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CADMIUM CONTENT OF PHOSPHATE ROCKS AND FERTILIZERS (a)

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1. Introduction

Worldwide public awareness and concern regarding protecting the environment have increased, and the global fertilizer sector is subject to increasing scrutiny and accountability. Among the primary environmental issues confronting fertilizer producers, marketers, promoters, and users are concerns over the presence of cadmium and other potentially hazardous elements in phosphate rock and phosphate fertilizers.

Almost all phosphate fertilizers are produced from phosphate rock. “Phosphate rock” is a general term used to describe naturally occurring rocks that contain significant amounts of phosphate minerals. The term is also used to describe naturally occurring ores or beneficiated concentrates that can be used for fertilizer production and chemical processing.

About 16 elements associated with phosphate rock and fertilizer are potentially hazardous to human health. The more common potentially hazardous elements found in phosphate rocks include arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), selenium (Se), mercury (Hg), uranium (U), and vanadium (V). In sufficient concentrations arsenic, cadmium, lead, mercury, and uranium are considered highly toxic when ingested and/or inhaled [Lewis, 1993]. When phosphate rocks are used as fertilizer (direct application) or as feedstocks to produce fertilizers, these potentially hazardous elements are entrained in processes and may be redistributed in products and byproducts. Ultimately, all or part of these elements are applied to the soil or must be managed as wastes, such as phosphatic tailings and phosphogypsum.

Of the more common potentially hazardous elements associated with phosphate rock and fertilizers, cadmium is certainly the element of most concern at the present time. Cadmium naturally occurs at trace levels in a broad spectrum of rock types that comprise the crust of the earth. Cadmium is particularly enriched in some coal, zinc, and phosphate rock deposits. The cadmium content of the original phosphate rock, type of processing, and any secondary processing within a specific process dictate the redistribution of cadmium to products, byproducts, and wastes.

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While cadmium is the element of most concern in phosphate rock and fertilizers at the present time and will be the main focus of this paper, the contents of several other potentially hazardous elements in phosphate rock and fertilizers are also the cause of concern. In the author's experience, the other elements generating the most concern are uranium, arsenic, and lead.

2. The Cadmium Issue

Cadmium is recognized by the World Health Organization (WHO) as a carcinogen by inhalation; no evidence exists to link cadmium to cancer by oral ingestion, and there is no evidence of genotoxicity [Anonymous, 2001a]. Cadmium has no known function in the human body. Cadmium accumulates in the kidneys with a half-life of 10-35 years. According to WHO, the critical concentration of cadmium in the renal cortex that would produce a 10% prevalence of low-molecular weight proteinuria in a general population is about 200 mg/kg and would be reached after a daily dietary intake of about 175 µg/person for 50 years. The provisional tolerable weekly intake (PTWI) has been set at 7 µg/kg of body weight.

Itai-itai disease is a well-known health hazard induced by cadmium in cadmium-polluted areas in the Jinzu River Basin in Toyama Prefecture, Japan. The main clinical features of Itai-itai disease are osteomalacia accompanied with osteoporosis and multiple proximal renal tubular dysfunctions. Citizens of the area consumed rice grown on the floodplain of the river downstream of a lead-zinc mine, which disposed of its wastes in the river basin. Exposure of the citizens began in the early 20th century. Recognition of cadmium as the prime factor in the disease did not occur until the mid-20th century.

Cadmium poisoning is also known from industrial environments, primarily in zinc mining and processing, both in Europe and North America. For an overview of the history and other aspects of the cadmium issue, the reader is referred to the abstracts and proceedings of the SCOPE Workshop on "Environmental Cadmium in the Food Chains: Sources, Pathways, and Risks" [Anonymous, 2001b; Syers and Gochfield, 2001].

Just as cadmium tends to build up in the human body with continued exposure, cadmium concentrations can build up in the soil. Cadmium exposure and buildup in agricultural soils are of extreme concern, particularly in Europe, and member states in the European Union (EU) have instituted mandatory and/or voluntary limits on the cadmium contents of fertilizers and/or limits on cadmium inputs to soils (Table 1) [Hutton and de Meeûs, 2001].

While fertilizers are certainly not the only source of cadmium in the environment, fertilizers are a significant source that is most assuredly viewed as a source of cadmium that can be controlled. Similar to Europe, cadmium concentrations in fertilizers have become an issue in the United States, particularly in California, Texas, and Washington.

Cadmium is produced commercially as a byproduct of the zinc industry; there are no mineral deposits that are mined exclusively for cadmium. In 2001 world cadmium production was estimated at 18,700 mt [USGS, 2002]. Cadmium metal prices have been falling since 1995

(US \$4.05/kg) to a price of approximately US \$0.34/kg in 2001 (average New York dealer price for 99.95% purity in 5 short ton lots).

Like zinc, cadmium is almost always divalent in stable compounds. The ionic radius of cadmium in the +2 state is 0.97 angstroms. This ionic radius is very similar to calcium; in the +2 state the ionic radius of calcium is 0.99 angstroms. Cadmium may substitute for calcium in calcium-bearing compounds and minerals.

Cadmium is widely dispersed in the rocks that comprise the earth's crust at levels generally less than 1 ppm [Adriano, 1985; Carmichael, 1982; Turekian, 1972; Turekian and Wedepohl, 1961]. Among the various igneous rock types, basalts contain the highest average cadmium contents (0.22 ppm). Among the general types of sedimentary rocks, shales and pelitic rocks have relatively higher cadmium contents (up to 1.4 ppm). Because cadmium naturally occurs in the minerals comprising the bedrock of the earth, cadmium naturally occurs in soils.

Relatively high cadmium contents are associated with zinc, copper, and lead sulfide ores. The cadmium content of such ores is usually dispersed within the mineral sphalerite (ZnS), and zinc sulfide deposits are the most cadmium enriched of the various metal sulfide ores. The cadmium content of sphalerite samples can range from less than 100 ppm to several thousand ppm. The USGS [USGS, 2000] estimates that world resources of cadmium are 6×10^6 million mt based on zinc resources containing about 3,000 ppm cadmium.

Cadmium is concentrated and/or removed at several stages in the processing of sulfide ores. In modern facilities most of the cadmium reporting to gaseous emissions and dust will be contained. The potential to disperse cadmium in the environment exists in sulfide mining, processing, and waste storage (mining and processing).

Coal formation is generally recognized to result from a rapid burial of plant material in coastal marsh or deltaic environments. Absorption processes and ion exchange during the life of the plants and later during decay results in the concentration of several elements including cadmium. While many coals have cadmium contents on the order of <1 to 3 ppm, high cadmium content coals (Western Interior, United States; New South Wales, Australia) may contain 20-30 ppm cadmium [Wixson, 1977].

The potential to redistribute cadmium in the environment exists in coal mining, processing, waste storage (mining and processing), and the burning of coal. Although there are several sources of cadmium in the environment, zinc ores and coal are probably the most significant sources. Wixson [1977] indicates the primary atmospheric sources of cadmium probably rank as follows: smelter > incineration of plastics and pigments > fossil fuel, including coking > steel mills > metallurgical.

Cadmium naturally occurs in soils at levels up to about 20 ppm [Wixson, 1977]. The cadmium content of soils is undoubtedly influenced by the cadmium content of the parent bedrock, and cadmium often appears to be enriched in the overlying soil [Adriano, 1985]. Cadmium contents of soils can be enriched in soils over zinc and lead deposits and particularly enriched in soils with a high organic content near zinc sulfide deposits [Meyer and Evans, 1973].

While not specifically addressed by this paper, much of the concern over several other of the potentially hazardous elements in fertilizers such as lead and arsenic appears to be, in part, from their presence in micronutrient additives. Micronutrient sources can be derived from base metal (zinc, copper, and lead) primary processing or secondary recovery operations. Of course, high levels of cadmium can be present in zinc micronutrient sources.

3. World Production of Phosphate Rock

World production of phosphate rock concentrate and unbeneficiated phosphate rock for chemical processing and direct application was estimated to be 133.0 million mt (145.5×10^6) (Table 2) in 2000 [USGS, 2002]. Over the last 20 years, 80%-90% of world phosphate rock output has been delivered to the world fertilizer industry. The remaining production is mainly directed to the animal feed and chemical industries. Prior to the breakup of the former Soviet Union (FSU) in the late 1980s, world production of phosphate rock was over 160×10^6 mt.

Twelve countries dominate world phosphate rock production. The production of other countries (11.3×10^6 mt) is approximately 8.5% of the world total. Of the total 2000 production of the top 12 countries (121.7×10^6 mt), approximately 18.8×10^6 mt (15.4%) came from igneous phosphate rock deposits in Russia, Brazil, and the Republic of South Africa. The remaining production (102.9×10^6 mt or about 85%) of the top 12 producers originated from sedimentary deposits.

The exact amount of phosphate rock reserves for each deposit and the world is rather uncertain; these types of data are often privileged information and can often only be obtained indirectly. The reserve data in Table 2 were derived mostly from a United States Geological Survey (USGS) source [USGS, 2002]. Where USGS data were not available for a particular deposit, other sources were used and it was assumed that the quoted reserves were producible under current technical and economic conditions.

4. Cadmium in Sedimentary and Igneous Phosphate Rocks

Almost all phosphate fertilizers are produced from naturally occurring phosphate rock. Phosphorus occurs in trace amounts in nearly all rock types but is concentrated in association with certain basic and ultrabasic igneous intrusions, igneous carbonatites, sedimentary phosphorites, and insular deposits.

The most prevalent phosphate minerals in igneous and sedimentary phosphate rocks that are commercially produced are species of the apatite family. In igneous phosphate deposits the three primary species of apatite that are found are chlorapatite, hydroxylapatite, and fluorapatite. Igneous apatites are commonly substituted with strontium and rare earth elements. Sedimentary apatites are found as two species. Carbonate-fluorapatite (francolite) is the most abundant species and is found in association with a broad spectrum of marine and freshwater deposited

sedimentary rocks. The hydroxyl-containing sedimentary apatites or hydroxyl-fluor-carbonate apatites are typically associated with insular or cave deposits where bird or bat guano may have contributed to formation [Van Kauwenbergh, 1995].

Whatever their origin, igneous or sedimentary, apatites can be highly substituted and have variable compositions. More than 25 elements are known or proposed to substitute in the apatite structure [McClellan, 1980]. The more common potentially hazardous elements found in phosphate rocks include arsenic, cadmium, chromium, mercury, lead, selenium, uranium, and vanadium. The exact residence of these elements may be speculative. Often the only indication of an association is a positive correlation with varying phosphate contents. These elements may be substituting within the apatite structure, substituting in other minerals associated with phosphate deposits, or may be adsorbed on the surface of apatite and other minerals. Divalent calcium (Ca) may be substituted in the apatite structure by divalent cadmium, mercury, or lead or by other cations such as vanadium, chromium, or uranium if compensating substitutions take place. Phosphorus (P^{+5}) may be substituted by arsenic or vanadium and chromium if compensating substitutions take place. Work by Sery et al. [1996] utilizing fluorescence-yield extended x-ray absorption fine-structure (EXAFS) spectroscopy indicates cadmium atoms are located within the apatite framework at both Ca crystallographic sites and are not adsorbed at mineral surfaces or grain boundaries.

Some of these elements may be enriched in the weathered portions of phosphate deposits. Leaching, secondary uptake, and enrichment of uranium are known from the Florida deposits [Altschuler et al., 1958]. McArthur [1980] worked with samples of unweathered and weathered Moroccan and Queensland (Australia) phosphate rock and noted that elements such as uranium and rare earth elements (REE) are generally removed during weathering, and secondary enrichment and element retention are common features in weathered samples. Lucas et al. [1980] noted increases in vanadium, chromium, zinc, lead, and other elements from nonweathered to weathered facies in the Moroccan phosphate deposits. Selective leaching of the carbonate component of carbonate-containing phosphate rock beds downdip of the highly weathered ore zone in the Togo deposit suggests a portion of the cadmium content (approximately 25%) is associated with the calcite component [Van Kauwenbergh, 1997]. Phosphate and cadmium become more concentrated with leaching of the carbonate-containing bed and removal of calcite.

In Table 3, the results of an IFDC study by Van Kauwenbergh [1997] are compared with the results of a similar study by Altschuler [1980] that compared the trace element compositions of sedimentary phosphorites with an average shale. Shales are the most abundant sedimentary rocks. Sedimentary rocks constitute about 8% of the volume of the crust of the earth, and shales are estimated to constitute about 53% of the total volume of sedimentary rocks [Carmichael, 1982].

Altschuler [1980] compared the trace element compositions of phosphorites with an average shale through the use of concentration and depletion factors. When the average concentration of an element determined for a phosphate rock group (sedimentary or igneous) is greater than the values given for standards (shales in the case of sedimentary phosphate rocks; basalts, granites, and crustal abundance in the case of igneous phosphate rocks), the average concentration of the element for the phosphate rock group is divided by the concentration of the standard; the resulting value is termed the enrichment factor. When the concentration given for an element in a standard is greater than the average concentration determined for a particular phosphate rock group, the concentration of the element in the standard is divided by

the average value determined for the phosphate rock group; the resulting value is termed the depletion factor.

The phosphate rock data used by Altschuler [1980] are not strictly analogous to the data used in the Van Kauwenbergh [1997] study. Altschuler used data from sedimentary phosphorite deposits from 18 sedimentary basins. Many of these samples were unprocessed ores and contained relatively low amounts of P_2O_5 . The data used in the Van Kauwenbergh [1997] study were obtained mainly from processed concentrates with relatively high P_2O_5 contents.

Altschuler [1980] considered an element in phosphorites enriched or depleted if the enrichment or depletion factor compared with an average shale is greater than two. Using these criteria, Altschuler considered arsenic, chromium, and vanadium to have normal abundances in phosphorites when compared with an average shale. Mercury was considered depleted. Cadmium, lead, selenium, and uranium were considered enriched. Cadmium and uranium had the highest enrichment factors of 60 and 32, respectively.

The enrichment and depletion factors determined in the Van Kauwenbergh [1997] study are similar to those of Altschuler [1980]. A slightly different shale was used for comparative purposes [Carmichael, 1982]. Using these criteria that depletion or enrichment factors of less than two are normal abundances, chromium, mercury, and vanadium are considered in normal abundance in sedimentary phosphate rocks when compared with an average shale. Lead is the only element considered depleted in sedimentary phosphate rocks. The depletion of lead (2.4) and normal abundance of mercury (1.0) are the two most significant differences between the previous study of Altschuler [1980] and the Van Kauwenbergh [1997] study.

The Van Kauwenbergh [1997] study indicates arsenic, cadmium, selenium, and uranium are considered enriched in sedimentary phosphate rocks. Arsenic is only slightly enriched with an enrichment factor of 2.0. The enrichment factor of selenium (8.0) is only slightly more than the value (7.7) found by Altschuler [1980]. Cadmium and uranium are the most enriched potentially hazardous elements in sedimentary phosphate rocks and show enrichment factors of approximately 69 and 30, respectively.

Eighty-five percent of the sedimentary phosphate rock deposits surveyed exhibit arsenic concentrations below 20 ppm (85%). Chromium concentrations are generally below 300 ppm (97%). Mercury data indicate that 90% of the sedimentary phosphate rock deposits surveyed have concentrations of <400 ppb. Lead data indicate a maximum number of deposits at <2 ppm with concentrations ranging up to 26 ppm.

More detailed chemical data for the cadmium contents of 35 sedimentary phosphate deposits in 20 countries are given in Table 4. Most of the data available are for countries that are among the top 12 world producers of phosphate rock. However, limited data are available for the Chinese sedimentary deposits, and there were no data available for sedimentary deposits in the FSU.

Concentrations of cadmium in sedimentary phosphate rocks from specific mines or ores are plotted in Figure 1 with respect to the number of deposits on which data were available. Fifteen of the sedimentary phosphate rock deposits surveyed (42.8%) exhibit concentrations of <10 ppm cadmium. Nine deposits exhibit concentrations of 10-19 ppm cadmium. Phosphate rocks from three deposits have between 20 and 29 ppm cadmium, and four

deposits exhibit cadmium concentrations between 30 and 39 ppm. Only four deposits in the data set exhibited cadmium concentrations that were greater than 50 ppm.

From the data in Table 4, it is apparent that cadmium concentrations in sedimentary phosphate rocks can vary widely between deposits within a particular country. Concentrations of cadmium can also vary widely within a particular deposit area. The overall average of the sedimentary deposits surveyed is 20.6 ppm cadmium with a range of 0.5-150 ppm cadmium.

Data on the potentially hazardous element contents of igneous phosphate rocks are summarized in Table 5 and compared with the crustal abundances and abundances of the chosen elements in granitic and basaltic rocks. Granites and basalts are two of the most common igneous rocks that form the crust of the earth.

More detailed chemical data for the cadmium contents of 11 igneous phosphate rock deposits in nine countries are shown in Table 6. The average cadmium concentrations of all the igneous deposits were below 2.5 ppm. While igneous phosphate rocks have much lower cadmium contents than sedimentary phosphate rocks, they are still enriched in cadmium. Based on a worldwide average of 1.5 ppm cadmium, igneous phosphate rocks exhibit an enrichment factor of 7.5 compared with crustal abundance [Van Kauwenbergh, 1997].

5. Future World Production

Some generalities can be made concerning world phosphate reserves and future world production of phosphate rock with respect to potentially hazardous element contents. Of the current top twelve producers of phosphate rock, nine produce from sedimentary deposits; six of these nine sedimentary producers are export oriented.

The present world production mix for the top 12 producing countries of approximately 85% sedimentary phosphate rock and 15% igneous phosphate rock is in response to several factors. Sedimentary phosphate rock is simply more abundant than igneous phosphate rock. Many of the sedimentary deposits can be mined by low-cost surface methods. Major sedimentary deposits are often located near a coast, increasing the economic viability of export. Development of sedimentary deposits near coasts will continue to be more favorable than deposits that are far inland, a category that includes many igneous phosphate deposits. The use of igneous phosphate rocks that contain lower concentrations of cadmium and other potentially hazardous elements may be a desirable alternative; however, substantially increased world production of igneous phosphate rock is not foreseen to be a viable option to replace the use of sedimentary rock.

With the notable exceptions of arsenic and lead, sedimentary rocks simply contain more potentially hazardous elements from igneous phosphate rocks (Table 7). In absolute terms, igneous phosphate rocks potentially contain more arsenic and lead.

The low content of cadmium and other potentially hazardous elements may be one factor to stimulate increased production and/or development of phosphate deposits. However, it is suggested that established producers have a distinct advantage in terms of capital investment and expertise, and those established sedimentary phosphate rock producers with ample reserves would continue to supply most of the phosphate rock to the world market.

6. Manufacture of Phosphate Fertilizers and Potentially Hazardous Elements Contents

At the present time, nearly all phosphatic fertilizers are manufactured from naturally occurring phosphorus-containing minerals. Phosphate rock must generally be treated to convert the phosphorus to water-soluble or plant-available forms. There are various methods to process phosphate rock (Figure 2); the most important methods are described in the following sections. For more detailed information concerning the cadmium content of phosphate products produced from specific phosphate rock sources, see Van Kauwenbergh [2001].

6.1. Single Superphosphate

Single superphosphate (SSP), also called simple, ordinary, or normal superphosphate, is the simplest and oldest of manufactured phosphate fertilizers. Ground phosphate rock is treated with sulfuric acid in a comparatively simple plant to produce a product usually containing about 18% P_2O_5 . The importance of SSP has steadily declined, having dropped far behind high-analysis ammonium phosphates and triple superphosphate (TSP) in world production due to the comparative cost advantage of shipping high-analysis phosphate fertilizers.

Sulfuric acid is not usually a raw material that carries trace elements or heavy metals [UNIDO, 1978]. If sulfuric acid from zinc or lead sulfide smelting is used for manufacturing SSP fertilizers, there is a potential of introducing lead, cadmium, and other impurities in the process.

All the potentially hazardous elements present in the phosphate rock will be transmitted to the SSP product. No byproducts or wastes are removed from the system.

6.2. Wet-Process Phosphoric Acid

Wet-process phosphoric acid (WPA) became important in fertilizer production in the early 1950s when TSP was established as an effective, economical, high-analysis fertilizer. WPA is usually produced in large complexes often near the phosphate rock deposits. A large part of the acid is used near the sites of rock production to produce nongranular and granular TSP and granular ammonium phosphates.

The ground phosphate rock is reacted (digested) as a slurry with sulfuric acid in multiple-reaction tanks or in a compartmented single tank. Slurry from the reaction system is filtered to remove the calcium sulfate that is precipitated in the reaction. The dihydrate WPA process results in the precipitation of byproduct calcium sulfate as the dihydrate form (gypsum). Other WPA processes are operated at higher temperatures resulting in the precipitation of calcium sulfate in the hemihydrate or the anhydrite form. The filter cake is washed to recover the P_2O_5 as phosphoric acid at a concentration usually ranging from 28% to 30% P_2O_5 for the dihydrate process or 40% to 50% P_2O_5 for the hemihydrate and anhydrite processes.

The filter acid is concentrated to 52%-54% P_2O_5 (merchant grade) for shipping and for use in producing phosphate fertilizers. For ammonium phosphate production at the site, a

concentration of about 40%-45% P_2O_5 is sufficient. Wet-process superphosphoric acid, used mainly in preparation of liquid fertilizers, is prepared by concentration to 68%-72% P_2O_5 content.

In Florida, the calcium sulfate that is removed from the reaction slurry in production of WPA usually is disposed of by storage in huge piles (stacks). Large areas of land are required for storage. Central Florida-produced gypsum must be stacked because the radioactivity of the material exceeds 10 picocuries/g, the United States Environmental Protection Agency (EPA) limit for gypsum; gypsum-exhibiting radioactivity above these levels cannot be used for agricultural or other purposes and it must be contained at controlled locations. North Carolina gypsum falls below the 10 picocuries/g limit and some of this gypsum is used for agricultural purposes; the bulk of the gypsum is slurried with tailings and used to back fill the mine. In many locations, gypsum is disposed of by dumping into rivers or the ocean. In Japan and a few other locations, the calcium sulfate hemihydrate is processed to the dihydrate form and used in the production of wallboard and other similar building materials.

When producing phosphoric acid, cadmium in the phosphate rock will report to both the acid product and to the calcium sulfate byproduct. When using a dihydrate process, approximately 55%-90% of the cadmium originally contained in the rock is transmitted to the phosphoric acid [IFDC, unpublished data] (Table 8). Becker [1983] indicates about 80% of the original cadmium in the phosphate rock is found in the filter acid when using the dihydrate process, and only 50% of the original cadmium is found in the filter acid using hemihydrate systems.

Cadmium concentrations are also an issue in gypsum disposal. Target limits for cadmium in gypsum disposed of in the North Sea are 0.5 g cadmium/mt of phosphogypsum [Hutton and Meeûs, 2001].

Depending on the process used and the intended end use of the phosphoric acid, the acid may or may not be clarified and concentrated (or concentrated and clarified). Clarification may remove significant amounts of cadmium as sludge. Becker [1983] indicates rather high concentrations of cadmium are found in the sludge precipitated from 30% P_2O_5 acid.

Depending on the phosphate rock source, degree of concentration, type and amount of clarification, and utilization of purification processes, phosphoric acids can have cadmium contents ranging from 1 ppm to over 130 ppm. In general, the use of high cadmium content rocks will result in high cadmium concentrations in the phosphoric acid products.

It is very important to note that many clarification or other purification processes will produce two acid streams. The cleaned acid stream will usually be used to produce diammonium phosphate (DAP), liquid fertilizers, or for other chemical products. The sludge- and impurity-containing stream will be utilized in applications that are more tolerant of impurities such as TSP, monoammonium phosphate (MAP), or ammonium phosphate sulfate (APS) production. These sludges/precipitates may have high P_2O_5 contents, and high P_2O_5 recovery may be essential to the economic viability of the entire processing scheme.

6.3. Triple Superphosphate

Triple superphosphate (nominally 46% P_2O_5) is made by acidulation of phosphate rock with phosphoric acid. The phosphoric acid is usually produced from the same phosphate rock. Like

SSP, TSP is a straight product of the reaction between acid and the rock where no byproducts are removed from the process (with the exception of fluorine). All potentially hazardous elements contained in the rock and in the acid will be present in the final product. Depending on the phosphate rock source, TSP can have from <10 ppm to over 100 ppm cadmium contents. Triple superphosphate is sometimes made by some commercial manufacturers of WPA to process sludge from the clarification of phosphoric acid.

6.4. Ammonium Phosphates

Ammonium phosphates were first produced in significant quantities during the early 1960s. Ammonium phosphate became the leading form of phosphate fertilizers in the United States in 1971 and in the world by 1977. The main ammonium phosphate fertilizers are DAP, MAP, and APS.

Diammonium phosphate and MAP are produced by reacting WPA and ammonia. The standard DAP grade for international trade is 18-46-0 (18% N, 46% P₂O₅, 0% K). High impurity contents in the phosphoric acid can lead to the formation of impurity-phosphate compounds in the process so that the phosphate is not completely available for reaction with ammonia. Therefore, clarification/purification of phosphoric acid may be required to achieve the standard N grade. MAP is produced in a variety of grades. Unlike DAP there is no standard for international trade. A typical MAP grade is 11-52-0. Production of MAP can be very similar to that of DAP although several process variations are possible.

Ammonium phosphate-sulfate essentially consists of MAP and ammonium sulfate formed by the reaction of ammonia, phosphoric acid, and sulfuric acid, although solid ammonium sulfate can be used in place of sulfuric acid. The best known grade is 16-20-0.

In manufacturing ammonium phosphates, metal impurities precipitate upon ammoniation of WPA. The compositional form and relative abundance of these metal salts depend upon both acid composition and operative parameters during ammoniation and granulation. Cadmium is thought to precipitate along with other divalent metals as (M²⁺ NH₄PO₄²⁻) compounds. These compounds are generally expressed as anhydrous compounds.

Depending on the phosphate rock source, phosphoric acid processing scheme, and use of any clarification/purification processes, DAP products can have cadmium contents ranging from 1 ppm to over 100 ppm. Monoammonium phosphate and APS products may contain over 200 ppm cadmium due to the fact that MAP and APS production are also used for sludge processing similar to the case of TSP. Monoammonium phosphate and APS production does not require that the sludge be separated from the acid, and all the sludge is fed into the neutralization system.

7. NPK Fertilizers

Numerous examples of the cadmium contents of NPK fertilizers are found in the literature. However, it is practically impossible to determine what phosphate sources and what production processes were used. NPKs can be produced by numerous methods, including bulk blending, steam granulation, and chemical granulation, in conjunction with nitrophosphate and APS production or by other processing schemes. The phosphate products discussed in the

previous sections are used as raw materials in the production of NPKs by steam granulation, bulk blending, chemical granulation, and with APS production. It should be noted that NPK facilities are generally designed and run as zero effluent/waste facilities. That is, liquid effluents, solid spillage, etc., are integrated with production so that no waste is produced; some particulate matter may be carried from such sites, but the amount of this material is typically minimal. Any cadmium or other potentially hazardous elements in the raw materials are redistributed in the products.

Nitrophosphates are produced using several process variations, the most common being the Odda Process. Basically, phosphate rock is dissolved with nitric acid. The resulting phosphoric acid intermediate is generally utilized internally within the fertilizer complex to produce a number of multinutrient granular products. Calcium is removed from the system as calcium carbonate, calcium ammonium nitrate (CAN), or calcium nitrate. The level of calcium removal from the nitric/phosphoric acid solution controls the water solubility of the phosphate in the finished product. Insolubles (silica sand, etc.) are removed from the system and may be sold as construction materials. Any cadmium or other potentially hazardous elements present in the phosphate rock are redistributed to products and coproducts.

8. Removal of Potentially Hazardous Elements

8.1. Cadmium

There are two main opportunities to remove cadmium prior to the production of fertilizers. Cadmium can be removed from the phosphate rock prior to processing, or it can be removed during or after the production of phosphoric acid.

Limited work at IFDC has indicated that neither common beneficiation techniques nor selective leaching are feasible methods to remove cadmium from phosphate rock. The only known method to effectively remove cadmium from phosphate rock is by calcination.

Removal of cadmium from phosphate rock by calcination is governed by the known physical properties of cadmium metal and cadmium oxide. Cadmium can be removed from phosphate rock by calcination most effectively at temperatures between approximately 850° and 1150°C under either an inert atmosphere or reducing conditions. The higher end of the temperature range is needed for the most effective cadmium removal.

Significant research has been performed in the area of calcination [Henin, 1984; Walker and Tuffley, 1974; Frankenfeld and Peter, 1985; Plassen and Baechle, 1983a, 1983b; Friedrich et al., 1983; Friedrich and Baechle, 1983; Plassen and Schimmel, 1987; Smidth, 1986; Smith, 1980], and several patents have been granted. To the author's knowledge the only facility that has been built in the world to remove cadmium was installed (75 mtph) on the Island of Nauru for Nauru Phosphate Corporation. The exact cost of calcination is not known, but in 1992 untreated Nauru phosphate rock sold for approximately US \$50/mt while calcined product sold for over US \$90/mt.

The exact costs for calcining phosphate rock by various methods to remove cadmium are not known; companies promoting this option at one time probably have good figures. The cost

per metric ton of phosphate rock is probably in the US \$10-\$20/mt range, depending upon the scale of operations and treatment of wastes. Interest and research in this area have waned due to economic considerations and because of results from research in other areas that indicated alternate routes might be more cost effective.

Cadmium can be removed from phosphoric acid that is produced with sulfuric acid-based processes by a variety of methods, including co-crystallization with anhydrite, precipitation with sulfides, removal by ion exchange resins or liquid ion exchange, removal by solvent extraction, and separation by membrane technology.

In a comprehensive study, Davister [1992] contacted all known research groups/companies then involved in cadmium removal technology, assessed the various technologies, and developed general/average costs for co-crystallization with anhydrite, precipitation, ion exchange resins, and solvent extraction (Table 9). The results of this study indicate the cost advantages of the co-crystallization route [Becker, 1994]. Precipitation, ion exchange resins, and solvent extraction were all much more expensive methods for removing cadmium.

In the Davister study, the potential values of the rejects were used to offset the costs of treatment. Some caution should be used in applying the value of the cadmium-containing rejects as a way to reduce the cost per metric ton of P_2O_5 for the co-crystallization process. This part of the analysis was not as detailed as other aspects, and the value of cadmium and other elements to be recovered from the rejects and processed into marketable products may be highly variable. As mentioned in a previous section, in 2001 cadmium metal was worth a fraction of what it was worth 4 years earlier. If the reject material must be disposed of as a hazardous waste, overall costs may increase significantly.

In the co-crystallization with anhydrite process, concentrated phosphoric acid (50%-54% P_2O_5), including sludges, is heated and further treated with calcium phosphate and sulfuric acid. Impurities are precipitated as anhydrite with phosphate and metal substitutions.

A very favorable aspect of the process is the small amount of reject generated; Davister [1992] indicates that about 70 kg of reject is generated per metric ton P_2O_5 . It should be noted that a significant proportion of the cadmium will report to the calcium sulfate byproduct that is produced during the generation of the concentrated phosphoric acid that is fed to this coprecipitation process.

Baechle and Wolstein [1984] indicate it is more difficult to separate cadmium from solutions when the phosphate rock is digested with nitric acid. An extraction process used for the production of rare earths by Kemira Oy and a Czech process are mentioned as possible methods for cadmium separation. There were no examples or costs presented by Baechle and Wolstein.

A study conducted for the EU [Hutton and Meeûs, 2001] indicates the potential costs for various cadmium removal methods (Figure 3). The potential costs of decadmiation by calcination by neutral/reducing atmosphere and cocrystallization are similar to those given in this paper. It should be noted that the low costs associated with calcination under an oxidizing atmosphere may not be appropriate to further analyses; the method is not suitably effective in most cases (perhaps a 40%-50% reduction in cadmium contents) and may only be appropriate to reduce cadmium content in some cases to meet specific limits.

It should be stressed that the costs mentioned in this section and the EU study are only potential production costs; there have been no significant successful implementations of the technologies mentioned for fertilizer production to adequately assess all associated costs. The costs of processing or disposing of wastes are particularly uncertain. Furthermore, the production costs mentioned are not the added costs farmers will ultimately pay for product. Primary producers, secondary producers, brokers, distributors, etc., will expect to make a reasonable profit on their investments. If US \$10-\$20/mt P_2O_5 is added at the primary production level, the cost/metric ton P_2O_5 could very easily double by the time the fertilizer reaches the consumer.

9. Continuing Issues

European Union options under consideration to control cadmium contents in phosphate fertilizers include limits of 60, 40, or 20 mg cadmium/kg P_2O_5 (Table 10); these limits would be phased in or voluntarily implemented by predetermined dates [Hutton and Meeûs, 2001]. The author is not aware of any scientific basis for these proposed cadmium levels; risk-based analysis techniques do not appear to have been used to select these cadmium levels. The proposed cadmium levels appear to be a phased approach to lowering cadmium levels in fertilizers by eventually using the lowest cadmium content phosphate rocks available and/or using the best available techniques to lower cadmium contents to the lowest levels possible.

Use of low-cadmium raw materials has been determined to be the lowest cost option. The impact on the use of different rock sources can be seen in Table 10. Imposition of a 20 mg cadmium/kg P_2O_5 limit would limit use to igneous phosphate rock sources and a very limited number of very low cadmium content sedimentary sources.

Cadmium removal is considered costly. The European outlook, from a cautious health perspective and due to environmental concerns, is that cadmium removal may be necessary. When the costs of cadmium removal are calculated to the individual consumer level in Europe, the costs do not seem excessive.

Cadmium charges (taxes) have also been considered. Cadmium taxes are already levied in Sweden. Management of the cadmium levels of soils and crops in the EU is also under consideration. Such management might focus on soils with high levels of cadmium and crops that preferentially uptake cadmium.

The U.S. EPA, CDFA, and The Fertilizer Institute (TFI) have undertaken evaluations of potential human health risks as a result of exposure to metals in fertilizers. The risk assessments by these organizations share much of the same underlying science and methodologies. Details of these studies are available from TFI [Anonymous, 2001].

Collaboration among consultants working on behalf of TFI and CDFA resulted in a risk-based acceptable concentration (RBC) for cadmium of 10 ppm per 1% P_2O_5 in NPK products and 83 ppm per 1% of micronutrient. The RBC is the estimated maximum safe level of a particular metal present in a phosphate fertilizer product at 1% of the nutrient level. This cadmium value and other metal values have been recommended by the Association of American Plant Food Control Officials (AAPFCO) Board of Directors to be incorporated into the Statement of Uniform Interpretation and Policy (SUIP) #25, the fertilizer adulteration clause, and is the proposed AAPFCO standard (Table 11). Under the levels of this standard,

any phosphate rock commonly available on the world market can be processed to phosphate fertilizer by conventional means to produce fertilizers with acceptable cadmium levels.

The State of California has further agreed to phase in additional restrictions on metals in phosphate fertilizers over a 2-year period [Anonymous, 2001d]. For each percent of available phosphate (water-soluble + neutral ammonium citrate [NAC] P_2O_5) starting January 1, 2002, the allowable units will be 4 ppm arsenic, 6 ppm cadmium, and 20 ppm lead. Limits as of January 1, 2003 will be 3 ppm arsenic and 5 ppm cadmium; lead will remain at 20 ppm. On January 1, 2004, the limits will be lowered to final levels of 2 ppm arsenic, 4 ppm cadmium, and 20 ppm lead for each percent of available phosphate.

To contrast the proposed AAPFCO cadmium standard, the final California standard (4 ppm cadmium per 1% P_2O_5) and proposed EU standards, an example of a 10-50-0 MAP product can be used. Under the AAPFCO standard, the RCB would be 500 ppm cadmium. The final California standard would allow 200 ppm cadmium in a 10-50-0 MAP product. Under the proposed EU limits of 60, 40, and 20 mg cadmium/kg P_2O_5 , the limits would be 30, 20, and 10 ppm cadmium, respectively, in a 10-50-0 MAP product.

The differences in these maximum cadmium levels will undoubtedly spawn considerable debate. For one perspective on this issue, see the website of the California Public Interest Research Group [Anonymous, 2001e].

Even more basic to the cadmium issue is the considerable amount of debate within the medical research community concerning cadmium. Swedish researchers basically consider any cadmium intake unacceptable; any detection of proteinuria due to cadmium intake is indicated to eventually lead to a decreased quality of life. Swedish researchers consider the renal effects of cadmium irreversible [Friberg, 2001].

Belgian research [Bernard, 2001a; 2001b] indicates that renal effects are reversible. Belgian research indicates that the effects of cadmium intake are more disturbing from the perspective of incorporation in bone and joint tissue.

U.S.-based research [Chaney, Ryan, and Angle, 2001] indicates the assessment of the ultimate bioavailability of cadmium in foods is very complex. Most livestock and wildlife have no increase of cadmium in tissue used as food even when crop cadmium is increased substantially as long as the cadmium:zinc ratio is near natural levels. Zinc inhibits cadmium absorption and/or retention in tissue, even liver and kidney. Feeding studies, which used cadmium salt additions to diets, are not relevant to risk assessment because zinc was not increased simultaneously. Many of the toxic effects of high cadmium doses (without normal increased zinc) result from cadmium-induced zinc deficiency and are not relevant to risk assessment.

Similarly, the U.S. researchers concluded that risk to the food chain of soil cadmium is very dependent on the cadmium:zinc ratio of the soil. Most plant species exclude cadmium relative to zinc during formation of grain fruits or storage roots. However, rice grown in flooded soils has an opposite pattern in which grain cadmium is substantially increased, while grain zinc remains at background levels. Worldwide use of rice-based studies has resulted in an overestimation of risk from soil and food cadmium. The U.S. researchers indicate the ultimate risk from bio available crop cadmium should be the basis for any limits developed for cadmium in crops or soils.

10. Conclusions

Cadmium occurs at trace levels in some soils and a broad spectrum of rock types that comprise the earth's crust. Cadmium is particularly enriched in some coal, zinc, and phosphate rock deposits. Phosphate rock deposits provide the basis for most of the fertilizer production of the world. The bulk of phosphate rock mined in the world is used for the production of fertilizers. World production of phosphate rock is mainly based on sedimentary phosphate rock. World reserves of phosphate rock are dominantly sedimentary phosphate rock. World production and resources of igneous phosphate rock are located mainly in Russia, Brazil, and the Republic of South Africa.

Sedimentary phosphate rocks in general contain much higher concentrations of cadmium than igneous phosphate rocks. Igneous rocks are also enriched in cadmium; however, the average content of cadmium is much lower than that in sedimentary phosphate rocks. The concentration of cadmium in sedimentary phosphate rock can vary among the phosphate rock deposits of a given country and within a given deposit. Sedimentary phosphate rock will continue to supply most of the world's phosphate rock requirements in the future. Several major undeveloped sedimentary deposits have low contents of cadmium. It is suggested that if low cadmium content products are mandated in specific regions of the world, demand and costs will increase for low cadmium igneous and sedimentary phosphate rocks.

While igneous phosphate rocks have much lower cadmium contents than sedimentary phosphate rocks, igneous rocks can contain higher concentrations of arsenic and lead. If arsenic and lead are a cause of concern, the screening and selection of igneous phosphate rocks is suggested; treatment may be required and treatment may not be economic.

Straight phosphate fertilizers, like SSP and TSP, contain cadmium directly derived from the phosphate rock source. The amount of cadmium in the final products depends on the rock source. Because the production of SSP and TSP does not generate byproducts, all the cadmium in the raw materials (phosphate rock and acids) is transmitted to the final product.

If very low cadmium contents for phosphate fertilizers are mandated, the use of igneous phosphate rocks, the lowest cadmium content sedimentary phosphate rocks, or treated phosphate rock will be required to produce SSP or TSP. The only effective way to treat phosphate rock to remove cadmium is by calcination under a neutral or reducing atmosphere; this type of treatment is very expensive. With treatment of the phosphate rock by calcination, production of SSP and TSP may become uneconomic relative to processes that totally dissolve the rock wherein cadmium can be removed by less costly methods.

Phosphoric acid is an intermediate raw material for the production of many phosphate fertilizers and a source of potentially hazardous elements. Although WPA may be treated to remove some elements and clarified for some products, a significant portion of the cadmium generally remains in the acid (liquid phase) and is transmitted to the final products. In addition, WPA production generates significant amounts of byproduct calcium sulfate, which contains a proportion of original cadmium derived from the rock source. Disposal of cadmium-containing phosphogypsum is an issue.

Ammonium phosphates (MAP, DAP, and APS) will contain all the cadmium contained in the phosphoric acid source. If the phosphoric acid has been treated or clarified, less cadmium will be found in the final fertilizer products. Monoammonium phosphate and APS products may contain proportionally more cadmium because sludge, clarification solids, and other WPA byproduct streams that may be used for production of these fertilizers may contain high impurity levels. NPK products, whether formulated by use of finished phosphate products and/or intermediates or produced by nitrophosphate processes, will generally contain all of the cadmium introduced with the raw materials.

There are several technologically feasible means that have been developed to remove naturally occurring cadmium from phosphate rock and phosphoric acid and thereby reduce cadmium levels in phosphate fertilizer products. The most cost-effective means appear to be those involving cadmium removal from concentrated phosphoric acid. The investment and production costs of cadmium removal are significant. Further study is needed to determine the exact costs of removal processes, treatment/disposal of byproducts/wastes, and eventual added cost to the consumer. Other potentially hazardous elements can potentially be removed by methods proposed to remove cadmium; further study is also needed in this area.

The issue of cadmium will continue to be debated from a fundamental medical research level, from the perspective of cadmium incorporation in foods, and at the policy/administrative level of various government entities. Maximum cadmium levels proposed for adoption by the EU are very restrictive practically mandating use of very lowest cadmium content phosphate rocks as raw materials and/or the implementation of processing strategies to remove cadmium. Proposed U.S. RCBs for cadmium are much higher and would not restrict the use of most commercially available phosphate rock for the production of phosphate fertilizers by conventional processing techniques. Production schemes, which utilize high impurity content phosphoric acid streams or sludges in the production of impurity tolerant products, may result in products that will not meet proposed U.S. or State of California standards.

There is no substitute for phosphorus in agriculture. There is no substitute for phosphate rock in phosphate fertilizer production. There is a tradeoff in this scenario; the naturally occurring potentially hazardous elements found in phosphate rocks are simply inherent to the situation. Based on world demand for phosphate fertilizers and available resources/reserves, simply selecting sources of phosphate rock to avoid potentially hazardous elements or purchasing low potentially hazardous-element-containing products is not a viable solution in a world context.

The necessity of removing or restricting the level of potentially hazardous elements in phosphate fertilizer products should be carefully considered with respect to the risk to human health and costs/benefits of the entire situation. U.S.-based organizations have taken a risk-based approach to this issue. While technologically advanced and affluent countries may be able to set high standards with respect to impurity levels in phosphate fertilizer products, less affluent countries may be forced to take a more pragmatic approach.

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Table 1. Limit Values for Cadmium in Fertilizers and in Soil in the EU Member States

	Cd in Fertilizers	Cd Input to Agricultural Soil	Cd in Agricultural Soils
	(mg kg P ₂ O ₅)	(g/ha/a)	(mg/kg dry soil)
Austria	75	10 ^a /5 ^b	1.0
Belgium/Luxembourg	90	150	1.0-3.0
Denmark	47		0.5
Finland	21.5	3	0.5
Germany	40-90 ^c	16.7 ^d	1.0
Netherlands	^e		
Portugal	40-70 ^f		
Sweden	43 ^g	1.75 ^h	
United Kingdom		0.15 ⁱ	3.0 ^j

a. Arable land.

b. Grassland and vegetables.

c. Based on a voluntary agreement between government and industry.

d. Average over a period of 3 years.

e. OECD [1994] mentions a limit of 40 mg/kg phosphorus (17 mg/kg P₂O₅). According to a spokesman of VKP, there is no limit for the Cd content in P fertilizers in the Netherlands. Instead a voluntary agreement is in preparation.

f. Mentioned in OCED (1994); probably not a legal limit.

g. A voluntary limit of 21.5 mg/kg P₂O₅ has been introduced by the SLR.

h. Average for 7 years; will lower to 0.75 g/ha/year as from 2000.

i. With sewage sludge only.

j. Soils with a pH of 5 and above, treated with sewage sludge.

Source:Hutton and de Meeûs [2001]. See original reference for further explanation of the table and references within footnotes.

Table 2. World Phosphate Rock Production and Reserves

Country	2000 Production ^a , b	Reserves ^{a,b}	Reserve Base ^c	Comments
	(tonnes x '000)			
United States	38,600	1,000,000	4,000,000	Combined North Carolina, Florida, and Western United States
Morocco and Western Sahara	21,000	5,700,000	21,000,000	Reserves may be much larger
China	19,400	1,000,000	10,000,000	Reserves may be much larger
Russia	11,100	200,000	1,000,000	Production mainly from igneous deposits, Anonymous [1999], indicates 3.2 x 10 ⁹ of reserves in Kola area
Tunisia	8,340	100,000	600,000	Combined production and reserves of several mines
Jordan	5,510	900,000	1,700,000	Savage [1987] indicated 790 x 10 ⁶ tonnes of measured reserves
Brazil	4,900	330,000	370,000	Production from igneous deposits
Israel	4,110	180,000	800,000	Savage [1987] indicated 150 x 10 ⁶ tonnes of proven reserves
Republic of South Africa	2,800	1,500,000	2,500,000	Verster and van Luitingh [1997] indicate a resource base of 2.31 x 10 ⁹ tonnes of concentrate @ 38% P ₂ O ₅
Syria	2,170	100,000	800,000	
Togo	1,370	30,000	60,000	Hahotoe, Kpogame, and Dagbati areas
Senegal	1,800	50,000	160,000	Taiba 35 x 10 ⁶ tonnes product; Tobene 50 x 10 ⁶ tonnes product
All other countries	11,300	1,200,000	4,000,000	
Total	132,400	12,290,000	46,990,000	

a. Sources: USGS, 2002; IFDC unpublished data.

b. Economically recoverable materials producible under present conditions.

c. May encompass those parts of resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics.

Table 3. Potentially Hazardous Trace Element Abundances in Sedimentary Phosphorites, Sedimentary Phosphate Rock, and Average Shales

Element	Altschuler [1980]			Van Kauwenbergh [1997]			Enrichment or (Depletion) Factor
	Average Shale ^a	Average Phosphorite	Enrichment or (Depletion) Factor	Average Shale ^b	Sedimentary Phosphate Rock	Range	
	(ppm)			(ppm)			
As	13	23	1.8	6.6	13.2	3-79	2.0
Cd	0.3	18	60	0.3	20.6	1-150	68.7
Cr	90	125	1.4	100	129.2	16-1,000	1.3
Hg	0.4	0.055	(7.3)	0.4	0.4	0.010-99	1.0
Pb	20	50	2.5	20	8.4	1-55	(2.4)
Se	0.6	4.6	7.7	0.6	4.8	2-42	8.0
U	3.7	120	32.4	3.2	96.1	10-390	30.0
V	130	100	(1.3)	130	129.6	2-1,737	1.0

a. Turekian and Wedepohl [1961].

b. Carmichael [1982].

Table 4 . Phosphate and Cadmium Contents of Sedimentary Phosphate Rocks^a

Country	Deposit	No. of Samples	Average P ₂ O ₅	Average Cd	Range Cd
			(wt %)	(ppm)	
Algeria	Djebel Onk	2	28.8	22.5	13-32
Algeria	Djebel Kouif	1		12	-
Australia	Duchess	4	31.2	4.17	0.5-5
Burkina Faso	Kodjari	3	29.2	2.5	2-3
China	Kaiyang	1	35.9	<2	-
Colombia	Media Luna	1	30.1	9	-
Colombia	Sardinata	2	35.4	12	12-19
Egypt	Abu Tartur	3	29.89	5.67	3-10.5
Egypt	Hamrawen	1	22.2	15	-
Egypt	West Makamid	1	26.5	6	-
India	Mussoorie	2	25.0	8	-
India	Rajasthan	1	33.3	1	-
Israel	Zin	6	31.13	30.77	20-40
Israel	Undifferentiated	4	32.8	24.25	20-28
Israel	Arad	3	32.4	14.33	12-17
Israel	Oron	1	33.62	5	-
Jordan	El-Hasa	5	31.9	5.42	3-12
Jordan	Shidyia	1	30.5	6	6
Mali	Tilemsi	1	28.8	8	8
Mataiva Island		1	35.6	9	
Morocco	Undifferentiated	6	32.7	25.98	10-45
Morocco	Bu Craa	2		37.5	32-43
Morocco	Khouribga	10	32.6	15.06	3-27
Morocco	Youssoufia	6	31.22	23.17	4-51
Nauru		4	36.65	85.15	70-100
Niger	Parc W	2	34.3	4	<2-4
Peru	Sechura	4	30.2	25	11-41
Senegal	Taiba	12	35.91	86.67	60-115
Syria	Khneifiss	1	31.9	3	-
Tanzania	Minjingu	1	28.6	1	-
Togo		19	36.7	58.41	48-67
Tunisia		4	29.95	39.5	30-56
United States	Central Florida	27	32.1	9.13	3-20
United States	North Florida	7	31.0	6.14	3-10
United States	Idaho	7	31.7	92.29	40-150
United States	North Carolina	14	29.8	38.21	20-51
Venezuela	Recieto	1	27.9	4	-
Overall Sedimentary Averages ⁿ			31.3	20.6	0.5-150

a. Full details and references can be found in Van Kauwenbergh [1997].

Table 5. Potentially Hazardous Trace Element Abundances in the Crust, Granite, Basalt, and Igneous Phosphate Rocks^a

Element	Crustal Abundance ^b	Granite ^b	Basalt ^b	Igneous Phosphate Rock	Range	Enrichment or (Depletion) Factor Relative to Crust
			(ppm)			
As	1.8	1.5	2.0	121.4	3-1,300	67.4
Cd	0.2	0.2	0.2	1.5	1-5	7.5
Cr	100	4	200	26.9	1-100	(3.7)
Hg	0.08	0.08	0.08	0.06	1-500	(1.3)
Pb	20	5	20	15.0	4-36	(1.3)
Se	0.05	0.05	0.05	3.8	3-5	76
U	2.7	4.8	0.6	59.8	7-247	22.1
V	135	20	250	49.5	4-300	(2.7)

a. Van Kauwenbergh [1997].

b. Carmichael [1982].

Table 6. Phosphate and Cadmium Contents of Igneous Phosphate Rocks^a

Country	Deposit	No. of Samples	Average P ₂ O ₅	Average Cd	Range Cd
			(wt %)	(ppm)	
Brazil	Araxa	2	37	2.50	2-3
Brazil	Catalao	1	37.4	<2	
Burundi	Matongo	1	40.4	<2	
Finland	Siilinjarvi	1	39.50	<2	
S. Africa	Phalaborwa	5	38.6	1.3	1-1.6
Sri Lanka	Eppawala	3	36.43	2.17	0.5-5
Sweden	Kiiruna	2	35.3	0	<1-<5
Sweden	Grangessburg	2	37.85	1	-
Uganda	Sukulu Hills		38.6	1	-
Russia	Kola	5	39.2	1.25	0.3-2
Zimbabwe	Dorowa		33.1	1	1
Overall Igneous Averages			37.58	1.5	0.5-5

Full details and references can be found in Van Kauwenbergh [1997].

Table 7. Comparison of the Potentially Hazardous Trace Element Contents of Sedimentary and Igneous Phosphate Rocks^a

	Sedimentary Phosphate Rock	Igneous Phosphate Rock
P ₂ O ₅ (wt %)	31.2	37.4
As (ppm)	13.2	121.4
Cd (ppm)	20.6	1.5
Cr (ppm)	129.2	26.9
Hg (ppb)	375.4	61.6
Pb (ppm)	8.4	15.0
Se (ppm)	4.8	3.8
U (ppm)	96.1	59.8
V (ppm)	129.6	49.5

a. Average of averaged data for each individual deposit.

Table 8. Cadmium Distribution in Phosphoric Acid Production by the Dihydrate Process

Phosphate Rock	Cd Content (ppm)	Proportions Recovered (%) in	
		Acid ^{a,b}	Gypsum
Senegal ^c	78	75	25
Togo ^c	55	90	10
United States			
Central Florida ^d	5	67	33
North Florida ^d	8	60	40
North Carolina ^d	38	55	45
Western Region ^d	120	60	40

a. 28%-32% P₂O₅ filter-grade acid.

b. Based on total amounts of cadmium removed in acid and gypsum cake.

c. IFDC [unpublished data].

d. Wakefield [1980].

Table 9. Potential Costs of Cadmium Removal From Phosphoric Acids^{a,b,c}

Type of Treatment	Conditions	Investment (million US \$)	Cost /mt P ₂ O ₅ (US \$)
Co-crystallization with anhydrite	Without treatment of reject	3.30	8.65
	Without value of reject		5.65
	With value of reject	4.35	10.10
	With treatment of reject		5.65
	Without value of reject		5.65
Precipitation		4.25	20.00
Ion exchange resins	Partial treatment	6.20	25.00
Solvent extraction	Full treatment	6.30	27.00

a. Source: Davister [1992].

b. Capacity = 500 mt P₂O₅/24 h.

c. All costs in U.S. dollars, April 1, 1992.

Table 10. Impact on Different Rock Deposits According to the Hypothetical Limits of Cadmium in Fertilizers Proposed for the EU

Limit—Fertilizers (mg Cd/kg P ₂ O ₅)	Deposits (average in mg Cd/kg P ₂ O ₅)
60	Algeria—Djebel Onk (60) Morocco—Khouribga (55) Israel—Nhal Zin (61)
40	Florida (23) Israel—Arad (35) Morocco—Khouribga (37) Syria (22)
20	South Africa—Phalaborowa (2.7) Russia—Kola (2.8) Jordan—El-Hassa (13) Egypt—Abu Tartur (15)

Note: Above table based on average figures giving only a approximate values.

Source: Adapted from Hutton and Meeûs [2001].

Table 11. Proposed AAPFCO Recommended Metal Limits in Phosphate Fertilizers and Micronutrient Sources

Metals	ppm per 1% P ₂ O ₅	ppm per 1% Micronutrients
Arsenic	13	112
Cadmium	10	83
Cobalt	3,100	23,000
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1,900
Selenium	26	180
Zinc	420	2,900

Source: Anonymous [2001g].

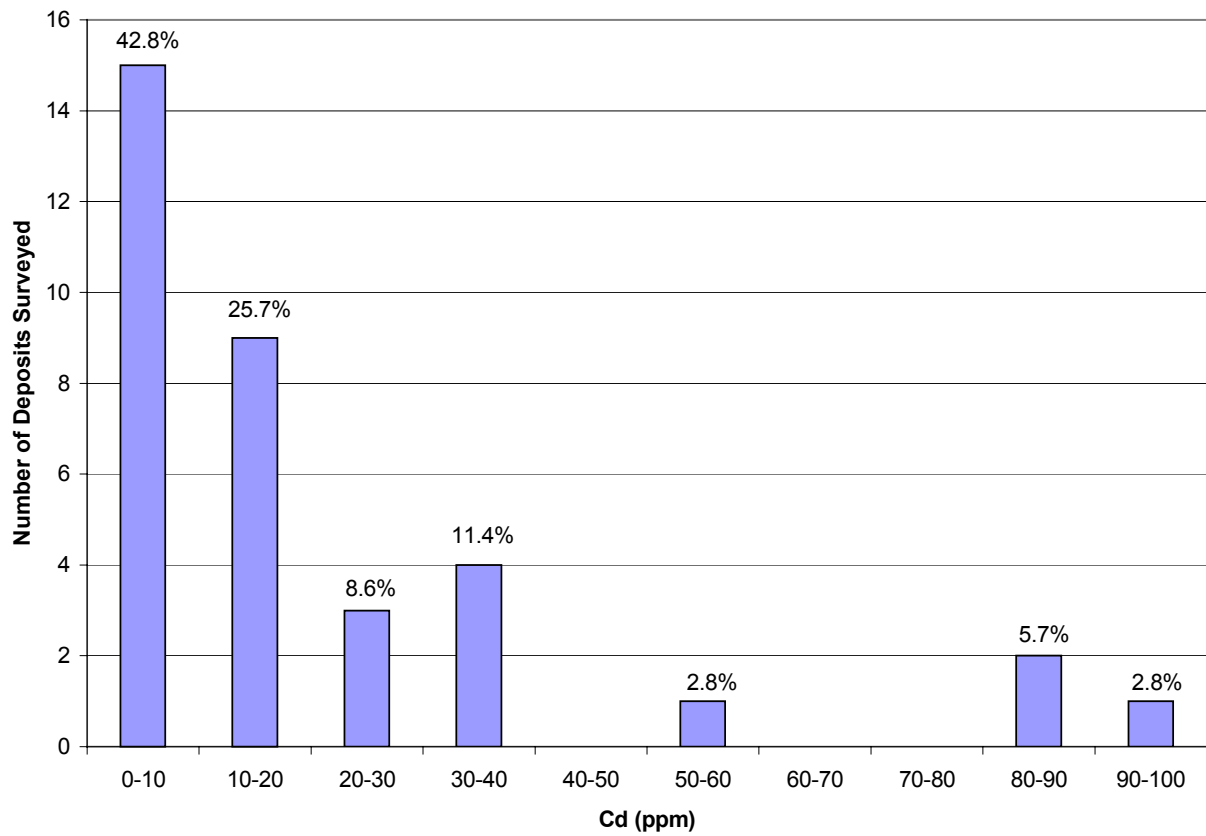
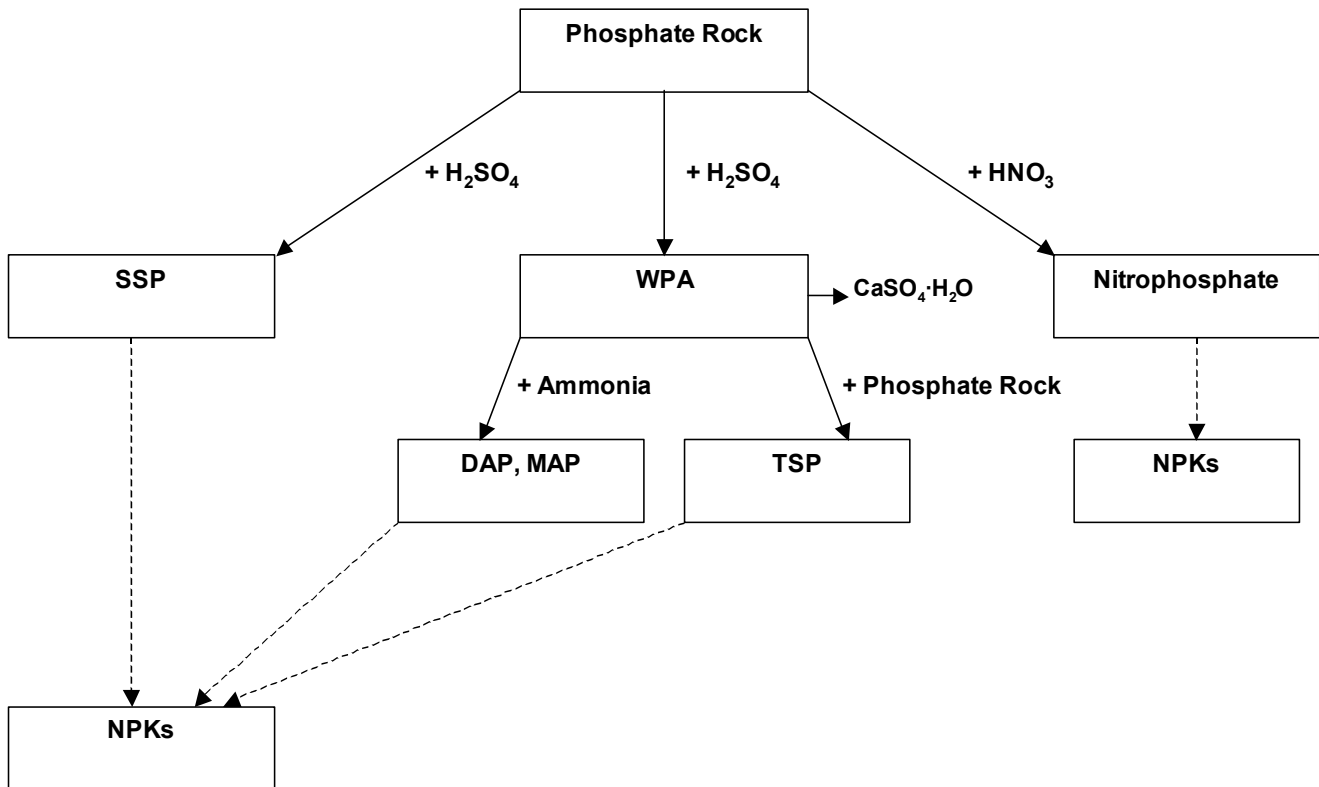
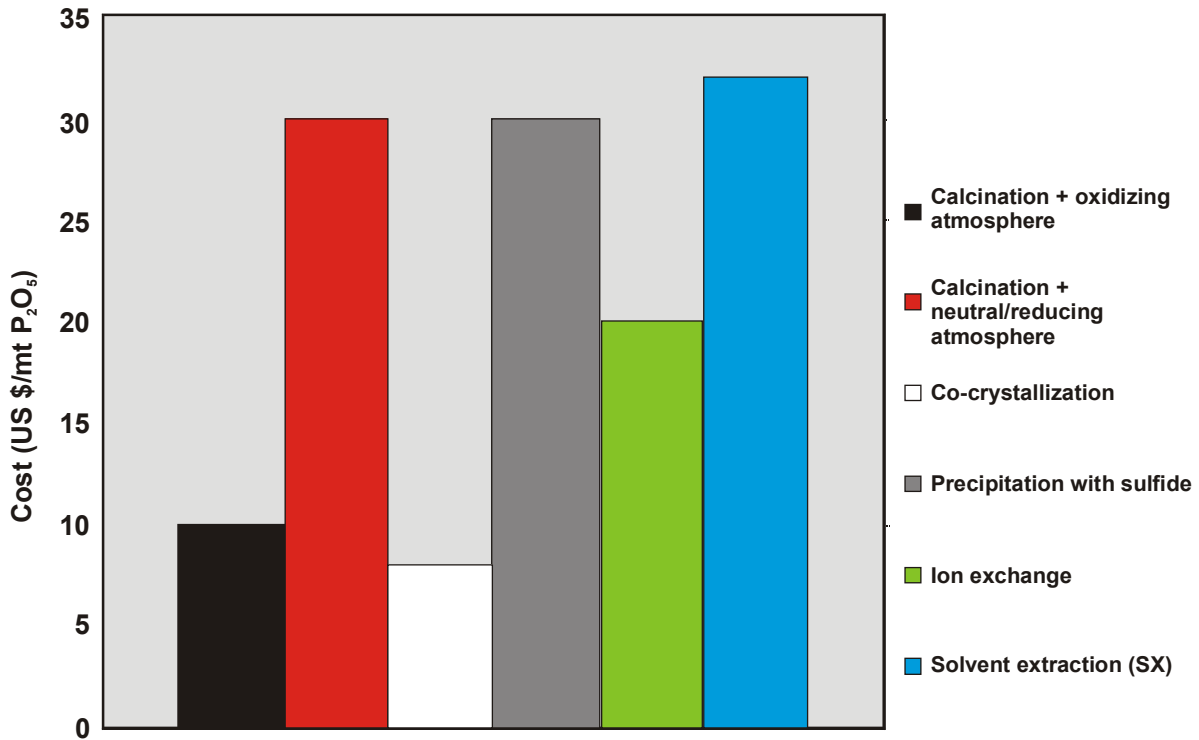


Figure 1. Concentrations of Cadmium in Sedimentary Phosphate Rocks Versus Number of Deposits Surveyed

Figure 2. Relationship of Phosphate Rock and Phosphate Fertilizers





Source:Hutton and Meeûs [2001].

Figure 3. Cost of Various Decadmiation Methods (US \$/mt P₂O₅)