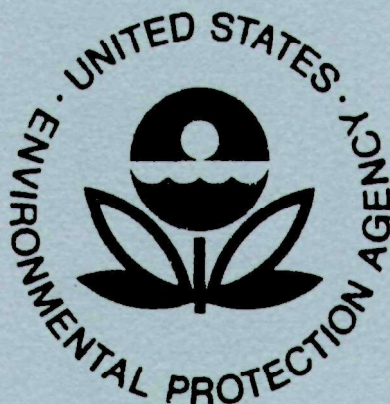


CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVES

**TASK VI - CADMIUM IN PHOSPHATE FERTILIZER
PRODUCTION**



**ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460**

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CHEMICAL TECHNOLOGY AND ECONOMICS IN
ENVIRONMENTAL PERSPECTIVES

Task VI - Cadmium in Phosphate Fertilizer Production

Contract No. 68-01-3201
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PREFACE

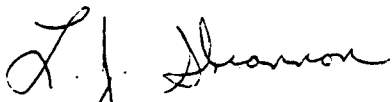
This report presents the results of Task VI of a project entitled "Chemical Technology and Economics in Environmental Perspectives," performed by Midwest Research Institute, under Contract No. 68-01-3201, for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Mr. Charles Auer was project officer for the Environmental Protection Agency.

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Approved for:

MIDWEST RESEARCH INSTITUTE



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CONTENTS

Preface	iii
Figures	vi
Tables	vii
1. Introduction	1
Objective	1
2. Summary and Conclusions	2
3. The Phosphate Fertilizer Industry	4
General history	4
Production and consumption of phosphate fertilizers	6
Fertilizer trends	6
References for Section 3	13
4. Current Data	14
Methodology	14
Manufacturing processes	15
Cadmium levels in phosphate ores and fertilizers	28
References for Section 4	36
5. Research Needs	39
Cadmium in phosphate rock	39
Mass balance studies	39
Cadmium removal	40
Smelter acid	40
Micronutrients	40

FIGURES

<u>Number</u>	<u>Page</u>
4-1 Generalized flow sheet of a phosphate rock mining and beneficia- tion plant	18
4-2 Wet process phosphoric acid flow sheet	20
4-3 Normal superphosphate flow sheet	23
4-4 Flow sheet for granulated triple superphosphate production . . .	24
4-5 Flow sheet for production of diammonium phosphate	26

TABLES

<u>Number</u>		<u>Page</u>
3-1	Current U.S. Ammonium Phosphate Producers	7
3-2	Current U.S. Normal Superphosphate Producers	8
3-3	Current U.S. Triple Superphosphate Producers	9
3-4	U.S. Phosphate Consumption	10
4-1	Cadmium Concentrations in Phosphate Ores	29
4-2	Cadmium Concentrations in Phosphate Fertilizers	33

SECTION 1

INTRODUCTION

Cadmium has been known for many years to be a highly toxic element; health problems attributed to cadmium exposure include proteinuria, pulmonary emphysema, hypertension, and liver and kidney damage. The need for precautions against human exposures in industrial operations involving cadmium or its compounds has long been recognized. Not until comparatively recent times, however, has concern been expressed over the possible human health effects of long-term exposure to low concentrations of cadmium, such as those that might develop through environmental routes.

One of the potential environmental sources of cadmium is the use of agricultural phosphate fertilizers, which may contain up to 100 ppm of cadmium. The commercial phosphate fertilizer production process has the potential, in fact, to increase the concentration of cadmium in the finished fertilizer above that which had existed in the phosphate rock starting material.

OBJECTIVE

This brief task was initiated to study the levels of cadmium concentration as phosphate rock is processed into the finished commercial fertilizer. The primary focus of this study was to determine if the concentration of cadmium in commercial phosphate fertilizers represented an increase over the levels initially contained in the phosphate rock and to identify specific points of increase in the process. If the cadmium levels were, in fact, found to increase as the phosphate rock is processed into fertilizer, the reasons for such increases and the sources of the increases were to be ascertained.

SECTION 2

SUMMARY AND CONCLUSIONS

The importance of phosphorus as a plant nutrient, essential for the growth of higher plants, has been long recognized, and commercial phosphate fertilizers have been produced for over 100 years. Essentially all phosphate fertilizers are obtained from a single raw material source, a calcium mineral known as apatite or phosphate rock. The phosphate rock is seldom used directly for fertilizer, and is normally chemically processed to one of several other forms for fertilizer use. Prior to about 1955, most of the phosphate fertilizer used domestically was in the form of normal superphosphate. Since that time, the use of normal superphosphate has steadily declined as it has been displaced by the more concentrated phosphate fertilizers, triple superphosphate (TSP) and the ammonium phosphates.

Cadmium occurs as a natural contaminant in the phosphate rock used in fertilizer production, and may be present in a form which is readily available for uptake by edible fruits and plants. Concern has developed that production methods may concentrate the cadmium in the finished fertilizer. This brief project was initiated to study the levels of cadmium as phosphate rock is processed into the commercial fertilizer and to determine if an increase in cadmium levels occurs. In general, the results of this study have shown that very little information is available on the levels and fate of cadmium as the ore proceeds through the various manufacturing steps.

Raw ore is generally classified as eastern or western ore. The cadmium levels in mined eastern ore average about 10 to 25 ppm, while in mined western ore, levels range from about 50 to 150 ppm, depending upon the type of ore. Some western ores have cadmium levels as high as 980 ppm; however, these ores are not extensively mined at the present time. Nevertheless, because of the tightening supply of high quality phosphate ores, domestic producers may be forced to shift to the less desirable low grade ores. The movement towards the use of lower grade ores may result in the future processing of raw phosphate rock containing a high cadmium content. Additional sources of potential cadmium contamination during processing are sulfuric acid and the addition of micronutrients. From the limited available data, it appears that by-product sulfuric acid from zinc, lead, and copper smelters is used, where available, in the processing of phosphate ore. Based on industry sources, an estimated

10% of the sulfuric acid consumed in phosphate ore processing is smelter acid. This is primarily true with the western ores. The cadmium content of the by-product smelter acid is not well defined; the levels reported in the literature range from 1 ppb to 60 ppm by weight. High levels are normally associated with zinc smelter processes. Very few data are available concerning the addition of micronutrients to phosphate fertilizers and any increase in cadmium levels resulting from such additions.

Thus, it is not currently possible to establish material balances or draw inferences about the concentrations of cadmium during the various stages of manufacture of phosphate fertilizers. Existing data do not indicate that a significant increase occurs in the cadmium to phosphorus ratio between raw materials and finished product as a result of current manufacturing operations. This conclusion is based on very limited data and must be considered tentative until corroborated by additional evidence. Studies designed to resolve the uncertainties of material balances and the question of possible enhancement of cadmium in phosphate fertilizer manufacture are currently planned by the Tennessee Valley Authority (TVA).

SECTION 3

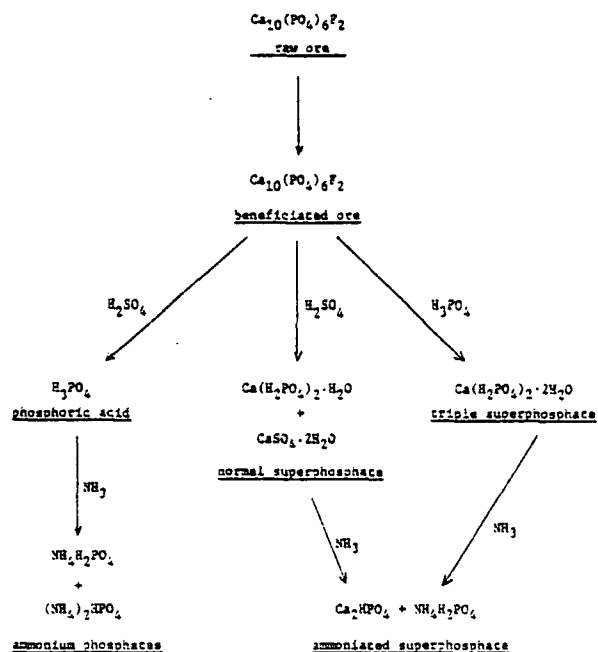
THE PHOSPHATE FERTILIZER INDUSTRY

GENERAL HISTORY

The importance of phosphorus as a plant nutrient, essential for the growth of higher plants, has long been recognized and commercial production of phosphate fertilizers has been practiced for over 100 years.^{1/}

Practically all of the phosphate fertilizers currently produced come from a single raw material--a calcium phosphate mineral commonly known as apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) or phosphate rock.^{1/} Organic materials were once a major source of phosphate, but their use has been discontinued as mined rock became more available and less costly.

A general flow diagram for the production of various types of phosphate fertilizers is shown below. Each of the steps in this diagram will be discussed later in Section 4.



Prior to approximately 1955, phosphate products (based on P_2O_5) were the major fertilizer nutrients consumed domestically. Since that time, nitrogen consumption has become predominant, but phosphates are still used on a large scale.^{2/}

During the past 20 years, there have been dramatic changes in phosphate fertilizer production facilities, costs, and industry image.^{3/} Prior to 1955, most of the phosphate nutrient was in the form of normal superphosphate, which contained about 16 to 20% P_2O_5 .^{3/} A low production cost and a single production method resulted in the manufacture of normal superphosphate by a large number of small plants located throughout the domestic market area. Since 1955, however, the market for normal superphosphate has steadily decreased, and its former share of the market has been taken over by more concentrated phosphate fertilizers. However, in order to manufacture the more concentrated fertilizers, it was necessary to modify the process and to increase the domestic production capacity of phosphoric acid, an essential intermediate. This demanded the production of greater quantities of sulfuric acid, as well as larger overall production facilities.^{3/}

Phosphoric acid is produced by two basic processes: (a) wet process, and (b) the electric furnace process. Although acid produced by each process is used in the fertilizer industry, the quantity of furnace process acid consumed is relatively small. Most of the furnace process acid is used in non-fertilizer applications. In contrast, almost all of the wet process phosphoric acid produced domestically is used in fertilizer processes.^{2/}

Triple superphosphate and ammonium phosphate facilities are generally large, multipurpose complexes located at or near the mine site. Triple superphosphate (46 to 48%, P_2O_5 content) contains approximately three times the P_2O_5 content of normal superphosphate. Ammonium phosphates are combination products which contain 46 to 61% P_2O_5 plus nitrogen values. Included are monoammonium phosphate (MAP) and diammonium phosphate (DAP) which differ in the degree of ammoniation attained during manufacture. The ammonium phosphates are currently the most widely used phosphate fertilizers in the United States.

Until 1970, finely ground (< 0.074 mm) phosphate rock was used domestically in relatively small quantities as a fertilizer.^{2/} Since domestic fertilizer prices are based on a citrate soluble P_2O_5 standard, ground rock (low in soluble P_2O_5) cannot compete with other products. However, there is still a significant demand for ground rock in foreign markets.

PRODUCTION AND CONSUMPTION OF PHOSPHATE FERTILIZERS

Current Producers

Tables 3-1, 3-2, and 3-3 show the top companies in each category in order of production capacity. The three types of fertilizers represented--ammonium phosphates, normal superphosphates, and triple superphosphates--account for nearly 100% of the phosphatic fertilizers presently in use.^{4/}

From the tables, it can be seen that approximately 40% of all fertilizers (i.e., normal superphosphates, triple superphosphates, and the ammonium phosphates) are produced in Florida. No other individual state produces more than 10% of the total. If the production is considered on a regional basis, the southeastern states of Florida, Georgia, Alabama, Tennessee, and North and South Carolina combine to manufacture approximately 60 to 65% of the total phosphate fertilizers.

Florida manufactures approximately 80% of all triple superphosphate. All other individual states produce about 10% or less of the total quantity. For normal superphosphate, three states (Florida, Georgia, and North Carolina) produce approximately 50% of the total domestic quantity. Florida and Louisiana combine to produce about 65% of all of the ammonium phosphates with no other state contributing more than 10% of the total U.S. production quantity.

Domestic Phosphate Fertilizer Consumption

Data showing the U.S. consumption of phosphate fertilizers during the period of 1970 to 1976 are presented in Table 3-4.

During the fiscal year periods from 1970 through 1976, domestic consumption of normal superphosphate decreased by about 54% while the rate for concentrated superphosphate remained relatively constant. Over the same period, the increases in the consumption rates for ammonium phosphates and for diammonium phosphates were about 24 and 43%, respectively.

FERTILIZER TRENDS

A brief discussion of processing trends in the industry and marketing trends and projections is presented in this subsection.

Processing Trends

Until recent years, fertilizer producers had an adequate supply of premium quality phosphate rock for which the existing chemical processes were designed.^{6/}

TABLE 3-1. CURRENT U.S. AMMONIUM PHOSPHATE PRODUCERS

Company ^{a/}	Location	Annual capacity (10 ³ tons)		
		By site	Total	Product
The Williams Companies				
Agrico Chemical Company, subsidiary	Donaldsonville, La.	1,540	1,540	DAP
CF Industries, Inc.				
Bartow Complex	Bartow, Fla.	1,000		DAP
Plant City Complex	Plant City, Fla.	435	1,435	DAP
Occidental Petroleum Corporation				
Occidental Chemical Company, subsidiary				
Florida operations	White Springs, Fla.	925		DAP
Jefferson Lake Sulfur Company, division	Plainview, Tex.	25		
Western division	Lathrop, Calif.	165	1,115	Mixtures
Baker Industrial Corporation				
	Conda, Id.	335		DAP
	Hahnville, La.	465		DAP
	Marseilles, Ill.	190	990	DAP
Olin Corporation				
Agricultural Products Division	Pasadena, Tex.	800	800	DAP and mixtures
Farmland Industries, Inc.				
Farmers Chemical Company, subsidiary	Green Bay, Fla.	435		
	Joplin, Mo.	245	680	Mixtures
Mississippi Chemical Corporation	Pascagoula, Miss.	630	630	Mixtures
International Minerals and Chemicals Corporation				
Agricultural operations	New Wales, Fla.	50		DAP and MAP
IMC Chemical Corporation, subsidiary	New Wales, Fla.	490	540	DAP and MAP
Brewster Phosphates				
	Geismar, La.	150		
	Luling, La.	385	535	
The Gardinier Companies				
Gardinier, Inc.				
U.S. Phosphoric Products	Tampa, Fla.	525	525	DAP and MAP
First Mississippi Corporation				
FIRSTMISS, INC., subsidiary	Fort Madison, Ia.	495	495	DAP and mixtures
W. R. Grace and Company				
Agricultural Chemicals Group	Bartow, Fla.	430	430	DAP and MAP
Standard Oil of California				
Ortho Division	Fort Madison, Ia.	200		APN
	Kennewick, Wash.	75		APN
	Richmond, Calif.	100	375	APN
United States Steel Corporation				
USS Agri-Chemicals Division	Cherokee, Ala.	245	245	DAP and mixtures
Mobil Corporation				
Mobil Chemical Company, division				
Phosphorus Division	Depue, Ill.	240	240	DAP
Simplot Company				
Minerals and Chemical Division	Pocatello, Id.	240	240	DAP and MAP

^{a/} These 16 companies produced 86% of the total annual ammonium phosphate production.

DAP = diammonium phosphate; MAP = monoammonium phosphate; and APN = ammonium phosphate nitrates.

Source: Directory of Chemical Producers - USA (1977).^{5/}

TABLE 3-2. CURRENT U.S. NORMAL SUPERPHOSPHATE PRODUCERS

Company ^{a/}	Location	Daily capacity (tons)	
		By site	Total
Kerr-McGee Corporation			
Kerr-McGee Chemical Corporation, subsidiary	Baltimore, Md. Cottondale, Fla. Jacksonville, Fla. Philadelphia, Penn.	500 500 500 500	2,000
United States Steel Corporation			
USS Agri-Chemicals Division	Albany, Ga. Chicago Heights, Ill. Columbus, Ga. Greensboro, N.C. Nashville, Tenn. Wilmington, N.C.	175 500 200 200 400 400	1,875
Esmark, Inc.			
Swift Agricultural Chemicals Corporation	Bartow, Fla. Dothan, Ala. Savannah, Ga. Wilmington, N.C.	300 700 190 500	1,690
International Minerals and Chemicals Corporation			
Rainbow Division	Americus, Ga. Florence, Ala. Hartsville, S.C. Spartanburg, S.C.	230 400 400 400	1,430
Gold Kist, Inc.	Clyo, Ga. Cordele, Ga.	400 400	800
Valley Nitrogen Producers, Inc.			
AFC Company, subsidiary	Bena, Calif.	300	
Agriform of Imperial Valley, subsidiary	Imperial, Calif.	400	700
The Gardinier Companies			
Gardinier, Inc.			
U.S. Phosphoric Products	Tampa, Fla.	600	600
Kaiser Aluminum and Chemicals Corporation			
Kaiser Agricultural Chemicals Division	Nashville, Tenn. Omaha, Neb. Riegelwood, N.C.	Not available Not available 600	600
Royster Company	Athens, Ga. Chesapeake, Va.	150 300	450
American Plant Food	Galena Park, Tex.	> 400	> 400
Indiana Farm Bureau Coop Associates, Inc.	Indianapolis, Ind.	400	400
Occidental Petroleum Corporation			
Occidental Chemical Company, subsidiary			
Western Division	Lathrop, Calif.	395	395
Columbia Nitrogen Corporation	Moultrie, Ga.	395	395
Stauffer Chemical Company			
Fertilizer and Mining Division	Tacoma, Wash.	300	300
The Williams Companies			
Agrico Chemical Company, subsidiary	Saginaw, Mich.	300	300

^{a/} These 15 companies produced 93% of the total daily normal superphosphate production.

Source: Directory of Chemical Producers - USA (1977).^{5/}

TABLE 3-3. CURRENT U.S. TRIPLE SUPERPHOSPHATE PRODUCERS

Company ^{a/}	Location	Annual capacity (10 ³ tons)	
		By site	Total
CF Industries, Inc. Plant City Phosphate Complex	Plant City, Fla.	930	930
W. R. Grace and Company Agricultural Chemicals Group	Bartow, Fla. Joplin, Mo.	665 100	765
The Gardinier Companies Gardinier, Inc. U.S. Phosphoric Products	Tampa, Fla.	745	745
The Williams Companies Agrico Chemical Company, subsidiary	Bartow, Fla.	675	675
Texasgulf Agricultural Chemicals Division	Aurora, N.C.	600	600
Occidental Petroleum Corporation Occidental Chemical Company, subsidiary Florida operations	White Springs, Fla.	460	460
Baker Industrial Corporation	Conda, Id.	340	340
International Minerals and Chemicals Corporation Agricultural operations	New Wales, Fla.	300	300
United States Steel Corporation USS Agri-Chemicals Division	Ft. Meade, Fla.	295	295
Engelhard Minerals and Chemicals Corporation Phillip Brothers Division Conservation Division	Nichols, Fla.	280	280
Farmland Industries, Inc.	Green Bay, Fla.	200	200
Royster Company	Mulberry, Fla.	180	180
Simplot Company Minerals and Chemical Division	Pocatello, Id.	120	120
Bordon, Inc. Bordon Chemical Division Smith Douglas	Piney Point, Fla.	70	70
Mississippi Chemical Corporation	Pascagoula, Miss.	50	50
Stauffer Chemical Company Fertilizer and Mining Division	Salt Lake City, Ut.	35	35

^{a/} These 16 companies accounted for 100% of the total annual production.

Source: Directory of Chemical Producers - USA (1977).^{5/}

TABLE 3-4. U.S. PHOSPHATE CONSUMPTION^{4/a/}

Fiscal year	Total P ₂ O ₅ consumption	P ₂ O ₅ in mixtures	Direct application materials			
			Superphosphate		Ammonium phosphates	Diammonium phosphates
			Normal	Concentrated		
1970	4,573,750	3,709,062	62,131	546,207	183,688	726,486
1971	4,803,443	3,943,372	55,009	555,960	178,878	814,938
1972	4,863,738	3,997,280	43,553	576,506	174,277	883,795
1973	5,085,162	4,237,591	35,328	569,353	201,423	1,073,198
1974	5,098,626	4,271,429	38,545	537,952	193,000	1,051,416
1975	4,510,979	3,717,825	36,355	530,598	175,899	1,038,091
1976p.	5,215,246	4,422,380	28,672	535,995	228,199	

a/ Quantities in short tons of P₂O₅.

This supply of phosphate rock was maintained by competition among mine producers, and the processor had wide flexibility in selecting sources of this raw material. This desirable situation appears to be rapidly fading.

Four factors are cited^{6/} as responsible for a recent worldwide trend towards the use of lower quality phosphate rock for fertilizer production. These factors are:

- * A two-step price surge during 1973 and 1974 in the price of phosphate rock.^{4/} The price increased from about \$7 to \$70 per ton.^{6/}
- * A change in processes used for mining and beneficiation of phosphate rock.
- * An increase in exploitation pressure on phosphate ore reserves to meet market demands.
- * An extension of phosphate rock production to more diverse ore types.

The principal causes of variability in phosphate rock properties are the diverse ore deposit characteristics.^{6/} Although all commercial phosphate raw materials are predominantly of the apatitic type, they differ with respect to the composition of the apatitic mineral, the presence of mineral impurities, the P₂O₅ concentration, and physical properties.

Because of the tightening supply of high quality phosphate ores, many domestic producers have abandoned their dependence on these ores. Instead, the fertilizer manufacturers are striving for maximum P₂O₅ recovery from inferior ores because the greatly increased market value of phosphate fertilizers makes this economically more attractive. This trend is resulting in a

gradual lowering of product quality because of phosphate rock blending, less beneficiation to reduce P_2O_5 waste, and the marketing of nonpremium grades (< 31% P_2O_5). This movement away from use of high quality raw materials appears to be permanent.^{6/}

Potential low-grade phosphate ore reserves include the Hawthorn Formation of Florida and currently unmined portions of the Phosphoria Formation in the western United States. However, new mining and processing techniques may have to be developed to utilize these low-grade but potentially useful sites.^{7/}

Because of this development, fertilizer processors must now deal with a complicated array of chemical and physical quality factors, which formerly were of only minor concern.^{6/} Physical quality factors of concern include phosphate rock texture, particle size, degree of crystallinity, and physical alteration. Important chemical quality factors are P_2O_5 levels, fluorine and carbonate content, and the degree of contamination by organic matter, chlorides, and inert mineral gangue (worthless material).

The presence of soluble iron and aluminum compounds, as well as the concentration of magnesium, can adversely affect both the processing and quality of the products. These compounds affect the chemistry of fluorine distribution as well as intermediate precipitation processes, and are often reported as insoluble phosphate compositions in the finished products.

Trace contaminants include heavy metals (i.e., cadmium, lead, zinc, mercury, etc.) and toxic elements (i.e., arsenic, selenium, vanadium, chromium, etc.) from minerals and acids, as well as radionuclides (i.e., uranium, thorium, radium, and radon). The concentrations of radionuclide impurities are generally too low to have any serious effect on processing or product grades.^{6/}

Following mining and beneficiation, western phosphate rock is almost always calcined to remove organic material prior to conversion to fertilizer. As the movement to the utilization of lower grade ores continues, the use of calcining techniques may become of increasing importance. However, calcination has the potential to volatilize cadmium and the volatilized cadmium is generally lost to the atmosphere since pollution control techniques for cadmium emissions are not usually practiced. Volatilization losses of cadmium are discussed in greater detail later in this report (see Section 4).

In the future, it appears that as the high quality weathered ore deposits of Florida, which have low cadmium content, are depleted, the lower grade deposits will be exploited for fertilizer usage. The western ores and possibly some of the lower grade ores of Florida and the Southeast will contain higher cadmium levels than the currently-mined Florida deposits.

Some experimental laboratory scale studies now under way at TVA are designed to identify and resolve fertilizer processing problems caused by new or increased impurities in phosphate rock raw materials.^{8/} Exploratory work is also under way toward improving the physical condition of phosphate rock that may be used for direct application to the soil.^{8/} Interest in direct application is reviving due to the development of a better understanding of methods for characterization of phosphate rock. It is now relatively easy to identify phosphate materials best suited for direct application. Recent studies have shown that one promising method for convenient application of pulverized rock is to suspend the rock in water, with or without added clay, and then apply the suspension to soil with the use of spray equipment common to the fluid fertilizer industry.

Marketing Trends and Projections

Total domestic phosphate fertilizer consumption was 5.2 million tons P_2O_5 in 1976.^{6/} Mixed fertilizer products continue to dominate the phosphate market and the use of diammonium phosphate has continued to expand. Production of normal superphosphate continues to decline in favor of higher analysis products. Concentrated superphosphates have remained at fairly stable production levels in recent years (1974 to 1976).^{6/} Projections described in the literature^{9/} indicate that domestic consumption of phosphate fertilizers will grow at a compound rate of 3%/year from 1976 through 1980 and reach almost 6 million tons of P_2O_5 by 1980.

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SECTION 4

CURRENT DATA

METHODOLOGY

Midwest Research Institute (MRI) was provided with a preliminary literature survey by Radian Corporation. Data bases searched by computer included: Agricola/Cain, 1970-; Compendex, 1970-; NTIS, 1964-; and Pollution Abstracts, 1970-. Manual and machine searches were made for Biological Abstracts, 1955-; Chemical Abstracts, 1955-; Monthly Catalog, 1972-; and Soils and Fertilizers, 1974 to February 1977. Also reviewed were the Radian Library holdings, the University of Texas at Austin holdings, and Books in Print. MRI conducted a search of the Smithsonian Science Information Exchange, Inc. (SSIE) to identify ongoing research in the areas of interest.

Information was obtained from previous reports for the Environmental Protection Agency (EPA), National Science Foundation (NSF), Department of the Interior, and Energy Research and Development Administration (ERDA), as well as many technical journals. Other periodicals surveyed were: Agrindex, Bioresearch Abstracts, Biological and Agricultural Index, Bibliography of Agriculture, Phosphorus and Potassium, Phosphorus and the Related Group V Elements, Phosphorus and Sulfur and the Related Elements, and Fertilizer Abstracts.

Information was obtained during a personal visit to TVA's National Fertilizer Development Center at Muscle Shoals, Alabama. A large percentage of the research and development effort on fertilizers is conducted at this site.

Fifteen companies and numerous individuals in the U.S. fertilizer industry were contacted in order to obtain information concerning specific procedures, materials, and chemical analyses. Among those companies were: Beker Industries (Conda, Idaho), Valley Nitrogen Producers, Inc. (Helm, California), Agrico Chemical Company, a subsidiary of The Williams Companies (Donaldsonville, Louisiana), and Monsanto Industrial Chemicals Company (Soda Springs, Idaho). Other companies contacted for information were located in Florida, North Carolina, Idaho, Missouri, Kentucky, California, Louisiana, and Utah.

Contacts were also made with the Agronomy Department of Kansas State University, the Potash-Phosphate Institute, the Lawrence Livermore Laboratory at the University of California, the Idaho Division of the Environment, The Fertilizer Institute, and various offices of the Bureau of Mines, EPA, and the Geological Survey.

MANUFACTURING PROCESSES

A discussion of phosphate ore mining, ore beneficiation, and commercial fertilizer production processes is presented in this subsection to provide a foundation for further discussions relative to the potential for the enhancement of cadmium levels throughout the entire process.

Ore Mining

Phosphorus is mined in the United States almost entirely in the form of phosphate rock from sedimentary deposits. About 80 to 90% of the domestically mined phosphate rock is used in fertilizer for agricultural purposes. The remainder is used to make phosphoric acid based chemicals, such as detergents, water softeners, animal feed supplements, flame retardant compounds, and various other compounds.

Domestic phosphate mining operations are conducted in the eastern states of Florida, North Carolina, and Tennessee, and in the western states of Idaho, Montana, Utah, and Wyoming. In 1976, the production distribution pattern was 84% from Florida and North Carolina, 4% from Tennessee, and 12% from the western states.^{1/} Of the percentage shown for Florida and North Carolina, essentially all of this is from Florida. Thus, Florida is the major mining site for phosphate ore.

Most phosphate rock is mined by open-pit methods, in which the overburden is stripped with draglines and the phosphate rock removed.^{3/} The mined rock, known as matrix, is then placed into a previously prepared sluice pit, and high pressure water is used to break up the matrix to produce a slurry of approximately 40% solids. The matrix slurry is pumped through movable steel pipelines for distances up to 6 miles to a beneficiation plant. At some mines the matrix is loaded into trucks or railroad cars and hauled to beneficiation plants.

In some western locations, phosphate rock is mined by underground techniques; however, these operations account for only a minor part of total domestic production.^{3/}

Commercial phosphate rock contains one or more phosphatic minerals such as fluorapatite or tricalcium phosphate and numerous impurities. The phosphate deposits are usually mixed with clay and sand.^{2/} The Florida phosphate

deposits are generally shallow and occur principally as a consolidated conglomerate mixed with sand and clay.^{3/} The Tennessee brown rock deposits are a weathered phosphatic limestone, while the North Carolina deposits are found in phosphatic clays, limestones, and sands. The western phosphates occur as a folded and faulted shale member of the Permian Phosphoria Formation.

It is not possible to be explicit regarding specific associations of cadmium with phosphates because of the lack of published information on this subject. Cadmium may be associated with the apatite, sulfides, organic matter, or any combination of these. Extensive anionic and cationic substitutions in the apatite are possible.^{4/} Cadmium may substitute for calcium in the apatite structure, but it can also occur with other heavy metals in sulfides (e.g., pyrite (FeS_2) and troilite (FeS)), as well as inorganic matter.^{5/} Pyrites are commonly associated with marine phosphate deposits and demonstrate the impact of weathering. Pyrite pseudomorphs found in phosphate pellets from shallow deposits indicate a change from the sulfide of the original pyrite to the oxide. More deeply buried deposits which have not undergone weathering, will still contain pyrites.

Recent work by Martin et al. shows either that: (a) cadmium and phosphorus (as PO_4^{3-}) are taken up together by phytoplankton in an approximate ratio of 1 mg phosphorus for each 1 μg of cadmium; and/or (b) cadmium is taken up by adsorption. This relationship between phosphorus, a vital nutrient, and cadmium could partially explain the presence of cadmium in phosphate deposits.^{6/}

Another factor in the differences in cadmium levels of eastern and western ores may be attributed to their contrasting geological histories. Both the eastern and western ores are due, at least in part, to marine deposits. However, a more dynamic environment in the West, including volcanic eruptions and tectonic disturbances, could have resulted in lava, ash, and upward moving ore solutions penetrating the western phosphate deposits. This would lead to western ores of generally lower quality and likely containing more cadmium. Apparently due to high humidity and high rainfall, extensive water leaching of the shallow Florida ores has resulted in lower cadmium levels.^{7/} By contrast, the western ores existed in a dryer climate and occurred in deep deposits. These factors resulted in minimum weathering of the ore and anaerobic conditions in the deposits. Both sulfate reducing bacteria, which form the highly insoluble cadmium sulfide, and the strong adsorption properties of the organic matter combine to retain and stabilize the cadmium in the western deposits.^{7/}

Ore Beneficiation

Methods of beneficiating phosphate rock differ to some extent with each operating company.^{3/} Beneficiation is defined as the processing of ores for the purpose of (a) regulating the size of the desired product, (b) removing unwanted constituents, and (c) improving the quality, purity, or assay grade

of a desired product. Factors which influence the type of beneficiation methods used include: the matrix particle size and analysis; the ratio of phosphate, clay, and sand in the matrix; and the preference of the operator for certain equipment. In general, the initial treatment consists of separating coarse-sized phosphate rock from the clay, sand, and fine-sized phosphate. This operation, conducted in a washer plant, separates the matrix into three components: slimes, fine phosphate and sand, and coarse phosphate. A generalized flow sheet is given in Figure 4-1.

The coarse phosphate separated from the washer is stockpiled for use in all types of phosphate fertilizer plants.^{3/} Fine-sized material, consisting of sands, clay, and phosphate, is generally deslimed to remove the clays and then sent to a flotation plant where the fine phosphate is recovered by flotation. Small quantities of sodium hydroxide, fatty acids, fuel oil, amines, kerosine, and sulfuric acid are utilized in the flotation process. The remainder of the material, referred to as sand tails, is then discarded in the slime ponds. The slimes, containing about 4 to 6% solids, are generally pumped to slime ponds constructed in mined out areas. These slimes, which cannot be effectively beneficiated, can contain up to one-third of the P_2O_5 originally present in the mined ore.^{3/}

Following mining and beneficiation, western phosphate rock and some eastern ores are almost always calcined to remove organic material prior to conversion to fertilizer. The average total weight loss from the beneficiated ore due to ignition is reported to be about 10%.^{4/}

Calcining can also be effective against all three types of cadmium association in the phosphate rock, either by lattice decomposition or rearrangement. The cadmium will be free to vaporize, but since total evolution of cadmium is not observed, it must be partially condensed and perhaps reprecipitated. Calcining of the original apatite ($\sim 800^\circ\text{C}$) to form fluorapatite involves a complete recrystallization which will free any cadmium in the original ore.^{4/} At temperatures of 500°C , cadmium in the organic matter will be released, and any sulfides will decompose around 700 to 800°C .

Calcination in the West is generally carried out at 900 to 1000°C . These temperatures can potentially remove (via volatilization) up to 67% of the cadmium. Some calcination is also performed in North Carolina; however, operating temperatures are generally in the range of 600 to 800°C .

Calcination is generally conducted in rotary kilns similar to cement kilns. The exhaust gases, containing volatilized cadmium probably in the form of cadmium fluoride, are discharged from the kilns through a waste gas stack (commonly 100 to 150 ft high) and vented to the atmosphere. Pollution control

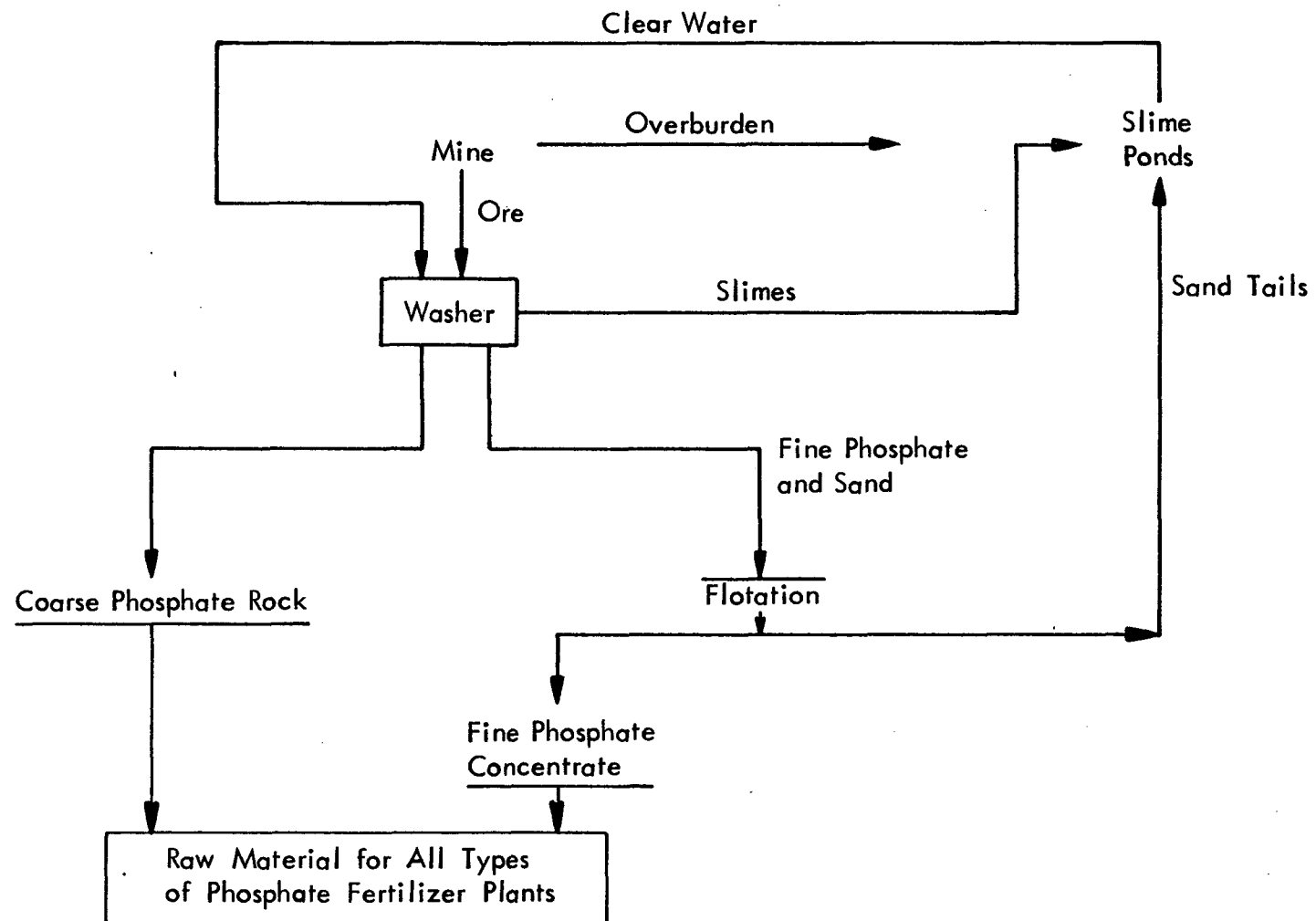


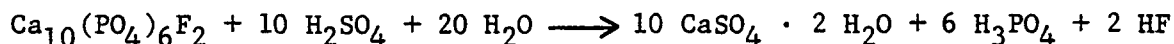
Figure 4-1. Generalized flow sheet of a phosphate rock mining and beneficiation plant.^{3/}

for cadmium emissions is not generally practiced in the United States during calcination of phosphate rock; therefore, most of the evolved cadmium is apparently discharged to the atmosphere.^{4/}

The plant product sent to storage is analyzed for particle size, P₂O₅ content, sodium, potassium, arsenic, and fluoride. Common shipping grades are 31 to 35% P₂O₅.^{3/}

Wet Process Phosphoric Acid Production

This process is the principal source of fertilizer phosphoric acid in the United States.^{3/} Beneficiated phosphate rock is reacted with a strong mineral acid (normally sulfuric acid) to convert the tricalcium phosphate to orthophosphoric acid (H₃PO₄) as shown in the reaction^{3/}:



Depending on reaction conditions, the calcium sulfate can crystallize out as an anhydrite (CaSO₄), a hemihydrate (CaSO₄ · 1/2 H₂O), or a dihydrate (CaSO₄ · 2 H₂O) commonly referred to as gypsum. Processes have been developed for each of these three forms. In the United States, only the dihydrate process has achieved any commercial significance, because this form is more easily filtered, retains less P₂O₅, and is more economically attractive.^{3/}

A flow sheet typical of the dihydrate processes showing the basic operations is given in Figure 4-2. Pulverized beneficiated phosphate rock, containing 30 to 35% P₂O₅, is continuously fed to a reaction system where it is mixed with sulfuric acid and a recycle stream of dilute phosphoric acid. In most plants, the concentration of the sulfuric acid used is between 77 and 98%.

In the digestion tank(s) the rock and acid react to form gypsum (dihydrate) and phosphoric acid. To obtain complete reaction of the rock, the rock-gypsum-acid slurry is rapidly circulated between the digestion tanks or the compartments of a single tank at 75°C. Retention time in the digester is in the range of 3 to 8 hr. The extraction of P₂O₅ from the refined ore normally exceeds 96% and the strength of phosphoric acid produced is in the range of 30 to 32% P₂O₅.

The acid slurry flows from the digester to a filter system where gypsum is removed.^{3/} Operating conditions are normally controlled so that the gypsum is easily filtered and retains a minimum of trapped P₂O₅. Typically the filter system yields two phosphoric acid streams: a 30 to 32% P₂O₅ product stream and a stream containing about 20% P₂O₅ which recycles to the digester.

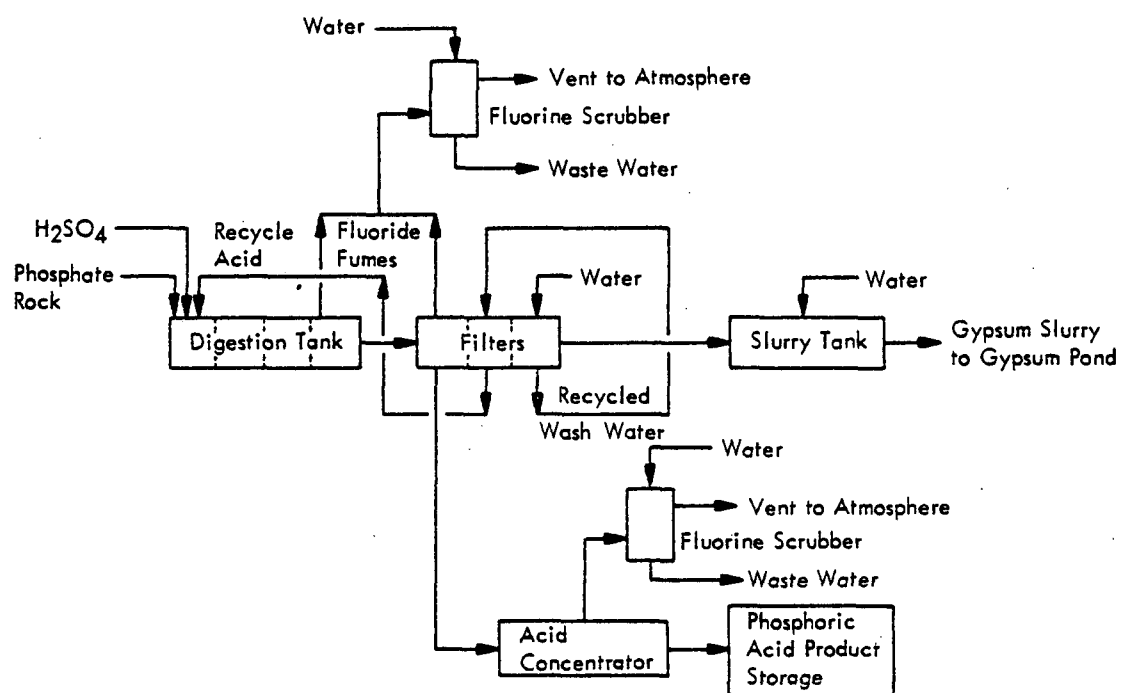


Figure 4-2. Wet process phosphoric acid flow sheet.^{3/}

The 30 to 32% P_2O_5 product stream from the filter is evaporated to give a phosphoric acid product containing about 54% P_2O_5 .^{3/} After concentration, the phosphoric acid becomes supersaturated with respect to impurities such as iron and aluminum phosphates, soluble gypsum, and fluosilicates.^{8/} These impurities are present in amounts sufficient to create an accumulation problem during acid storage. Thus, it is necessary to remove these precipitated impurities before the acid can be considered a marketable product. The removal process involves holding the phosphoric acid product under controlled temperature conditions followed by physical separation of the impurities (e.g., centrifugation). The separated solids are normally used as an additive in dry fertilizer production, principally in diammonium phosphate and to a lesser extent in the manufacture of superphosphate products.^{9/}

The wet process phosphoric acid plant produces large tonnages of gypsum (on the order of 4.5 tons of gypsum per ton of P_2O_5 product). It is the general practice to store this gypsum in diked areas called gypsum ponds. These ponds are entirely separate from the slime ponds used in phosphate rock mining and beneficiation operations. The slurried gypsum from the filter is pumped to these ponds where the gypsum settles to the bottom. The clarified water is recycled back to the various parts of the process.^{3/}

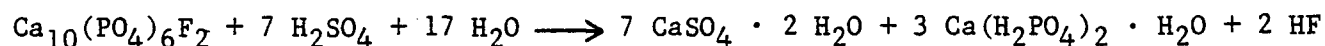
Electric Furnace Phosphoric Acid

Phosphoric acid produced by the electric furnace process is of higher purity than acid produced by the wet process,^{3/} and, at the present time, finds only limited use in the fertilizer industry.^{3/}

While there are a number of companies which produce furnace grade phosphoric acid, the processes used by the various producers are quite similar. Basically, the furnace processes involve the reaction of phosphate rock with carbon and silica in an electric furnace to form elemental phosphorus.^{3/} The elemental phosphorus, which volatilizes from the furnace, is collected and oxidized to P_2O_5 .^{3/} The P_2O_5 is absorbed in water to give a concentrated orthophosphoric acid with a 54% P_2O_5 content.

Normal Superphosphate Production

Basically, the production of normal superphosphate involves the reaction of beneficiated phosphate rock with sulfuric acid to form monocalcium phosphate.^{3/} The overall reaction which occurs can be expressed as:



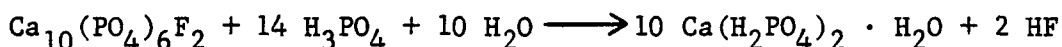
The monocalcium phosphate is water soluble and the phosphate is available for plant uptake from the soil solution. No attempt is made to separate the calcium sulfate from the monocalcium phosphate.^{3/}

Both batch and continuous processes have been developed for producing normal superphosphate and a number of modifications of each process exists.^{3/} Figure 4-3 shows a flow sheet which is typical of the continuous normal superphosphate process. Phosphate rock (98% < 0.147 mm) is fed at a controlled rate to a mixer where it is thoroughly mixed with sulfuric acid which has been diluted to about 75%. The rock-acid slurry discharges from the mixer to a pug mill where additional mixing occurs and the reaction between the rock and acid starts. From the mill, the slurry discharges to a slow moving conveyor where the reaction continues and the slurry hardens to a plastic-like mass. As this mass leaves the conveyor, it is cut into chunks and transferred to a storage area for final curing. From the storage area, the normal superphosphate product is fed to a pulverizer where it is crushed and screened. In some cases, it is desired to produce a granular product. The superphosphate can be granulated before or after curing, but granulation before curing is the preferred route.^{3/}

Triple Superphosphate Production

Triple superphosphate (TSP) contains about three times as much P_2O_5 as normal superphosphate, because no calcium sulfate is formed in the TSP. The two principal types of TSP produced domestically are run-of-pile (ROP) and granular triple superphosphate (GTSP).^{8/} Most modernized and newly established plants are of the GTSP type.

TSP is made by the reaction of beneficiated phosphate rock with phosphoric acid to give soluble monocalcium phosphate.^{3/} The overall reaction can be expressed as:



TSP can be manufactured by either batch or continuous processes, but most commercial production is by the continuous process. Various modifications of the continuous process exist, but the basic operations are identical in each case.^{3/}

A flow sheet typical of the production of GTSP by the continuous process is presented in Figure 4-4. Beneficiated phosphate rock is ground (75% < 0.074 mm) and then mixed with phosphoric acid. The resultant slurry is fed to a continuous belt where it solidifies. The discharge from the belt is crushed and sent to a storage pile for curing. The cured product is then ground and screened. The screened material is passed to a granulator where it is mixed with water and steam. The resultant wet granules are discharged to an air dryer where the water is evaporated to give a hard, dense, granular product.^{3/}

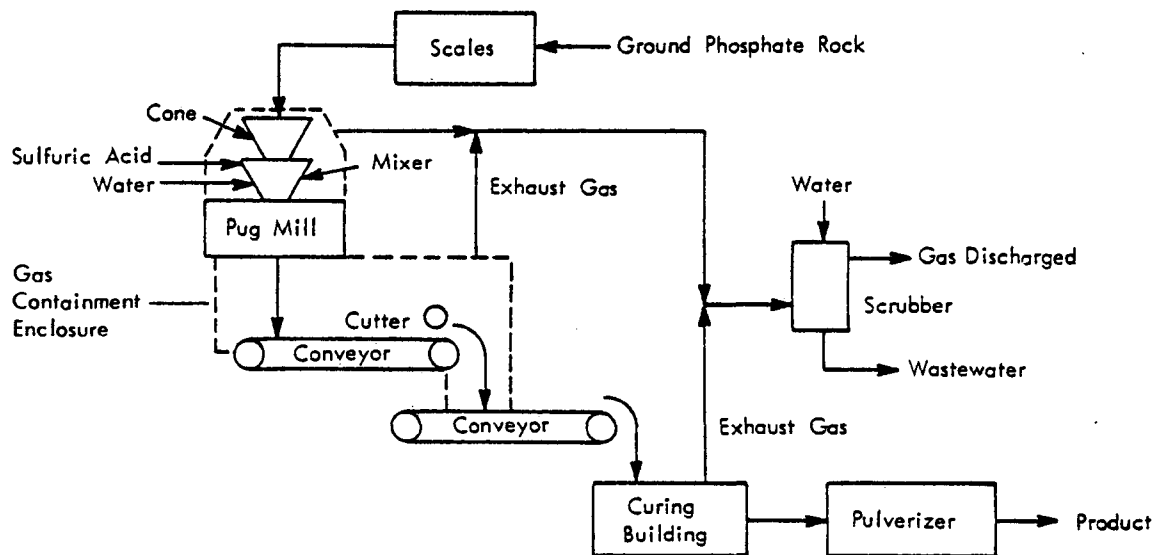


Figure 4-3. Normal superphosphate flow sheet.^{3/}

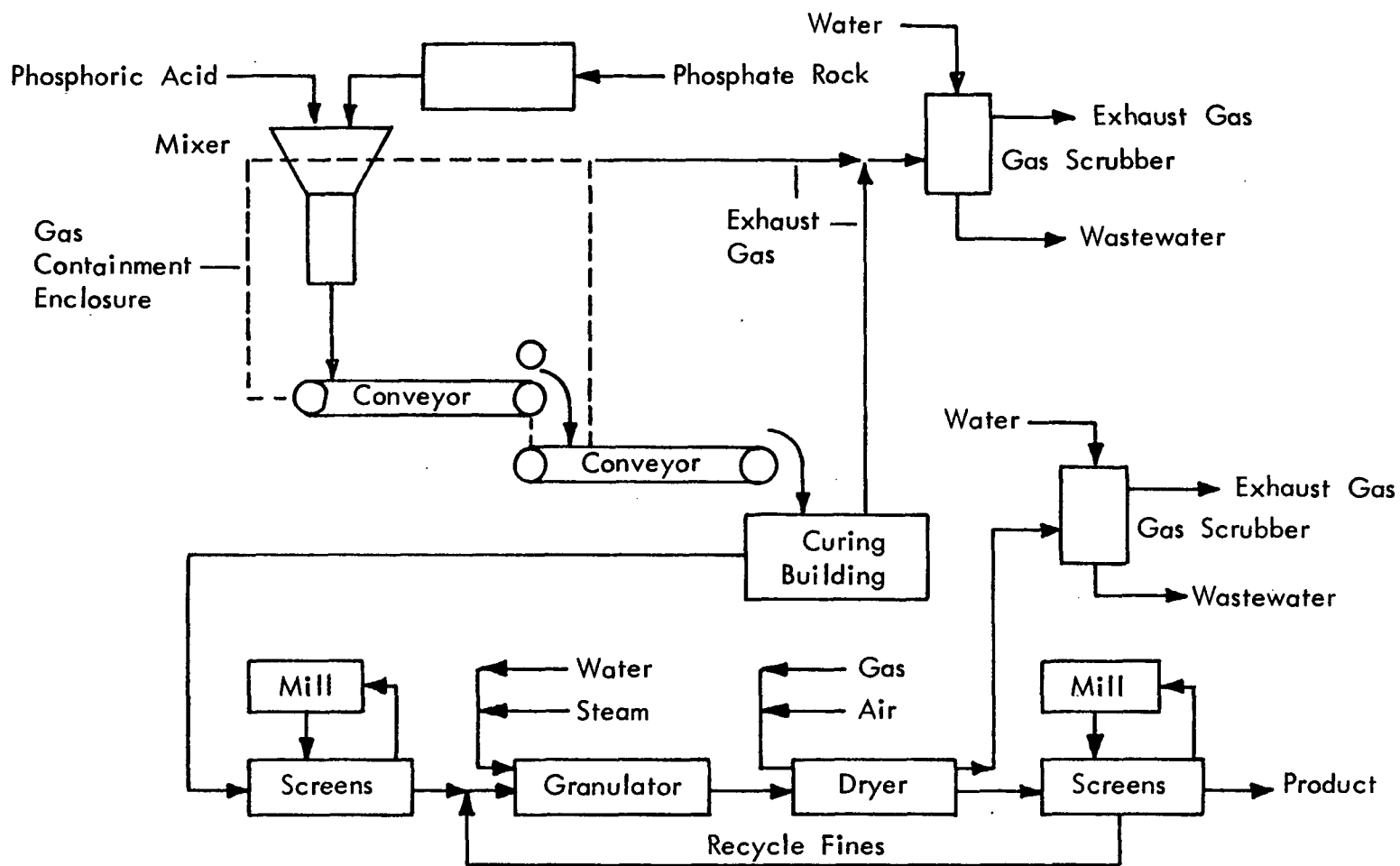


Figure 4-4. Flow sheet for granulated triple superphosphate production.^{3/}

Production of Ammonium Phosphates

The ammonium phosphates have become one of the two major sources of fertilizer phosphate. The principal advantages which have led to their increasing popularity include low production costs, good physical and chemical properties, and high nitrogen and phosphate content.^{3/}

Ammonium phosphates are normally prepared by neutralization of phosphoric acid with ammonia.^{3/} The product obtained depends on the ratio of phosphoric acid and ammonia used, and may be monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), diammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, or a mixture of the two. The ammonium phosphates can be made from either furnace or wet process phosphoric acid; most ammonium phosphates intended for fertilizer use are based on wet process acid.

Several processes can be used to produce ammonium phosphates.^{3/} The ammoniator process developed by TVA is typical of the processes used to prepare diammonium phosphate. The flow sheet for the TVA process is shown in Figure 4-5. In this method, wet process phosphoric acid (about 40% P_2O_5) is introduced to the system through a gas scrubber where it serves as a scrubbing medium for the off-gas from the process. The acid solution discharged from the scrubber is partially neutralized in a reactor with anhydrous ammonia to form a slurry. The slurry is pumped to an ammoniator-granulator where it is sprayed over a bed of recycled fines. An excess of anhydrous ammonia is added in the granulator until the product has a $\text{NH}_3:\text{PO}_4$ ratio of 2:1. The solidified diammonium phosphate product flows from the granulator to a dryer, then to screening, and finally is sent to storage. The common grades of diammonium phosphate are 16% N, 48% P_2O_5 , and 18% N, 46% P_2O_5 .^{8/}

Ammoniated Superphosphate Production

Ammoniated superphosphates are produced by reacting normal superphosphate or TSP with ammonia (usually in the form of an ammoniating solution). The final product composition can be controlled by varying the ratio of feed materials. In addition, it is possible to incorporate other fertilizer materials such as urea, ammonium nitrate, and potassium chloride into the production scheme to make a wide range of fertilizer materials.^{3/}

The reactions involved in ammoniated superphosphate production are quite complex.^{3/} The overall effect is to convert the monocalcium phosphate in the superphosphate to dicalcium phosphate and the ammonia to monoammonium phosphate. Two secondary reactions can occur if calcium sulfate is present in the superphosphate (as is the case with normal superphosphate): (a) production of monocalcium phosphate, and (b) production of tricalcium phosphate. The reactions are controlled to minimize the formation of the insoluble tricalcium phosphate.^{3/}

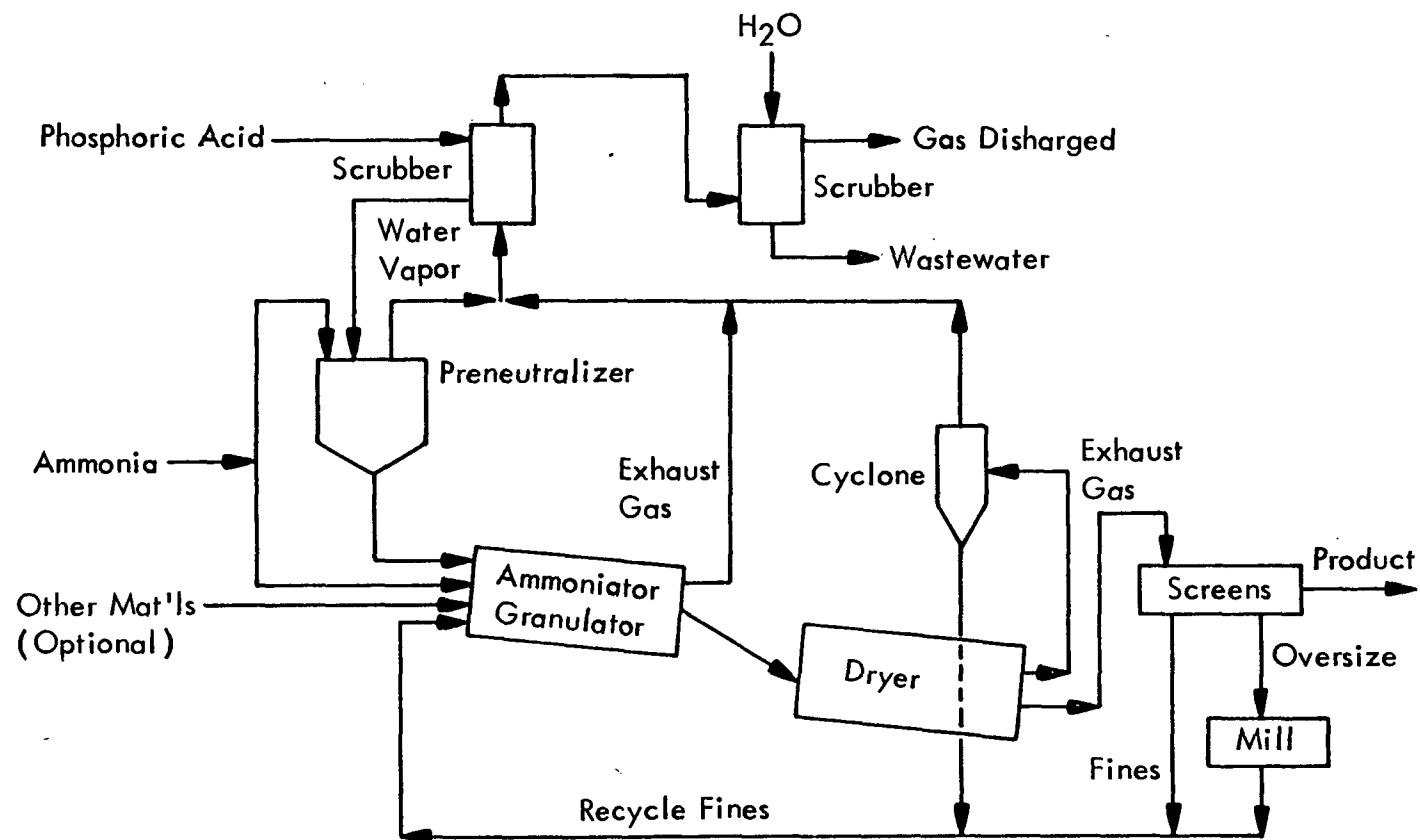


Figure 4-5. Flow sheet for production of diammonium phosphate.^{3/}

Nitric Phosphate Production^{2,10/}

Interest in nitric phosphate production has been limited in the United States because of a preference for higher grade and more rapid acting fertilizers and for economic reasons.

These products are made by dissolving phosphate rock in nitric acid (or nitric acid plus sulfuric or phosphoric acid), neutralizing the resulting slurry with ammonia, and granulating. Part or all of the calcium present in the phosphate rock remains in the product and may lead to complications in the process chemistry.

The basic chemical reaction depends on the amount of nitric acid used. If excess acid is required to provide the amount of nitrogen needed in the product, the principal reaction products are calcium nitrate and phosphoric acid. If excess acid is not required, and supplemental sulfuric or phosphoric acid is not used, a $\text{HNO}_3:\text{CaO}$ mole ratio of 1.8:1 is sufficient for good process operation. In this case, the reaction produces monocalcium diphosphate, calcium nitrate, and phosphoric acid. Neutralization with ammonia ideally converts all phosphate to dicalcium phosphate and all of the calcium nitrate to ammonium nitrate.

This mixture is acceptable agronomically, but the combination of calcium nitrate with ammonium nitrate is too hygroscopic for practical fertilizer use. Most of the variations in nitric phosphate production are concerned with removal of the calcium nitrate or its conversion in situ to a less hygroscopic compound.

Micronutrient Addition to Fertilizers

Zinc, copper, iron, and manganese are added to fertilizers used in regions of the United States where soil deficiencies of these essential plant nutrients exist. Cadmium is not commonly associated with salts of copper, iron, or manganese; however, zinc may contain significant concentrations of cadmium. From July 1, 1975, to June 30, 1976, 17,400 tons of zinc, as elemental zinc, were added to fertilizer.

Most micronutrients are field mixed today. Retail distributors purchase bulk phosphate, nitrogen, potash, and micronutrients, and custom mix these materials for the farmer-user.

Although micronutrient-supplemented fertilizers may be used in any region where soil deficiencies exist, the majority of zinc-supplemented fertilizers are used on irrigated corn grown in the high plains area of eastern Colorado, western Kansas, and Nebraska. Zinc is also typically added to fertilizer used for rice production.

Zinc application rates vary with need. The range of application rates varies from 2 to 10 lb of elemental zinc per acre and averages about 5 lb/acre in the high plains area.

Micronutrient packages containing different ratios of the four micronutrients are also marketed. Zinc is typically present in these micronutrient packages as either zinc oxide or zinc sulfate.

Using the data on consumption of zinc for this purpose and assuming an average zinc level of 2% in fertilizers, it can be calculated that about 5% of all marketed fertilizer contains added zinc; this is the same level estimated by TVA.^{11/}

CADMIUM LEVELS IN PHOSPHATE ORES AND FERTILIZERS

Cadmium levels in manufactured phosphate fertilizers can vary with the ore source, with ore beneficiation processes, and with types of phosphate rock and other raw materials used in the manufacturing process. Most of the data available is for composite ore samples and for composited fertilizer samples. In general, very little information exists on the levels and fate of cadmium as the ore is carried through the various manufacturing steps.

Information on cadmium levels in phosphate ores and fertilizers was compiled by Swaine.^{12/} Other reviews that contain relevant analytical data include Athanassiadis,^{13/} Fulkerson and Goeller,^{14/} and Sargent and Metz.^{15/} More recent and extensive data can be found in Lee and Keeney,^{16/} Mortvedt and Giordano,^{17/} unpublished data by EPA Region X,^{18/} and Gulbrandsen in a final Environmental Impact Statement.^{19/}

Cadmium in Phosphate Ores

Most phosphate rock mined in the United States is classified either as eastern (Florida, the Carolinas, and Tennessee) or western (Idaho, Montana, Utah, California, and Wyoming). In general, cadmium concentrations in the eastern ores are lower than those of the West. Florida ores range from 2 to 15 ppm, while western ores normally range from 50 to 150 ppm but can contain up to 980 ppm. A brief discussion of the chemical and physical state of cadmium in phosphate ores and the differences between eastern and western ores was presented earlier in this section.

Available data on cadmium levels found in different phosphate ore deposits are compiled in Table 4-1.

Some recent data on phosphate ores in southeastern Idaho have been compiled by Gulbrandsen of the U.S. Geological Survey (USGS) and reported, in part, in an Environmental Impact Statement for that region.^{19,20/} The

TABLE 4-1. CADMIUM CONCENTRATIONS IN PHOSPHATE ORES

Origin	Concentration (ppm) ^{a/}	Reference
<u>Eastern ores</u>		
Florida	8-15	<u>c/</u>
	2-10	17
North Carolina	10-25	14
South Carolina	13	17
Tennessee	0.1-2	17
<u>Western ores</u>		
Southeastern Idaho		
Meade Peak	60-340	19
Mudstone	50	19
Carbonate	40	19
Phosphoria Formations	90	19
Vanadiferous zone ^{b/}	470-980	19
Unidentified site	60-100	<u>c/</u>
Unidentified sites	2-50; 100	17

a/ Given as a range where possible, single values are averages.

b/ These high cadmium deposits are not generally mined.

c/ Anonymous industrial sources.

phosphate deposits surveyed contained significant amounts of several toxic elements, such as cadmium, fluorine, uranium, vanadium, selenium, and the rare earths. Cadmium averaged 90 ppm for all samples in the survey with a maximum of 340 ppm in the Phosphoria Formation. In the vanadiferous zone, cadmium levels as high as 980 ppm were found. The vanadiferous zone was originally named for a clearly defined area in Wyoming which contained vanadium concentrations in excess of 1%. This definition has since broadened to denote any area rich in vanadium content. One such zone in southeast Idaho (Bloomington area) is presently being mined; however, the low grade phosphate rock is actually a by-product rather than the ore of primary interest. As the demand for phosphate rock and rare earth compounds continues, increased mining of these areas may result. Because of the increased cadmium levels, new or modified processing techniques may be required to reduce the impurity content. The USGS is presently doing a similar survey of the Florida ores.

Sources of Cadmium in the Manufacturing Process

In addition to the raw phosphate ores, there are other potential sources of cadmium that may contribute to the total level found in the end-product fertilizer. The major sources identified include the acids used in fertilizer production and the micronutrients added to fertilizers.

Cadmium can substitute for calcium in phosphate rock and can stay with the phosphate fraction during the beneficiation process and phosphoric acid manufacture.^{15/} Sargent and Metz^{15/} indicate that the solubility of cadmium in mineral acid prevents any significant cadmium removal during the acid clarification step. Fulkerson and Goeller,^{14/} however, point out that while zinc and cadmium are readily soluble in strong mineral acids, they are only slightly soluble in phosphoric acid and most fertilizer solutions containing phosphates. Nevertheless, cadmium and other impurities in the phosphate rock, once solubilized during acidulation, generally stay in solution in the phosphoric acid.

At Beker's Conda, Idaho, plant, a filtered solution of a "gyp water" outfall to the gypsum pond contained 2.5 ppm of cadmium.^{19/} In one of Beker's beneficiation ponds, the cadmium level was 0.01 ppm which compares to the EPA standard or recommended limit for drinking water of 0.01 ppm. Waste outfall from Monsanto's plant at Soda Springs, Idaho, contained cadmium at 0.002 ppm. The variability of cadmium levels in process waters from various plants emphasizes the need to identify cadmium sources and to compile an accurate accounting of cadmium. In these cases, the cadmium levels in process waters indicate that there is not a one-to-one transferral of cadmium from the ore to the acid or fertilizer.

A survey of the fertilizer industry indicated that zinc, lead, and copper smelter acids are used, where available, in fertilizer production. In most cases, however, smelter acids are not available in sufficient quantity to meet

the needs of a fertilizer production plant. Of the total U.S. production of sulfuric acid, 10.9% is smelter acid with about 3% resulting from zinc roasting.^{15/} About 43% of the annual production of sulfuric acid is consumed in P_2O_5 production. Based on discussions with phosphate fertilizer producers, we estimate that about 10% of the sulfuric acid used in fertilizer production is a by-product smelter acid. This 10%, however, accounts for about 40% of all smelter sulfuric acid.

Limited data are available regarding cadmium levels in by-product smelter acid. Hedley et al.^{21/} analyzed sulfuric acid produced by seven major lead, zinc, and copper smelters. Cadmium levels (by weight) were detected at 1 and 5 ppb in sulfuric acid from two copper smelters; 2, 11, and 114 ppb in three lead smelter acid samples; and 5, 5, 5, 10, and 17 ppb in five zinc smelter samples. Fulkerson and Goeller^{14/} report that zinc smelter acids may contain 20 to 60 ppm cadmium; however, no further information was provided regarding specific sites. More and better data are needed on the cadmium content of smelter sulfuric acid actually used in fertilizer production before the impact of this source on the level of cadmium in end-products can be assessed.

The sulfuric acid used principally in the preparation of phosphate fertilizers is manufactured from elemental sulfur. For this acid, elemental sulfur is mined by the Frasch process to yield a high purity (99.5-99.9%) product, which is burned in air to yield sulfur dioxide. The sulfur dioxide is then converted by the contact process to sulfur trioxide and reacted with water to yield high purity sulfuric acid.^{22/} Because of the source of the sulfur and the production process, the resultant acid contains only very low levels of heavy metal impurities including cadmium.^{23/}

Zinc is added as a micronutrient to fertilizers. Levels added are sufficient to result in application rates of 2 to 10 lb of elemental zinc per acre with 5 lb/acre being about average.

The source of zinc used by micronutrient packagers vary considerably depending on availability and cost. One major source is the recovered skimmings from the galvanizing industry. Slab zinc is used in galvanizing. The levels of cadmium in slab zinc vary from 0.001% (10 ppm) to 1.0% (10,000 ppm). This zinc may also contain 0.001 to 2.0% lead. Zinc used for galvanizing contains an average of about 0.035% (350 ppm) cadmium.^{15/} Another source of zinc used for micronutrients is the baghouse dust from the brass industry. Zinc used in brass production contains no more than 0.004% (40 ppm) cadmium.^{15/} However, because of the high volatility of cadmium, the concentrations of cadmium in baghouse dust is likely to be higher than that of the source zinc. One industrial supplier of the zinc sulfate used by the micronutrient packagers states that their zinc sulfate contains less than 10 ppm cadmium.

Because of the variability of sources of zinc used as a micronutrient, the quantities of cadmium which might be introduced in fertilizers from this source cannot be accurately estimated. However, the worst case would occur where zinc from the galvanizing process, containing 1% cadmium, is added to fertilizer at levels sufficient to result in an application rate of 10 lb of elemental zinc per acre. This application rate of high cadmium zinc material would result in application of 0.1 lb/acre cadmium. This compares to only 0.002 lb/acre of cadmium that would result from the application of 200 lb/acre of phosphate fertilizer containing 100 ppm cadmium.

Cadmium in Phosphate Fertilizers

Cadmium levels in representative southeastern and western fertilizers, reported by Wilson,^{18/} Mortvedt and Giordano,^{17/} Sargent and Metz,^{15/} and SCS Engineers,^{24/} are shown in Table 4-2. In some cases, fertilizer concentrations of cadmium correlate with the NPK guarantee.* However, one study by Lee and Keeney^{16/} found no correlation between cadmium levels and the P₂O₅ level of the fertilizer guarantee.

Williams and David^{25/} demonstrated a high correlation ($r = 0.954$) between cadmium in a set of New South Wales phosphate fertilizers (ranging from 18 to 91 ppm cadmium) and the precursor phosphate rock. The authors suggested that during processing, the cadmium in the phosphate rock is transferred to the phosphoric acid with little, if any, gain or loss of cadmium during manufacture (based on parts per million Cd/% P). This is the principal, if not only, literature reference to a mass balance study. Acid used in these samples was from a manufacturing process using elemental sulfur, rather than waste acid from smelter flue gas absorbers, and therefore did not contribute to cadmium contamination of the fertilizer. Williams and David^{25/} also cite a 1940 study by Walkley, which concluded that cadmium in Australian superphosphates (50 to 170 ppm) was due to both the phosphate rock and the sulfuric acid used in fertilizer manufacture. The highest cadmium concentration was from a process using acid from zinc concentrates.

A representative of the Beker Industries Corporation at Conda, Idaho, provided the following breakdown of cadmium concentrations in the wet process production of diammonium phosphate from western ore.^{26/} These figures are not necessarily representative of the Beker process.

* NPK denotes the nitrogen-phosphorus-potash content.

TABLE 4-2. CADMIUM CONCENTRATIONS IN PHOSPHATE FERTILIZERS

Origin	Concentration (ppm)	No. of samples	Reference
<u>Eastern</u>			
Unidentified			
TSP (0-45-0)	12-14		25
Diammonium phosphate (11-46-0)	6-14		25
Monoammonium phosphate (11-48-0)	6-7		25
Superphosphate mixture	5-7		25
North Carolina			
Diammonium phosphate (10-15-0)	30 17		17 17
<u>Unidentified</u>			
TSP (0-46-0)	7.2		15
Diammonium phosphate (18-46-0)	9.0		15
Diammonium phosphate (16-48-0)	14.3		15
Monoammonium phosphate (13-52-0)	3.5		15
<u>Western</u>			
Idaho			
Diammonium phosphate (10-15-0)	50 44		17 17
Unidentified			
TSP (0-45-0)	41-174	14	18
Diammonium phosphate (18-46-0)	50-156	10	18
Monoammonium phosphate (11-48-0)	44-90	3	18
Ammonium phosphate/superphosphate (16-20-0) (0-18-0)	22-42	4	18

<u>Process steps</u>		<u>% P₂O₅</u>	<u>ppm Cd</u>	<u>Cd/P₂O₅</u>
1	Beneficiation feed (raw ore)	26	140	5.38
2	Beneficiation ore	32	140	4.38
3	Beneficiation tailings	15	130	8.67
4	Calcined ore	33	120	3.63
5	Gypsum by-product	0.5	60	120
6	Pond water (recycled)	0.8	2	2.5
7	30% Phosphoric acid	27	90	3.33
8	Diammonium phosphate (18-46-0)	46	140	3.04

The presence of cadmium in the pond water and the gypsum by-product is evidence that cadmium does not stay totally with the phosphate, but becomes distributed throughout the system. The trend (Cd/P₂O₅ column) from Steps 1 → 2 → 4 → 7 → 8 indicates a gradual decrease in the association of cadmium with the phosphates as processing continues. The main transfer of cadmium is apparent in the gypsum by-product, probably a result of acid solubilization.

An anonymous industry source also provided the following data.

<u>Material analyzed</u>	<u>P₂O₅ content (%)</u>	<u>Cd analysis (ppm)</u>	<u>Cd/P₂O₅</u>
Calcined ore	33	100	3.3
Phosphoric acid	25	58	2.3
Phosphoric acid	44	109	2.5
Phosphoric acid	52	95-100	2.0
Superphosphoric acid	70	120	1.7
Monoammonium phosphate	48	83	1.7
Diammonium phosphate	46	90	2.0

Data from these two sources indicate that the Cd/P₂O₅ ratios are comparable for the fertilizers, phosphoric acids, and calcined ores. The second manufacturer also indicated that some of their other data show that cadmium precipitates in the gypsum and sludges (i.e., silicates, etc.) during the formation and concentration of wet process phosphoric acid. This also is consistent with the levels measured for gypsum by-product in the first set of data.

Based on the very limited available data, it appears that cadmium in the phosphate ore is carried through the various stages of fertilizer production with no evidence of major concentration or dilution.

Additional data are necessary in order to trace cadmium contamination and changes in concentration ($\text{Cd}/\text{P}_2\text{O}_5$) through fertilizer manufacturing. The bulk of data now available on fertilizers and ores cannot be directly compared in an effort to complete a mass balance. A carefully designed program to establish the pathways of cadmium in the process steps will identify and quantify cadmium emissions (air, ground, and water) as well as the introduction of other sources of cadmium.

TVA is planning a program to study the fate of cadmium as phosphate rock is processed into fertilizer products.^{27/} These studies will determine the ratio of cadmium to P_2O_5 in fertilizer products, raw materials, and intermediates. This program is still in the early planning stages. TVA will work with The Fertilizer Institute (Washington, D.C.) to obtain representative processing samples from fertilizer manufacturers and will conduct chemical analyses of these samples to determine the concentrations of cadmium, P_2O_5 , and possibly other constituents.

Future Trends and Long-Term Effects

As the demand for phosphate fertilizers continues in the future, the utilization of low grade phosphate rock will likely continue to increase. Impurities in these low grade ores consist not only of cadmium but organic matter, clays, heavy metals, etc. Cadmium levels will generally be higher as the deeper deposits are mined. These deposits are less weathered and higher in organic matter, conditions which facilitate the adsorption and retention of cadmium.

A method to reduce cadmium contamination in phosphate ores was developed in Australia by Walker and Tuffley.^{28/} The Australian method involves calcination to reduce cadmium levels to less than 20 ppm. The prime reason for this work was legislation introduced in Japan to limit cadmium in imported phosphate rock to 20 ppm. Walker and Tuffley found a temperature of 1150°C and an atmosphere of 0.5% oxygen provided the optimum conditions for single step cadmium and organic carbon removal from the beneficiated ore. Cadmium removal is enhanced by increasing the temperature in a $\text{N}_2\text{-CO}_2$ atmosphere. Since oxygen is required for the removal of carbon, the maintenance of a continual low oxygen concentration of 0.5% in the $\text{N}_2\text{-CO}_2$ atmosphere at a temperature of 1150°C provided the desired conditions for effective cadmium removal from the phosphate rock. The principal differences between this process and the one currently used in the United States lie in the higher temperatures and the different reaction atmosphere of the Australian process. Both of these factors lead to faster and more efficient cadmium removal from Australian phosphate ores.

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SECTION 5

RESEARCH NEEDS

This section briefly delineates the major areas in which new or additional data are required in order to resolve the questions regarding potential cadmium enrichment in the phosphate fertilizer manufacturing process. Additional areas will be discussed which may not be directly applicable to present manufacturing processes, but which may be important in assessing the current and future impacts of phosphate fertilizers on cadmium levels in the environment.

CADMIUM IN PHOSPHATE ROCK

Limited data are available concerning the geology and mineralogy of the cadmium compounds in the raw, unbeneficiated phosphate rock. This is particularly true for those raw ores from deep, unweathered deposits in which there is an appreciable organic component as compared to the shallow, weathered deposits. Data are required for the mineral forms of cadmium (e.g., crystal forms, host compounds, etc.) and the distribution between the apatite and other components of the raw ore. This information would provide a more refined view of the beneficiation process and the mechanism by which cadmium is transported through this process. If cadmium removal becomes necessary in the future, these data would provide the background for the determination of the most technically and economically sound method of removal. The USGS is currently conducting studies of the raw Florida phosphate ores.

MASS BALANCE STUDIES

From the information presented in this report, a detailed mass balance study is obviously needed to ascertain the fate and levels of cadmium as the raw ore is processed into a finished commercial fertilizer. At the present time, data in this area are very limited and until such data are developed, any conclusions concerning the changes in the level of cadmium during the phosphate fertilizer production process must be considered tentative. The TVA is currently in the very early planning stages of mass balance studies.

CADMIUM REMOVAL

As deposits of high grade (low cadmium) ores are depleted and industry turns to lower grade deposits, cadmium removal may become necessary. At the present time, certain beneficiated phosphate ores in the United States are calcined. Using data developed on the characterization of cadmium in the raw phosphate ore, engineering studies can be performed to determine the effects of calcining on the beneficiated ore, the most efficient calcination process, and, if calcination is, in fact, the best method for the removal of cadmium. In many other industrial processes, methods other than calcination are presently used to separate trace impurities from the host material.

As the cadmium levels in the phosphate rock increase, air emissions from calcination processes may pose a serious localized air pollution problem. If data are unavailable, studies should be conducted on the engineering aspects (e.g., retention time, temperature, calcining atmosphere, etc.), pollution control devices for emission control, and the fate of cadmium volatilized during calcining.

SMELTER ACID

Additional data are needed to detail the actual quantities of by-product smelter acid used in the manufacture of phosphate fertilizers, the geographical location of this consumption and its relationship to the source of the raw ore, and the levels of cadmium present in this by-product acid. Current reported data on cadmium levels in by-product smelter acid show a wide range of values (approximately 1 ppb to 60 ppm) so that it is extremely difficult to evaluate this material as a potential source of cadmium increase in the manufacturing process.

MICRONUTRIENTS

Zinc micronutrients may be a significant source of cadmium addition to the finished commercial phosphate fertilizer. Additional data are required concerning the sources of zinc used as a micronutrient additive (e.g., slag from galvanizing processes, bag dust from bronze manufacturing, etc.), the quantities used from each source, and the cadmium levels present in the zinc from each source. Currently, very limited data have been compiled concerning this potential source of cadmium.

