ELEMENTAL PHOSPHORUS

A.   Commodity Summary

Phosphorus is the twelfth most abundant element. Nearly all of the naturally occurring phosphorus compounds are salts of phosphoric acid. Apatite minerals comprise the majority of phosphate constituents in phosphate rock. Phosphate rock deposits occur as marine phosphorites, apatite-rich igneous rock, and modern and ancient guano. All domestic production is from marine phosphorites. According to the U.S. Bureau of Mines, nearly 93% of the phosphate rock sold or used by U.S. producers in 1991 was for the manufacture of wet-process phosphoric acid, single superphosphate, and triple superphosphate; the balance (approximately 7%) was used to produce elemental phosphorus. [1]

Solid elemental phosphorus exists in several allotropic forms -- white, red, and black. The most commercially important is white (elemental) phosphorus. Red phosphorus is also important commercially. Black phosphorus has been prepared only in a few laboratories. [2]

Phosphorus-based materials are used mostly in fertilizers, detergents, foods and beverages, and metal treatment coating. Elemental phosphorus is used as a process input to produce a wide array of phosphorus chemicals. Most phosphorus is converted to derivatives, including phosphorus sulfides and halides, phosphorus pentoxide, and phosphoric acid. Elemental phosphorus is used in the deoxidation and alloying of copper; and elemental phosphorus is used with ferrophosphorus in ferrous metallurgy. White phosphorus is also used in roach and rodent poisons, chemical warfare, and other military purposes. Generally, red phosphorus is made from white phosphorus. Red phosphorus is used for wooden and paper safety matches and in the manufacture of fireworks. [3]

According to the U.S. Bureau of Mines, there are only two domestic producers of elemental phosphorus. FMC operates a facility in Pocatello, ID and Monsanto operates a facility in Soda Springs, ID.

B.   Generalized Process Description

1. Discussion of Typical Production Processes

Phosphate rock is mined using both surface and underground mining techniques. A modern electric furnace process for the production of phosphorus consists of a sequence of four operations: preparing the furnace burden, charging and operating the furnace, collecting the liquid products, and collecting the gaseous products. [4]

2. Generalized Process Flow Diagram

White Phosphorus

Exhibit 2 presents a process flow diagram for the production of white phosphorus. The furnace burden must be porous enough to allow gases to escape from the reaction zone near the bottom of the furnace. To ensure this, one of several agglomeration methods must be employed. Phosphate-rock fines must be sintered and then crushed to size and screened. Another agglomeration method is nodulizing. In this process, phosphate fines are heated in a rotary kiln to incipient fusion. The tumbling in the kiln causes the material to cohere and form spheroidal agglomerates. A final method of agglomeration is formation of pellets by tumbling. The pellets can then be calcined in a rotary kiln. [5]

The agglomerated phosphate rock is charged to an electric arc furnace with coke as a reductant and silica as a flux. The reduction generates a calcium silicate slag and ferrophosphorus, which are tapped, and carbon monoxide offgases that contain volatilized phosphorus. Dusts are removed from the offgases using dry separation techniques such as electrostatic precipitation, and phosphorus is removed by condensation in the presence of recirculation water above the

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[1] David Morse, "Phosphate Rock," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 977-980.

[2] "Phosphorus and the Phosphides," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XVII, 1982, pp. 473-490.

[3] Ibid.

[4] Ibid.

[5] Ibid.

melting point of phosphorus. The carbon monoxide gases are subsequently burned, and phosphorus is decanted from the water and stored for sale. The recirculating water is neutralized, and a purge of mud and soluble impurities is removed and disposed.[6]

Red Phosphorus

While red phosphorus is usually manufactured by a batch process, continuous methods have been developed. In the batch process, white phosphorous is converted to red phosphorus in a steel or cast-iron vessel. The liquid phosphorus, which is protected by a layer of water, passes into the vessel, which then is closed. The vessel is heated gradually so that unconverted liquid phosphorus does not boil violently and erupt. A reflux condenser is used to retain the phosphorus. The mass remains fluid until almost half of the phosphorus has turned into red phosphorus. As the process continues, the mass thickens and solidifies. The mass is cooled and red phosphorus is removed. The material is then wet-ground and boiled with sodium carbonate solution to remove any traces of white phosphorus, which is flammable in air. The red phosphorus is sieved, washed on a rotary filter, vacuum dried, and stabilized by one of two methods. In the first method, red phosphorus is suspended in a sodium aluminate solution and then aerated. In the second method, magnesium oxide is precipitated onto the red phosphorus.[7]

FMC Facility Process

FMC Corporation is the world's largest producer of elemental phosphorus, producing about 240 million pounds of elemental phosphorus per year. Because of the large quantities of elemental phosphorus produced here and the importance of this facility in the market, FMC's process is described below and a process flow sheet is presented in Exhibit 3.

Storage and Preparation of Raw Materials

Storage and preparation of raw materials consists of stockpiling; screening and crushing; briquetting; calcining; and proportioning of the shale ore, coke, and silica. Shale ore arrives at the plant by railcar and is unloaded by a rotary car dumper. The ore is conveyed to the stacker for distribution on one of two storage piles. Ore is then collected from the piles by a reclaimer which deposits it on a conveyer belt. The conveyor belt carries the ore to crushing and screening. Ore is screened to remove oversized material which is then crushed to a uniform size and sent to the briquetting process. Fugitive dust from screening and crushing is collected by three baghouses. The briquetting process presses the crushed material into briquettes similar to the size and shape of charcoal briquettes. The briquettes are then routed to the calciners where they are heated to burn organic material, remove water, and harden. The calcined briquettes, called nodules, are cooled and either stockpiled for later use or fed directly to proportioning. Calciners are fueled by carbon monoxide which is generated in the electric arc furnace operation. Air emissions from the calciners go to one of two sets of scrubbers for removal of particulates and radionuclides. The primary scrubbers remove particulates and the John Zink scrubber removes polonium 210, a radionuclide. The nodules are routed from the calciners to the proportioning building where they are mixed with silica and coke, creating a mixture called burden. The burden is sent to one of five feed bins on each furnace. Fugitive dust from transfer points at the calciners and the proportioning building is collected by baghouses.[8]

Electrothermal Processing

The burden is then fed to one of four electric arc furnaces through feed chutes located on top of the furnaces. There are 10 feed chutes per furnace to distribute burden uniformly about the electrodes. Each furnace is equipped with three electrodes which heat the furnaces to reduce the phosphate to gaseous elemental phosphorus. Silica is used as a flux agent to bind with the calcium present in the phosphate ore and form slag. The coke reacts with the phosphate ore to form carbon monoxide and ferrophosphorus. The furnace offgas, which contains elemental phosphorus, carbon monoxide and particulates, passes through an electrostatic precipitator (ESP) for particulate removal. The gas is then passed through a primary condenser where the phosphorus is cooled by water sprays and condensed to a liquid. Each furnace is equipped with a precipitator and primary condenser. The majority of the phosphorus is condensed in the primary condenser. The gas stream leaving the primary condenser is combined with the gas streams from the other primary condensers at the carbon monoxide header. The combined gas stream, which is primarily carbon monoxide, flows to a second condenser for additional phosphorus removal. The carbon monoxide stream from the secondary

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[6] Ibid.

[7] Ibid.

[8] National Enforcement Investigations Center (NEIC), <u>Multi-Media Compliance Investigation, FMC Corporation - Phosphorus Chemicals Division, Pocatello, Idaho,</u> January 1994.

condenser is used as fuel for the calciners. Excess carbon monoxide goes to the roof flare and to the flare pit. Elemental phosphorus is gravity fed from the condenser to sumps in the furnace building. Phosphorus in the sumps is kept under water to prevent contact with air. Phosphorus is transferred from the sumps to one of seven storage tanks at the phosphorus loading dock by pumping water into the top of the sumps to displace the phosphorus and forced it out the bottom of the sump and into the bottom of the storage tanks. The phosphorus displaces water from the top of the storage tank, and this water flows back to the sumps to form a closed-loop system. The combined capacity of the seven storage tanks is 3,131,000 pounds of phosphorus. Phosphorus is pumped from the storage tanks into railcars for off-site shipment. FMC also has 12 underground storage tanks for long term storage of phosphorus. The phosphorus dock also processes sludge generated at the furnace building sumps, storage tanks, and in the returning railcars. The sludge is dried in a centrifuge and stored before being pumped back to the furnaces for phosphorus recovery.[9]

Air emissions from furnace operations result from normal furnace operation, furnace venting, and slag tapping. The electrothermal process generates carbon monoxide which is used as fuel at the calciners or vented to the flare pit. Furnace venting occurs during furnace maintenance/repair or process upsets. During maintenance/repair, the furnace is vented to the roof flare. Emissions to the flare bypass the carbon monoxide header. These emissions consist primarily of phosphorus pentoxide. Emissions from process upsets, such as furnace overpressurization, are vented to a pressure relief valve. These emissions are also primarily phosphorus pentoxide. Emissions from slag tapping are vented to the atmosphere through a Medusa scrubber followed by an Anderson scrubber.[10]

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

None identified.

4. Beneficiation/Processing Boundaries

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in Section B.

EPA determined that for the production of elemental phosphorus, the beneficiation/processing line occurs between agglomeration and electric arc furnace reduction because the agglomerated phosphate rock undergoes a significant thermal reaction inside the electric arc furnace to yield gaseous phosphorus. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C.   Process Waste Streams

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[9] Ibid.

[10] Ibid.

1.   **Extraction/Beneficiation Wastes**

Waste rock from mining.

Fugitive dust is generated from screening and crushing. FMC collects this dust in baghouses.[11]

2.   **Mineral Processing Wastes**

Surface impoundment waste solids are generated at a rate of 373 kg per kkg product.[12] Existing data and engineering judgement indicate that this waste does not exhibit characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further. Waste characterization data are presented in Attachment 1.

Slag quenchwater.   Prior to treatment, raw slag quenchwater may be toxic for cadmium and lead. Before being discharged, slag quenchwater may be lime treated to precipitate phosphates and fluorides.[13] We used the methodology outlined in Appendix A to estimate a low, medium, and high generation rate of 0 mt/y, 0 mt/y, and 1,000,000 mt/y. This waste may be recycled and is classified as a spent material. Waste characterization data for treated slag quenchwater are presented in Attachment 1.

Slag, a RCRA special waste, contains trace amounts of radioactive materials in a stable, calcium silicate matrix. For every pound of white phosphorus produced, four pounds of slag are produced. In 1991, this waste was generated at a rate of 2,867 metric tons per year.[14] At FMC, slag is tapped into the slag pit which is located next to the furnace building. The slag is allowed to cool before it is loaded and hauled to the slag storage piles. Some slag is screened and crushed for use in berm and road maintenance.[15]

Dust. Phosphatic dusts may be slightly enriched in radioactivity as well as volatilized, reduced heavy metals. Phosphatic dusts are normally sold for blending with fertilizer materials[16] and are classified as byproducts. Management includes storage in a wastepile and offsite landfill disposal.[17] Dust is generated at a rate of 4,400 metric tons per year (adjusted from a reported value to reflect changes in the sector). Dusts may exhibit the characteristics of toxicity for cadmium, ignitability, and reactivity.

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[11] Ibid.

[12] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Volume II, Chapter 8, 1980.

[13] U.S. Environmental Protection Agency, Op. Cite., Volume II, Chapter 8.

[14] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, Vol. I, August 1992, pp. I-2 - I-8.

[15] NEIC, 1992, Op. Cit.

[16] U.S. Environmental Protection Agency. "Phosphate Rock," from 1988 Final Draft Summary Report of Mineral Industry Processing Waste, 1988, pp. 2-120 - 2-127.

[17] U.S. Environmental Protection Agency, Technical Background Document, Development of Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, August 1989, pp. 3-4--3-6.

EXHIBIT 2

ELEMENTAL PHOSPHORUS PRODUCTION

Graphic Not Available.

Source: "Phosphorus: A Mineral Processing Waste Generation Profile."

Condenser phossy water discard may contain cyanide.[18] This waste water comes from furnace washdown, phosphorus dock operations, condensers, and furnace building sumps. At FMC, phossy water is collected in a tank and then discharged to ponds for solids settling. The water may eventually be recycled for use in the process areas. Sediments from the settling ponds are dredged and place in another pond.[19] The generation rate for this waste is 720,000 metric tons per year[20] (adjusted from a reported value to reflect recent changes in the sector). Waste characterization data are presented in Attachment 1. This waste is not expected to be hazardous.

Furnace offgas solids. These solids may be toxic for cadmium. In addition, the waste may also contain cyanide. The generation rate for furnace offgas solids is 24,000 metric tons per year[21] (adjusted from a reported value to reflect recent changes in the sector). FMC sends air emissions from the calciners to scrubbers for removal of particulates and radionuclides.[22] Waste characterization data are presented in Attachment 1. This waste may be recycled and is classified as a sludge.

Furnace offgas may contain elemental phosphorus, carbon monoxide, and particulates. At FMC, an electrostatic precipitator removes the particulates. Dust slurry from the four ESPs is discharged to ponds which are dredged.[23] Based on existing data and engineering judgement, this waste is not expected to be hazardous. Therefore, the Agency did not evaluate this material further.

Sludge is generated in the sumps and consists of a phosphorus water emulsion and particulates not removed by the ESPs. Generally, sludge is distilled in iron retorts of steam heated vessels to recover phosphorus. Recovered phosphorus is added to the product and phosphorus free residues from the retorts are landfilled. Sludge is generated at a rate of 25 kg per kkg product.[24] At FMC, the sludge is sent to the phosphorus dock where it is processed with sludge generated from furnace building sumps, storage tanks, and returning railcars. The sludge is dried in a centrifuge and stored before being pumped back to
the furnace for phosphorus recovery.[25] Existing data and engineering judgement suggest that this waste does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate it further.

Precipitator slurry scrubber water. FMC treats the scrubber water with lime and discharges it to calciner ponds for settling. The water is recycled back to the scrubbers from the calciner ponds.[26]
Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further. Waste characterization data are presented in Attachment 1.

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[18] U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Office of Solid Waste, August 1992, Vol. II, pp. 14-45 - 14-59.

[19] NEIC, 1992, <u>Op. Cit</u>.

[20] U.S. Environmental Protection Agency, <u>Op. Cit.</u>, 1992.

[21] <u>Ibid</u>.

[22] NEIC, 1992, <u>Op. Cit.</u>

[23] NEIC, 1992, <u>Op. Cit</u>.

[24] U.S. Environmental Protection Agency, <u>Op. Cite.</u>, Volume II, Chapter 8, 1980.

[25] NEIC, 1992, <u>Op. Cit</u>.

[26] <u>Ibid</u>.

EXHIBIT 3

PROCESS **A**T **FMC F**ACILITY

Graphic Not Available.

Source: Elemental Phosphorus Processing Waste Characterization Report for FMC Corporation, Pocatello, Idaho, 1991, pp. 1-4.

Waste filter media is generated by Anderson scrubbers. At FMC, the waste filter media is washed to reduce radionuclide levels before off-site disposal. Filter media wash water is discharged to the wastewater treatment tank and then to the calciner ponds.[27] Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Cooling water is generated from cooling of furnace domes by direct water spray. At FMC, this water is discharged via a permitted outfall.[28] Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Furnace scrubber blowdown. We used the methodology outlined in Appendix A of this report to estimate a high, medium, and low generation rate of 270,000 metric tons/yr, 0 metric tons/yr, and 0 metric tons/yr.[29] Management for this waste may include treating in a tank and sending the sludge to disposal impoundments.[30] This waste may exhibit the characteristics of toxicity for cadmium and corrosivity prior to treatment. Waste characterization data for raw furnace scrubber blowdown are presented in Attachment 1.

WWTP Sludge/Solids. This waste is not expected to be hazardous. Waste characterization data are presented in Attachment 1.

Surface impoundment waste liquids. This waste is not expected to be hazardous. Waste characterization data are presented in Attachment 1.

Spent furnace brick. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Non-contact cooling water is generated by cooling of the grates which transport the briquettes. At FMC, the noncontact cooling water is discharged via a permitted outfall.[31] This waste is a non-uniquely associated waste.

Waste ferrophosphorus is tapped from the furnaces. It is tapped into chill molds inside the furnace building and allowed to cool. After cooling, the ferrophosphorus is crushed and screened before being sold as a raw material to the steel industry.[32] Based on existing data and engineering judgement, this waste is not expected to exhibit characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

Process wastewater is a RCRA special waste.

WWTP liquid effluent is not expected to be hazardous. This waste may be discharged under NPDES. The generation rate for this waste stream is 1,520,000 metric tons per year[33] (adjusted from a reported value to reflect recent changes in the sector). Waste characterization data are presented in Attachment 1.

AFM Rinsate. The generation rate for this waste stream is 2,000 metric tons per year[34] (adjusted from a reported value to reflect recent changes in the sector). This waste may be toxic for cadmium and selenium. Waste characterization data are presented in Attachment 1.

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[27] Ibid.

[28] Ibid.

[29] U.S. Environmental Protection Agency, 1992, Op. Cit., pp. 14-45 - 14-59.

[30] U.S. Environmental Protection Agency, Technical Background Document, Development of Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, August 1989, pp. 3-4--3-6.

[31] NEIC, 1992, Op. Cit.

[32] Ibid.

[33] U.S. Environmental Protection Agency, Op. Cite., Vol. II, pp. 14-45 - 14-59.

[34] FMC Corporation LDR presentation for EPA/OSW, December 1994.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naptha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous), and other lubricants.

BIBLIOGRAPHY

Bartels, James J., and Theodore M. Gurr. "Phosphate Rock." From Industrial Mineral and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 751-763.

Elemental Phosphorus Processing Waste Characterization Report for FMC Corporation, Pocatello, Idaho. 1991. pp. 1-4.

FMC Corporation LDR presentation for EPA/OSW, December 1994.

Morse, David. "Phosphate Rock." From Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 977-980.

National Enforcement Investigations Center. Multi-Media Compliance Investigation, FMC Corporation - Phosphorus Chemicals Division, Pocatello,Idaho. January 1994.

"Phosphorus and the Phosphides." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XVII. 1982. pp.473-490.

U.S. Environmental Protection Agency. Technical Background Document, Development of Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes. August 1989. pp. 3-4--3-6.

U.S. Environmental Protection Agency. "Elemental Phosphorus Production." From Report to Congress on Special Wastes from Mineral Processing. Vol. II. Office of Solid Waste. July 1990. pp. 7-l - 7-24.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992. Vol. I. pp. I-2 - I-8.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992. Vol. II. pp. 14-45 - 14-59.

U.S. Environmental Protection Agency. "Phosphate Rock, Phosphoric Acid, and Phosphorus." From 1988 Final Draft Summary Report of Mineral Industry Processing Waste. 1988. pp. 2-120 - 2-127.

U.S. Environmental Protection Agency. Multi-Media Assessment of the Inorganic Chemicals Industry. Volume II, Chapter 8. 1980.