0.84	0.31				
Attack Tank Outside	GA	0.013	0.05				
Attack Tank Outside	GA	0.12	0.04				
Flash Cooler	GA	0.14	8.02				

Table VI
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3					
		F (particulate)	F (gaseous)	H_2SO_4	H_3PO_4	Cd	Cr
Flash Cooler	CA	0.05					
Flash Cooler Outside	GA	0.015					
Flash Cooler & Tank Cleaning	BZ			0.16		0.003	0.003
Flash Cooler & Tank Cleaning	BZ			3.31			
Flash Cooler & Tank Cleaning	BZ			0.16			
#9 Tank Cleaning	BZ					0.003	0.003

Table VII
Plant D
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3				
		U	V	As	Respirable free silica	Respirable dust
#9 Tank Cleaning	BZ		0.05	0.09		
#9 Tank Cleaning	BZ		0.05	0.10		
Flash Cooler Cleaning	BZ		0.03	0.07	0.015	0.43 (3.5% quartz, OSHA Std. 1.82)[1]
Flash Cooler Cleaning	BZ			0.06	0.06	0.17 (35.3% quartz, OSHA Std. 0.27)
#9 Tank Cleaning	BZ		0.03	0.07		
#9 Tank Cleaning	BZ		0.03	0.07		
Flash Cooler & Tank Cleaning	BZ		0.03	0.06		
#9 Tank Cleaning	BZ		0.05	0.10		
Flash Cooler & Tank Cleaning	BZ		0.03	0.06		
#9 Tank Cleaning	BZ		0.03	0.06		
Tie Bags	BZ		0.14			
Fill Bags	BZ		0.18			

Table VII
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3				
		U	V	As	Respirable free silica	Respirable dust
Fill Bags - Oversize	BZ		0.11			
Stacking - Oversize	BZ		0.04			
Tie Bags	BZ		0.06			
Stacking	BZ		0.09			
Inside Converter (Vacuuming Catalyst	BZ		0.03 0.09 0.39			
Flash Cooler	GA				0.51	0.55 (92.7% quartz, OSHA Std. 0.11)
North of Car Unloading Phosphate Rack (12% H_2O) Into Grizzly	GA	0.004				
North Flash Cooler, West of Phosphoric Acid Train Cleanout Just Outside Verticle Cover and Overhead	GA	0.004				

[1] OSHA Standard for respirable dust containing quartz = $\frac{10\ mg/m^3}{\%\ Respirable\ SiO_2 + 2}$

Table VIII
Plant D
Bulk Sample Analysis Results

Sample Type	% U
30% Sludge	0.028
54% Merchant Acid	0.046
Gypsum Cake	0.010
Wet Rock	0.026
40% Sludge	0.032
54% Sludge	0.042
Water	0.012
Rock #3	0.002
Rock #4	0.002

Table IX
Plant D
Radon Daughter Sample Results

Sample Location	Counts	Working Level
DAP Granulator	0	0.0
DAP Storage	0	0.0

Table X
Plant E
Environmental Data

Sample Location	Sample Type	Airborne Concentration - mg/m^3							
		F	Cd	Cr	U	V	As	Respirable free silica	Respirable dust
Sizer Operator	BZ						0.001		
Dryer Operator	BZ		0.001	0.001		0.008			
Assist Grinder Operator	BZ		0.001	0.001		0.008			
Assist Grinder Operator 4, 5, & 6	BZ		0.001	0.05		0.01			
Dryer Operator	BZ		0.001	0.001		0.008			
Grinder Operator 4, 5, & 6	BZ		0.001	0.001		0.01			
Ground Loader R.R. Section	BZ	0.88						0.08	3.63 (2.2% quartz, OSHA Std. 2.38)
Dry Rock Distributor	BZ	0.46						0.09	2.02 (4.5% quartz, OSHA Std. 1.55)
3 & 4 Ball Mill Operator	BZ	0.49							
4, 5, 6 Grinder Operator	BZ	0.67							

Table X'
(continued)

Sample Location	Sample Type	Airborne Concentration - mg/m^3							
		F	Cd	Cr	U	V	As	Respirable free silica	Respirable dust
3 & 4 Ball Mill Operator	BZ	0.21							
Assist Grinder Operator 4, 5, & 6	BZ	0.70							
Dry Rock Distributor	BZ							0.04	0.45 (9.0% quartz, OSHA Std. 0.92)
Ball Mill	GA		0.005	0.005		0.04			
Ball Mill	GA		0.006	0.006		0.04			
#6 Raymond Mill 1st Floor	GA		0.007	0.007		0.05			
Sizer Control Room	GA		0.002	0.002		0.01			
Top of Sizing Screens	GA		0.001	0.001		0.008			
Ball Mill	GA						0.005		
Across From Top of Sizing Screens	GA						0.002		
Catwalk Above Ball Mill	GA				0.514				
1st Floor	GA				0.149				
Grinder Contol Room #3 & 4 Ball Mill	GA				0.022				

Table XI

Plant E

Radon Daughter Sample Results

Sample Location	Counts	Working Level
Environmental Services Trailer	0	0.0
Dryer Control Room	0	0.0
Dry Rock Distributor	0	0.0
Scale House Lunch Room	0	0.0
Grinder Control Room	0	0.0
Raymond Mill	0	0.0
Tunnel (#32)	0	0.0
Tunnel (#81)	0	0.0
Car Loading #2 Drying Bin	0	0.0
Administrative Office	0	0.0

APPENDIX B

Process Flowsheets

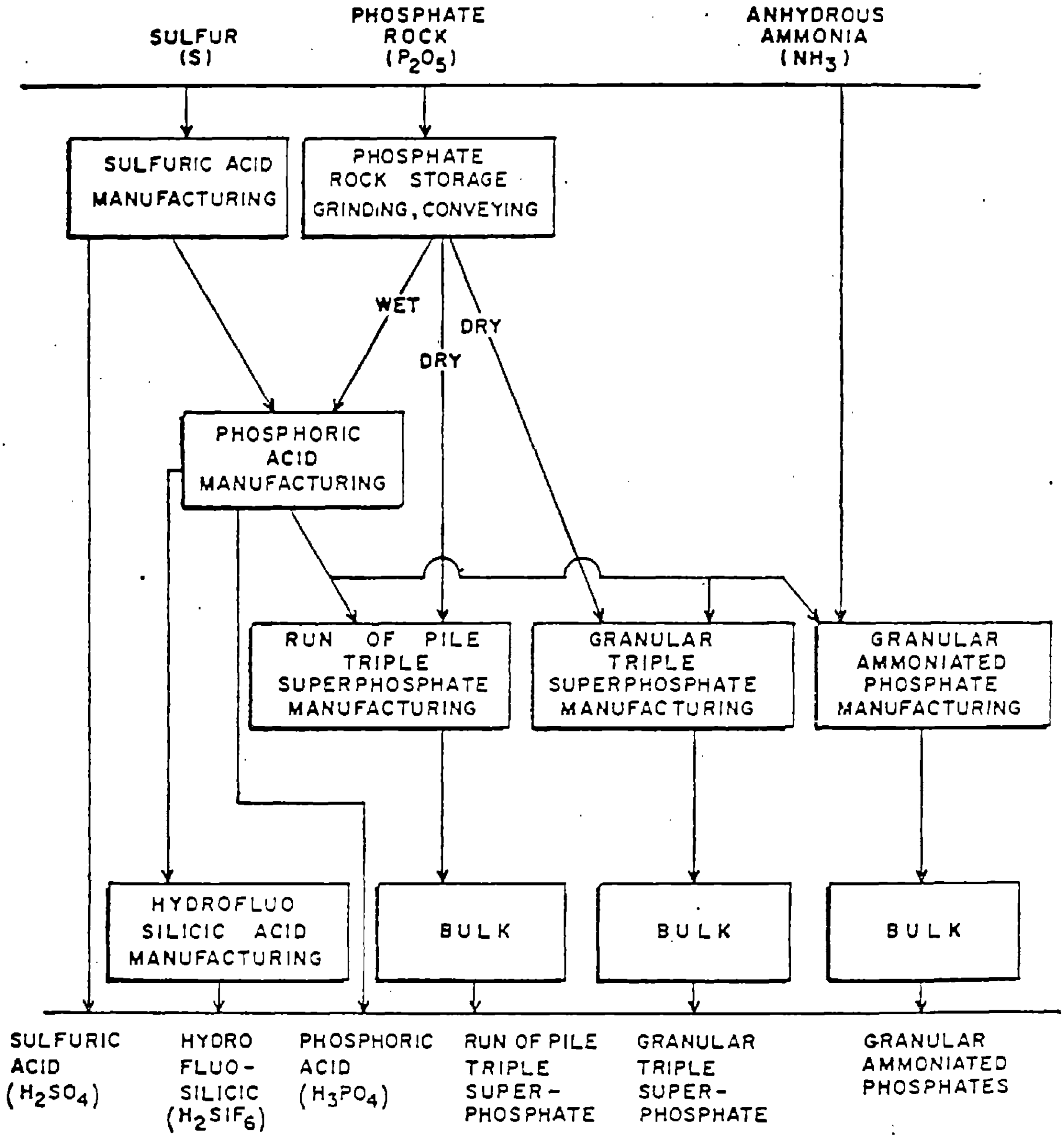

Figure 1. Phosphate Chemical Operations

Reference: All figures from "Control Technology Assessment - Phosphate Fertilizer Mining and Process Industry", unpublished NIOSH Report, 1980.

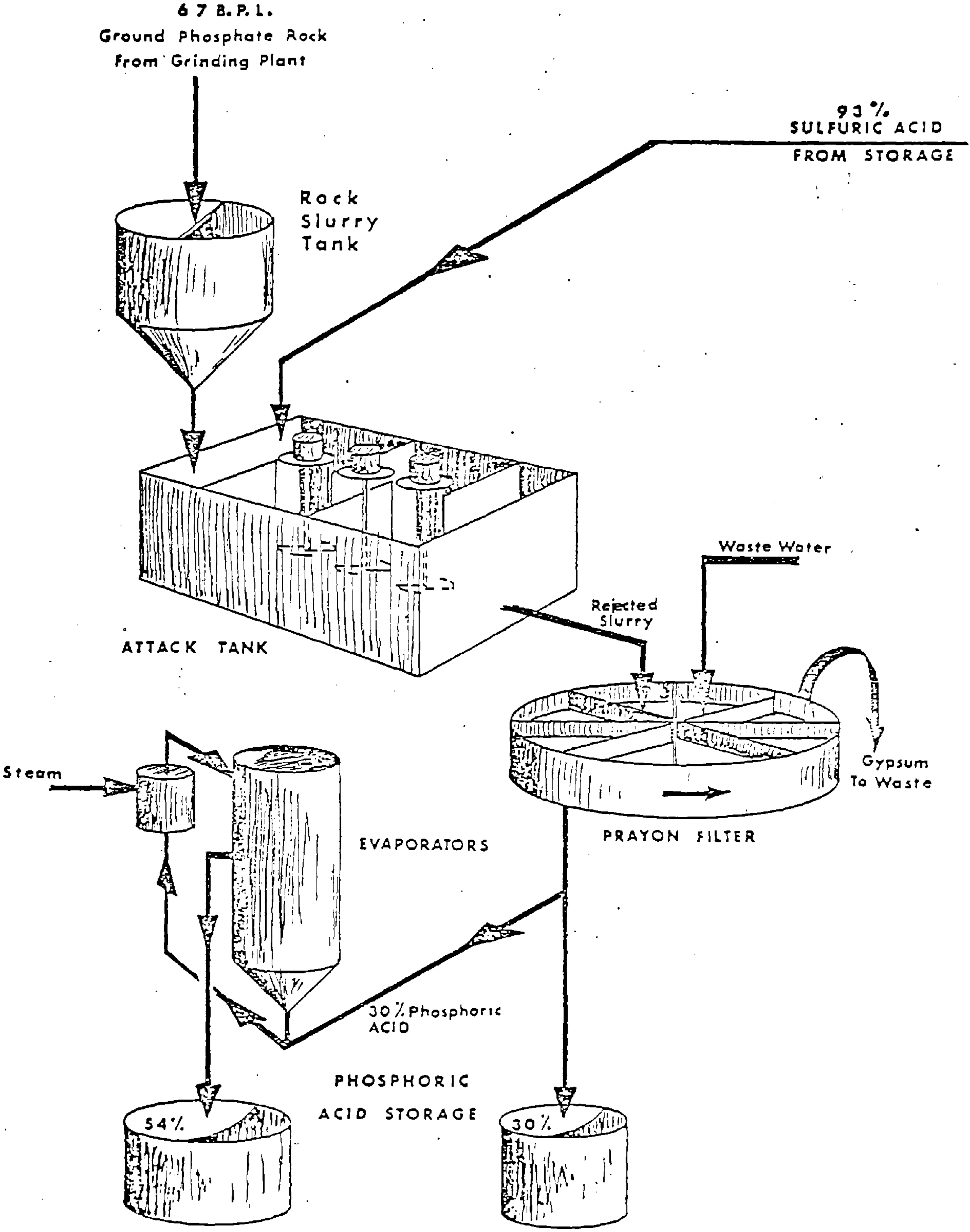

Figure 2. Phosphoric Acid Manufacturing

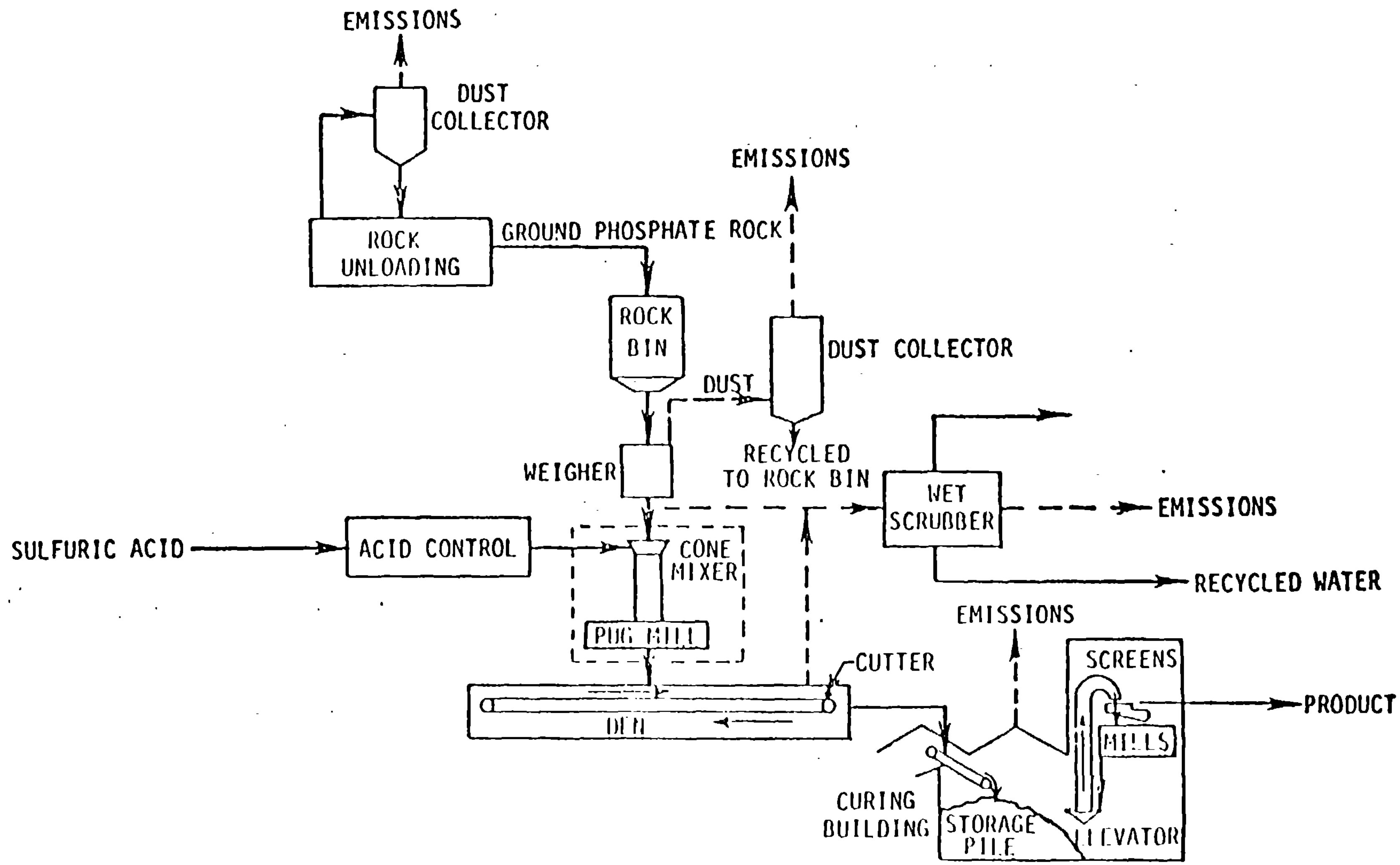

Figure 3 . Normal Superphosphate Process Flow

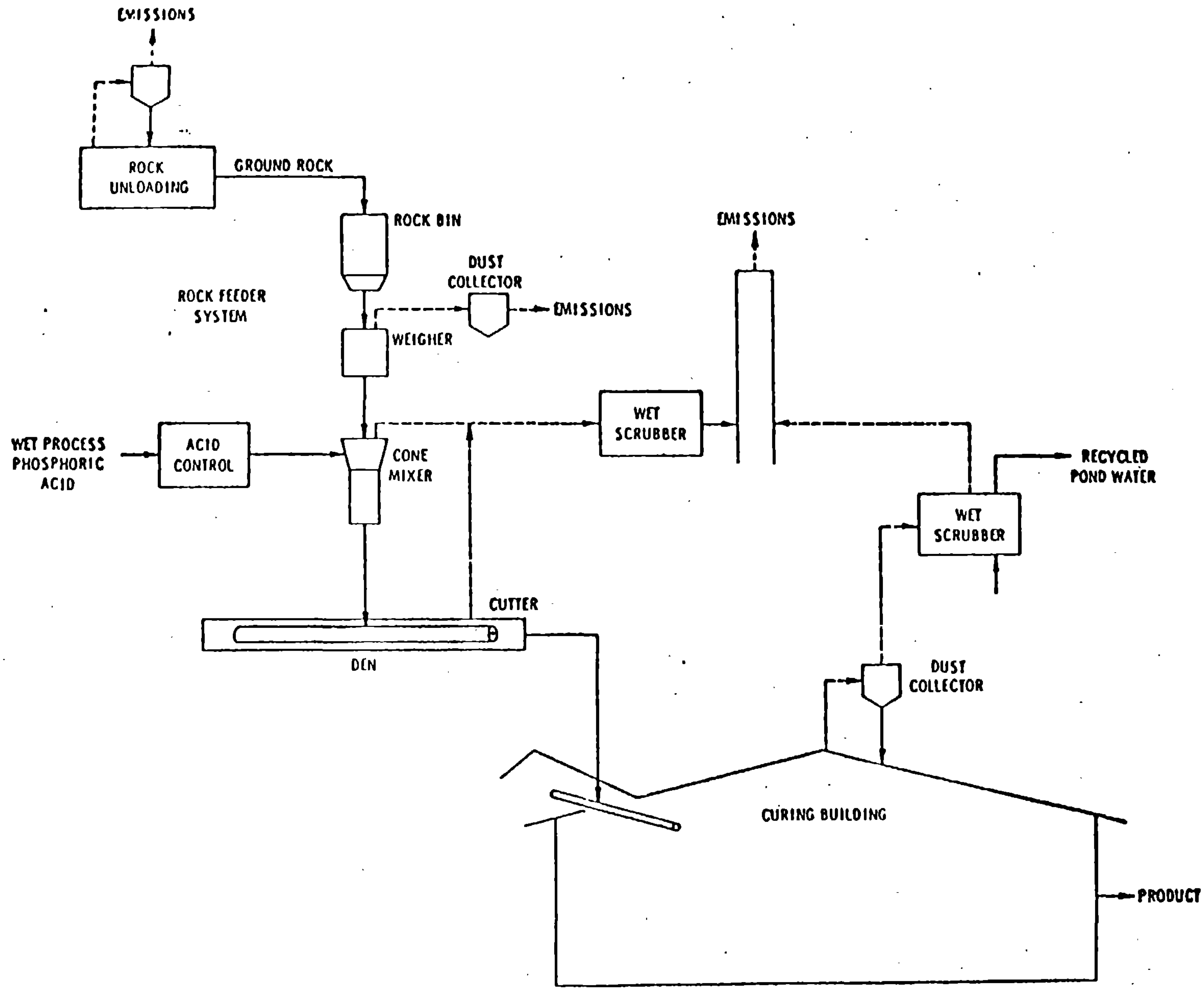

Figure 4. ROP-TSP Production Facility

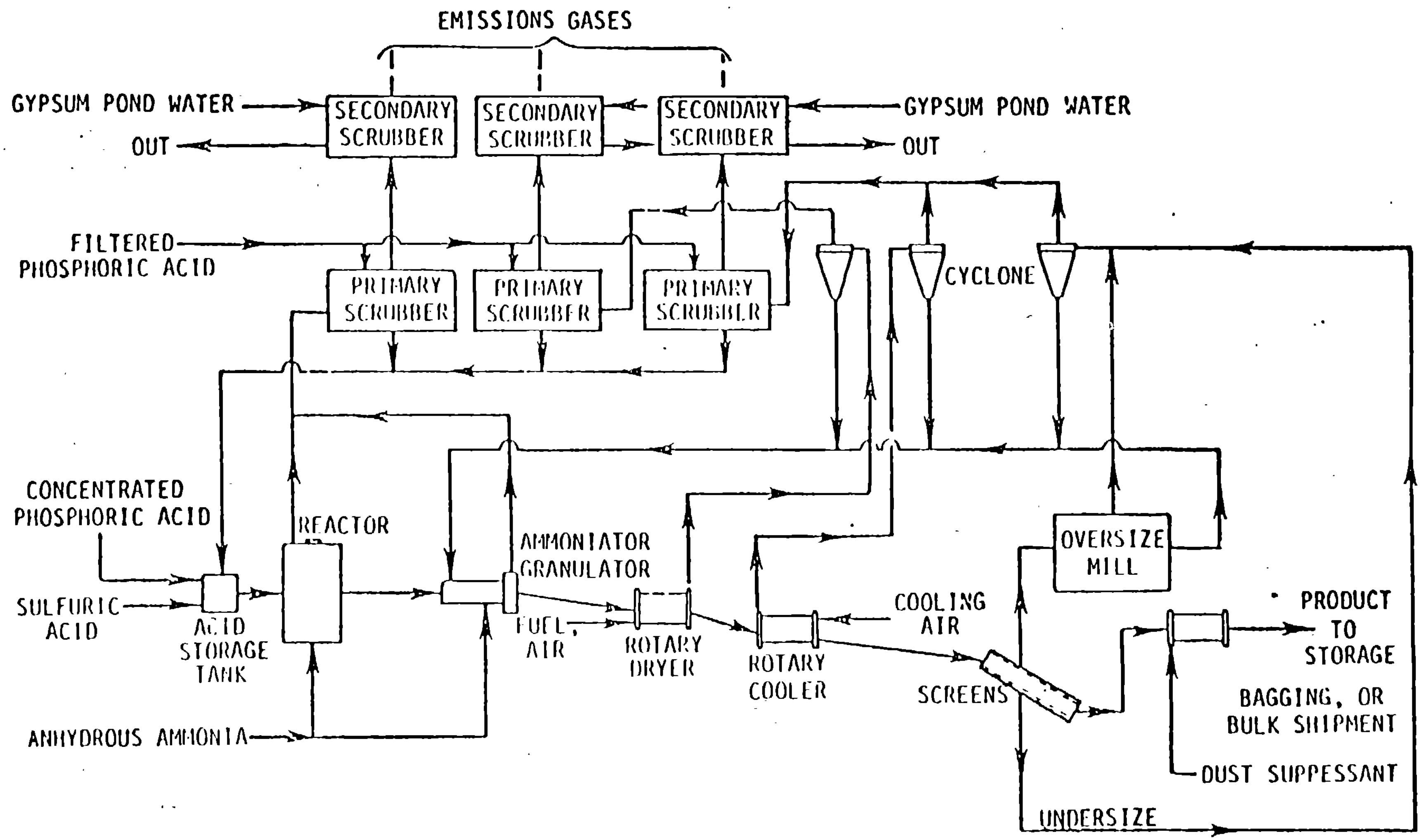

Figure 5 . TVA Ammonium Phosphate Flow