ELEMENTAL PHOSPHORUS

A. Commodity Summary

Phosphorus is the twelfth most abundant element, almost all of which occurs as salts of phosphoric acid. Phosphate rock deposits occur as marine phosphorites, apatite-rich igneous rock, and modern and ancient guano. Apatite minerals comprise the majority of phosphate constituents in phosphate rock. All domestic production is from marine phosphorites. According to the U.S. Bureau of Mines, nearly 93 percent 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 percent) 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 largest U.S. producer of phosphorus, there are four domestic producers of elemental phosphorus. FMC operates a facility in Pocatello, ID and Monsanto operates a facility in Soda Springs, ID. The remaining two facilities are owned and operated by the Rhone Poulenc Basic Chemical Company and the Occidental Chemical Company.[4] These are located Silver Bow, MT and Columbia, TN, respectively.

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.[5]

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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] FMC Corporation. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[5] Kirk-Othmer Encyclopedia of Chemical Technology. Op. Cit.

2. Generalized Process Flow Diagram

White Phosphorus

Exhibit 2 presents a process flow diagram for the production of white elemental phosphorus. The furnace burden must be porous enough to allow gases to escape from the reaction zone near the bottom of the furnace. Several agglomeration methods must be employed to prepare phosphate rock fines for the electric furnace. The 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.[6]

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 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.[7]

Red Phosphorus

Although red phosphorus is usually manufactured by a batch process, continuous methods are now being used. 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.[8]

FMC Facility Process[9]

FMC Corporation is the world's largest producer of elemental phosphorus, producing about 240 million pounds of elemental phosphorus per year. Under normal operating conditions, this process operates 24 hours per day, 365 days per year.[10] 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. This information was provided by FMC. The Agency may not necessarily agree with FMC's characterization of its waste streams.

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[6] Ibid.

[7] Ibid.

[8] Ibid.

[9] The processes discussed in this technical background document pertain to production at the FMC Pocatello, ID plant, and may not be fully representative of industry practices employed by the other three domestic phosphorous producers.

[10] FMC Corporation. Op. Cit. January 25, 1996.

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 first screened to remove oversized material and 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, which are fed to the calcining process. FMC Pocatello's calciners are sintering operations in which the briquetted shale is heated to form a coherent mass without melting. The calcining operation is therefore principally an agglomeration method. The process occurs in grate calciners in which the briquettes are carried on moving grates or pallets through the calcining zone where hot gases are pulled through the feed bed (the briquettes) and grate. Because the briquettes ride on the moving pallets they undergo little or no tumbling or other motion during this process. Water and carbon dioxide are given off during this process, but the temperatures are carefully controlled below the fusion point of the phosphate shale. Temperatures above the fusion point result in a phenomenon known as "fusing the bed" in which the briquettes on the pallets fuse into a single, rigid mass that cannot be handled in FMC's downstream material handling equipment. FMC calcines the ore for two reasons: (1) to harden the briquettes, thereby limiting briquette breakage; and (2) to drive off moisture content and carboniferous matter. (The carbon is driven off as carbon dioxide.) Calcining does not chemically alter the phosphate shale.

It is important to harden the briquettes during calcining to reduce breakage and allow proper flow of gaseous reaction products in the furnaces. Hardened (calcined) phosphate shale briquettes (nodules) are choke-fed into the furnace following mechanical conveyance and mixing with coke and silica. Significant breakage can occur to improperly hardened nodules during drops from one conveyor to the next and as the nodules are forced into the tops of the furnaces. Phosphate in the shale nodules, which is unchanged chemically during calcination from phosphate in the as-received mined shale, is reduced in the furnaces with coke to form elemental phosphorus and carbon monoxide. This occurs near the bottom of the furnaces in the plasma arcs at the tips of the carbon electrodes. Gas-phase reaction products, primarily elemental phosphorus and carbon monoxide, percolate up from the reaction zones through gas channels in the incoming bed of phosphate nodules, coke, and silica. Nodule fragments, formed by breakage from broken or improperly calcined briquettes, can plug these gas channels, interfering with proper, steady-state furnace operation.

It is also important to drive off water during calcining of the briquettes to prevent volatilization of steam in the high temperature furnaces and to prevent an unwanted side reaction involving water and elemental carbon. In the calciners, water content is reduced from about 11 percent in the incoming phosphate shale to less than 1 percent in the hardened briquettes or nodules. The dried and hardened nodules are conveyed and fed to the phosphorus furnaces, which operate at very high temperature. At the top, where the nodules, coke, and silica are being choke-fed, the temperature is about 400ºC, while near the bottom, temperatures can reach 1500ºC in the plasma-arc zones. If wet briquettes were allowed to enter the furnaces, steam would be uncontrollably and possibly explosively volatilized. At these temperatures, and in the reducing conditions found inside the furnaces, water and elemental carbon can undergo the watergas reaction to form hydrogen and carbon monoxide. This is a very destructive side reaction that can consume both coke, a reagent necessary for the reduction of phosphorus shale to elemental phosphorus, and the furnace electrodes and sidewall refractory bricks (both of which are solid carbon). Finally, water generated in the furnaces can cause increased corrosion in downstream process equipment.

Although less important than water removal, it is also necessary to drive off carboniferous material during calcination. Volatilization of these materials in the furnaces can create severe furnace pressure excursions. During calcining of phosphorus shale, quantities of low boiling point metals may be volatilized.[11]

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[11] FMC Corporation. Op. Cit. January 25, 1996.

EXHIBIT 2

ELEMENTAL PHOSPHORUS PRODUCTION

(Adapted from: Phosphorus, A Mineral Processing Waste Generation Profile.)

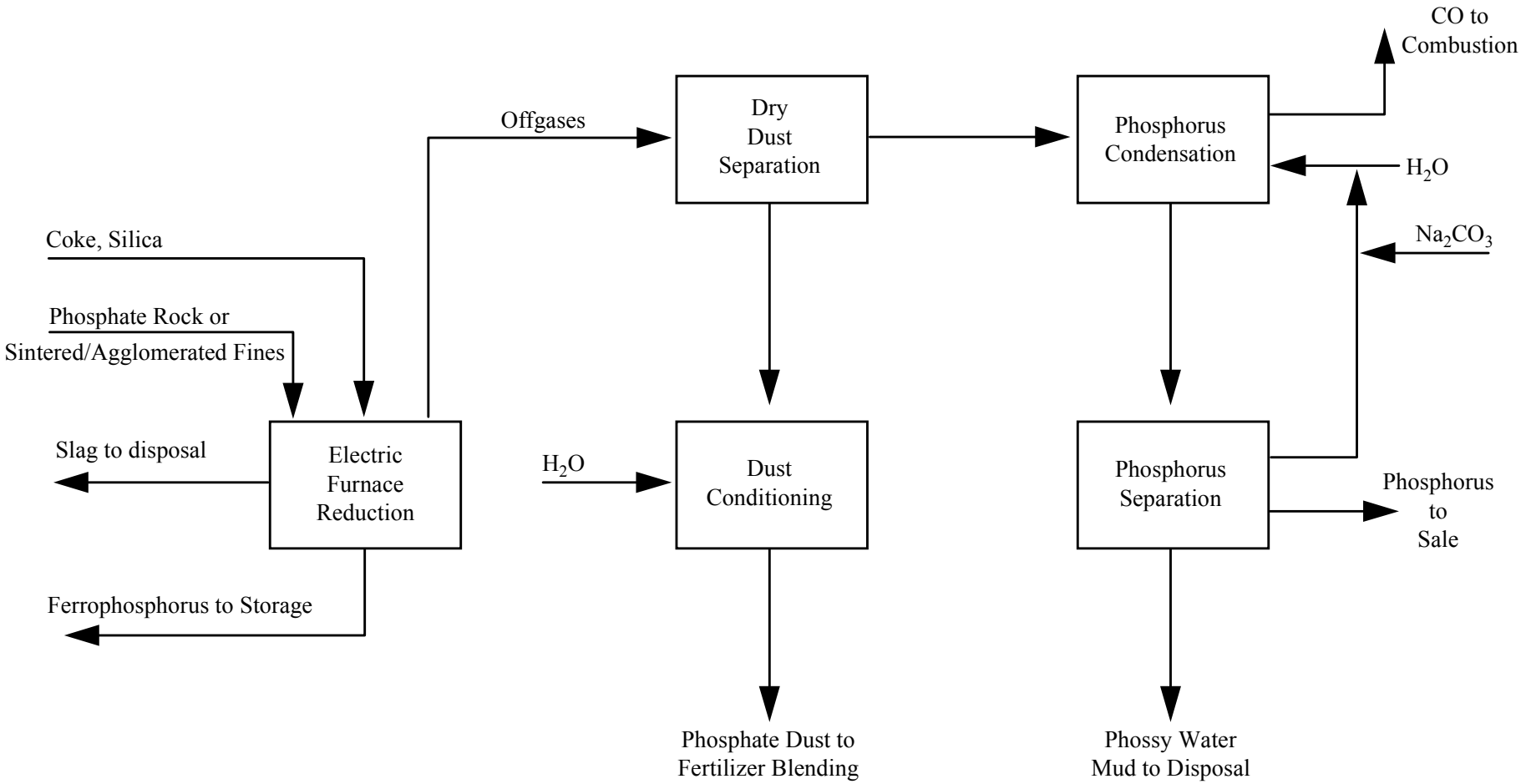
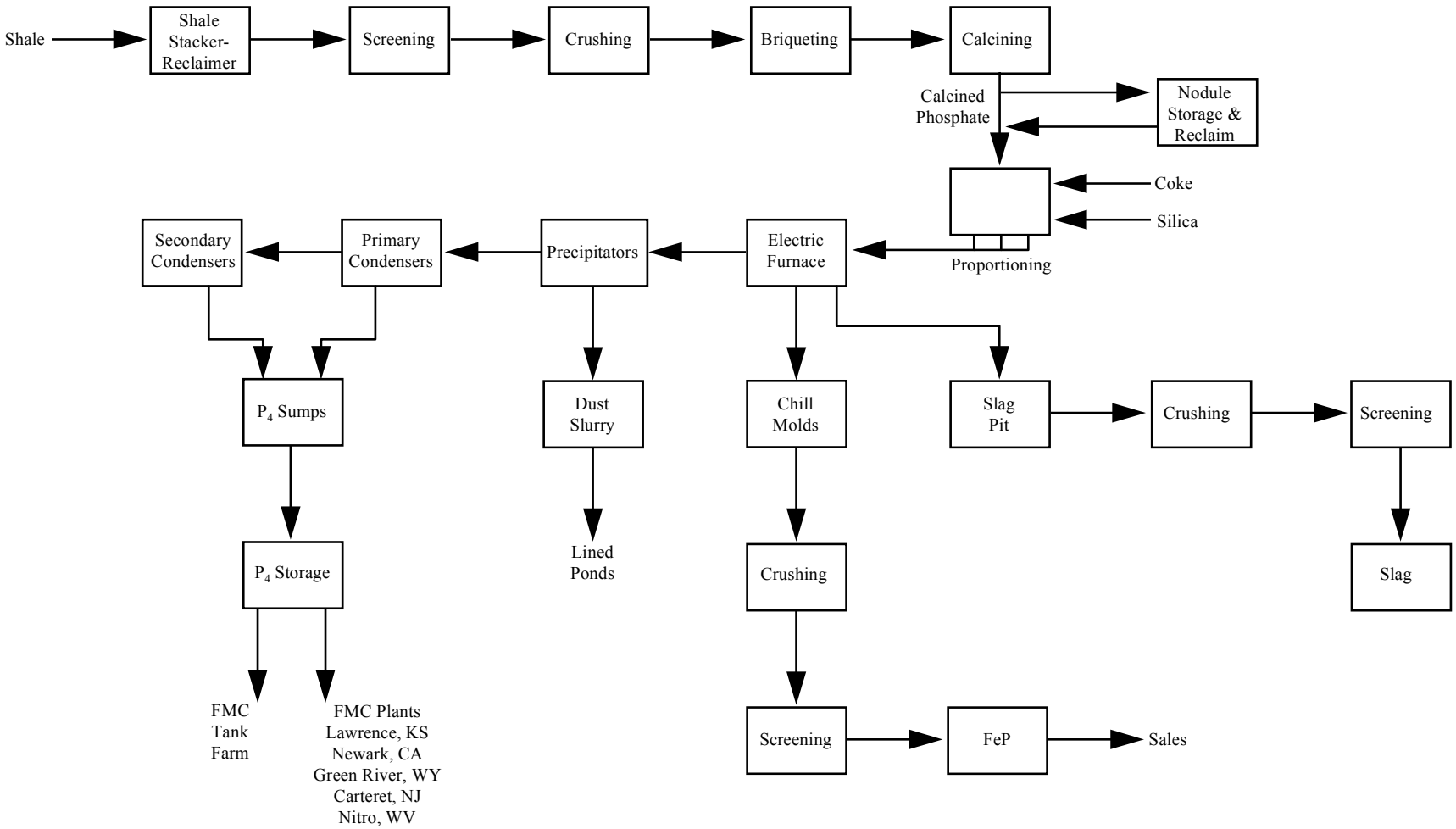


EXHIBIT 3

PROCESS AT FMC FACILITY

(Adapted from: Elemental Phosphorus Processing Waste Characterization Report For FMC Corporation, 1991, pp. 1-4.)



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 that heat the furnaces to reduce the phosphate to gaseous elemental phosphorus. Silica is used as a fluxing 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 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.[12]

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.[13]

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

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.

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

[13] Ibid.

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.

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. Calcining is recognized as a beneficiation activity in the production of phosphorous. It is one of the final activities performed prior to the chemical change of phosphate ore into the elemental phosphoro\us product.[14] Because EPA has determined that all operations following the initial "processing" step (in this case, the introduction of proportioned ore into the electric furnace) in the production sequence also are 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 downstream of 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

1. Extraction/Beneficiation Wastes

Fugitive dust is generated from screening and crushing. FMC collects this dust in baghouses.[15]

Calcining offgas solids. FMC sends air emissions from the calciners to scrubbers for removal of particulates and radionuclides.[16] It should be ruled that if calcining at FMC drivers off more than water and carbon dioxide, it is not a beneficiation activity (See 40 CFR 261.4(b)(7).

2. Mineral Processing Wastes

Surface impoundment waste solids are generated at a rate of 373 kg per kkg product.[17] Existing data and engineering judgment 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.

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[14] FMC Corporation. Op. Cit. January 25, 1996.

[15] NEIC. Op. Cit. 1994.

[16] Ibid.

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

Slag, a RCRA special waste, contains trace amounts of radioactive materials in a stable, calcium silicate matrix. For every pound of white phosphorus produced, eight to ten pounds of slag are generated. In 1988, this waste was generated at a rate of 2.6 million metric tons per year.[18] 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.[19]

Dust. Phosphatic dusts may contain slightly elevated levels of radioactivity as well as volatilized, reduced heavy metals. Phosphatic dusts are normally sold for blending with fertilizer materials[20] and formerly were classified as byproducts. Past management practices have included storage in a waste pile and offsite landfill disposal.[21] 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.

Furnace offgas solids. This waste may contain cyanide. The generation rate for furnace offgas solids is 24,000 metric tons per year[22] (adjusted from a reported value to reflect recent changes in the sector). Waste characterization data are presented in Attachment 1. This waste may be recycled and formerly was classified as a sludge.

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.[23] 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.[24] Existing data and engineering judgment 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.[25] Existing data and engineering judgment 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, Report to Congress on Special Wastes from Mineral Processing, Volume II: Methods and Analysis, Office of Solid Waste, July 1990, p. 7-3.

[19] NEIC, 1994, Op. Cit.

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

[21] 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.

[22] Ibid.

[23] U.S. Environmental Protection Agency, Op. Cit., Volume II, Chapter 8, 1980.

[24] NEIC, 1994, Op. Cit.

[25] Ibid.

Cooling water is generated from cooling of furnace domes by direct water spray. At FMC, this water is discharged via a permitted outfall.[26] Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Furnace scrubber blowdown. FMC generates this waste at the rate of 43.4 million gallons per year.[27] Management for this waste may include treating in a tank and sending the sludge to disposal impoundments.[28] 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.

Furnace building washdown. This waste is generated from numerous sources in the furnace building. The term "furnace building washdown" is a generic term used at the FMC facility to designate water collected in the V-3600 tank from numerous sources throughout the furnace building. The water is eventually discharged into a RCRA Interim Status MTR pond. Water is used in condensing elemental phosphorus from the furnace off-gas stream, water seals on pressure relief devices and overfill protection systems, electrical transformer and furnace cooling, furnace tapping fume scrubber systems, conveying and storage operations to keep phosphorus under water cover, slurrying and transporting electrostatic precipitator solids, cleaning (rinsing) of process equipment to ensure maximum performance, and other miscellaneous uses such as pump packings and steam condensate. The V-3600 tank is the back-up water collection point for some of these streams, which do not normally report to this tank. The discharge from the V-3600 tank collectively has been known as "furnace building washdown" because waters from numerous sources in the furnace building are the primary components of this stream. This stream is generated continuously during process operations. Contaminants in this stream originate from the mineral feedstocks (phosphate shale, silica, and coke) used at Pocatello to produce elemental phosphorus. This stream does not contain outside contaminants such as solvents or acidic or caustic cleaning agents. The furnace building washdown occasionally exhibits the Toxicity Characteristic for cadmium (D006). The TSS average is .08 percent, and it is also considered a wastewater for LDR purposes. Furnace Building Washdown contains elemental phosphorus and NORM. The FMC facility generates approximately 79 million gallons of this waste a year.[29]

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. This waste is completely recycled at FMC.

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

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.[30] Based on existing data and engineering judgment, this waste is not expected to exhibit characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

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[26] Ibid.

[27] FMC Corporation. Op. Cit. January 25, 1996.

[28] 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 to 3-6.

[29] FMC Corporation. Op. Cit. January 25, 1996.

[30] Ibid.

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[31] (adjusted from a reported value to reflect recent changes in the sector). Waste characterization data are presented in Attachment 1.

Andersen Filter Media (AFM). Andersen Filter Media (AFM) is a felt-like material that is used in the Andersen scrubbers to filter fine particulate. Andersen Cleanable Media High Efficiency Air Filter (CHEAF) scrubbers are used in series with the Medusa Scrubbers to further clean fumes from furnace tapping and phosphorus dock loading and operations. Andersen Filter Media is used in these scrubbers to filter fine particulates. The AFM is generated at a rate of 420 cubic yards per year. The material fails the TCLP for cadmium and sometimes arsenic, chromium, lead and selenium and is a RCRA hazardous waste.[32]

AFM rinsate. This waste stream has been eliminated by FMC as a waste reduction process modification.

FMC generates three additional waste streams, as described below, which may or may not be typical of other phosphorus producers.[33]

Precipitator slurry. The elemental phosphorus product exits the furnaces as a gas along with the carbon monoxide produced in the furnace reaction. The furnace off-gas also includes entrained solids and solids that have volatilized in the furnace and condensed as the off-gas cools. Electrostatic precipitators are used to remove these furnace off-gas solids prior to the water spray condensers that remove the elemental phosphorus as a liquid. At FMC, these solids collect in a vessel at the bottom of the precipitator, known as the slurry pot, where water is added with a mixer to form what is termed precipitator slurry. The slurry pot acts as a gas seal on the precipitators to prevent in-leakage of air. Some elemental phosphorus condenses in the slurry pot and the solids contain low volatile metals such as cadmium and zinc in elevated levels. Historically, precipitator slurry has been sent to ponds where the solids settle out and the water is recycled. FMC produces 43 million gallons of precipitator slurry (may be combined with NOSAP slurry as discussed below) each year. Although there are elevated levels of metals in the precipitator slurry, the solids typically do not fail a Toxicity Characteristic Leaching Procedure (TCLP) test, unless there are extenuating circumstances, in which case it will fail for cadmium (D006).

Based on preliminary data, EPA has indicated that precipitator slurry is ignitable (D001) and reactive (D003). The slurry also contains NORM and elemental phosphorus and should be managed accordingly. The TSS in the precipitator slurry typically exceed 1 percent, and the TOC concentration present in the precipitator slurry does not exceed 1 percent. Therefore, the slurry is considered an LDR non-wastewater.

NOSAP Slurry. In 1994 and 1995 as part of its waste minimization efforts, FMC developed and installed the NOSAP, which is a modification to the electrostatic precipitator and the slurry pot. Lime slurry is added to the slurry pot to control the pH of the slurry to a set point of pH 12. The lime reacts with the phosphorus to form phosphites and phosphine gas, thus reducing the concentration of phosphorus to below 1000 ppm. The lime also prevents the metals from becoming leachable and ensures the slurry will not fail the TCLP test. The resulting slurry that has gone through this process is known as NOSAP slurry. Based on preliminary data, EPA has indicated that NOSAP slurry is reactive (D003). If all precipitator slurry went through the NOSAP process, FMC would produce only 22 million gallons per year since the NOSAP slurry has a higher solids content. The solids in NOSAP slurry are the same as precipitator slurry with the exception of the effect of the lime. The NORM content is the same and there is still some residual phosphorus content. NOSAP slurry that does not meet specifications is a component of precipitator slurry. The TSS in the NOSAP slurry typically exceed 1 percent, and the TOC in the NOSAP slurry does not exceed 1 percent. Therefore, the NOSAP slurry is a non-wastewater for LDR purposes.

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

[32] FMC Corporation. Op. Cit. January 25, 1996.

[33] FMC Corporation. Comment submitted in response to the Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. May 12, 1997.

The maximum volume of precipitator slurry and NOSAP slurry that would be generated in one year would be 43 million gallons.

Phossy water. This water waste stream is called phossy water by FMC. Phossy water may carry the D003 RCRA waste code for reactivity. It is possible that phossy water could exhibit the TC for cadmium (D006) upon process upset. As a result of its contact with phosphorus, phossy water contains suspended phosphorus and other dissolved solids. In addition, the phossy water contains NORM. The majority of phossy water is recovered for reuse, but excess phossy water is generated from two locations within the facility. Due to the presence of elemental phosphorus, the solids in phossy water may spontaneously oxidize and ignite if dewatered. The TSS in the phossy water typically exceed 1 percent, and the TOC in the phossy water does not exceed 1 percent. Therefore, the phossy water is a non-wastewater for LDR purposes. FMC generates 89 million gallons total of the phossy water per year. Solids in phossy water settle out, and are considered to be mineral processing wastes, because the 1984 rule states that a waste of a mineral process waste is a mineral process wastes. Based on available data, solids from phossy water may be a hazardous waste.

Although other phosphorous manufacturers may generate the following waste streams, FMC does not do so at its facility: phosphatic dust, condenser water discard, precipitator slurry scrubber water, WWTP liquid effluent, and WWTP sludge/solids.

D. Non-uniquely Associated Wastes

Non-contact cooling water is generated by cooling of the ore calciner grates that transport the briquettes. At FMC, the noncontact cooling water is discharged via a permitted outfall.[34] This waste is a non-uniquely associated waste. 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), and acidic tank cleaning wastes. 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.

E. Summary of Comments Received by EPA

New Factual Information

Three commenters provided additional factual information about the elemental phosphorous production process (COMM 42, 70, 78)). This information, where appropriate, has been included in sector report.

Sector-specific Issues

Two commenters disagreed with the Agency's assertion that certain wastes generated during elemental phosphorous production are RCRA ignitable and reactive (COMM 42, COMM 70). One of these commenters has since agreed to treat certain wastes as ignitable and reactive (COMM 70).

One commenter stated that water recycled from ponds on-site should not be considered a hazardous waste, because it does not fit any one criteria that would make it a hazardous waste under the RCRA statute definitions (COMM 70).

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[34] NEIC, 1994, Op. Cit.

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ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT SOLIDS - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	-	-	-	0/0	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	-	-	-	0/0	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	-	-	-	0/0	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	10,000	10,000	10,000	1/1	-	-	-	0/0	-	-
Phosphate	200,000	386,667	480,000	3/3	-	-	-	0/0	-	-
Silica	50,000	50,000	50,000	2/2	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	5.00	5.53	5.80	3/3					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SLAG QUENCHWATER - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	11.60	11.60	11.60	1/1	11.50	11.50	11.50	1/1	-	-
Antimony	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	-	-
Arsenic	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	5.0	0
Barium	0.05	0.05	0.05	0/1	0.050	0.050	0.050	0/1	100.0	0
Beryllium	0.005	0.005	0.005	0/1	0.0050	0.0050	0.0050	0/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.012	0.012	0.012	1/1	0.011	0.011	0.011	1/1	1.0	0
Chromium	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	5.0	0
Cobalt	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	-	-
Copper	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	-	-
Iron	3.60	3.60	3.60	1/1	3.34	3.34	3.34	1/1	-	-
Lead	0.35	0.35	0.35	1/1	0.17	0.17	0.17	1/1	5.0	0
Magnesium	5.72	5.72	5.72	1/1	5.72	5.72	5.72	1/1	-	-
Manganese	1.54	1.54	1.54	1/1	1.52	1.52	1.52	1/1	-	-
Mercury	0.00010	0.00010	0.00010	0/1	0.00020	0.00020	0.00020	1/1	0.2	0
Molybdenum	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	-	-
Nickel	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	-	-
Selenium	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	1.0	0
Silver	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	5.0	0
Thallium	0.250	0.250	0.250	0/1	0.25	0.25	0.25	0/1	-	-
Vanadium	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	-	-
Zinc	3.13	3.13	3.13	1/1	2.94	2.94	2.94	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	5.00	5.00	5.00	1/1	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	41.30	41.30	41.30	1/1	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	5.78	8.29	10.80	2/2					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - CONDENSER PHOSSY WATER DISCARD - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.424	64.39	220	5/5	5.70	11.90	16.10	3/3	-	-
Antimony	0.016	1.76	4	3/5	0.050	0.71	1.30	3/4	-	-
Arsenic	0.0024	1.27	3	3/5	0.031	0.12	0.25	3/5	5.0	0
Barium	0.120	16.09	90	5/6	0.15	0.86	3.20	5/6	100.0	0
Beryllium	0.005	0.026	0.05	2/4	0.005	0.014	0.025	1/3	-	-
Boron	14	14.000	14	1/1	9.400	9.400	9.400	1/1	-	-
Cadmium	0.002	324	3200	11/11	0.067	0.17	0.40	6/6	1.0	0
Chromium	0.014	33.15	250	8/8	0.049	0.23	0.40	5/6	5.0	0
Cobalt	0.013	0.15	0.5	2/4	0.050	0.15	0.25	0/2	-	-
Copper	0.017	20.98	100	5/5	0.005	0.08	0.25	1/4	-	-
Iron	1.2	20.26	53	4/4	0.87	4.02	6.49	3/3	-	-
Lead	0.024	13.49	48	7/7	0.125	0.64	1.80	2/4	5.0	0
Magnesium	6.83	32.22	64	6/6	6.4	13.23	17.00	3/3	-	-
Manganese	0.23	1.77	3.8	4/4	0.25	0.95	1.85	2/4	-	-
Mercury	0.00010	0.1506	1	3/7	0.00010	0.000175	0.0002	1/4	0.2	0
Molybdenum	0.035	0.17	0.5	2/4	0.05	0.15	0.25	0/2	-	-
Nickel	0.046	6.93	45	5/7	0.02	0.09	0.25	2/5	-	-
Selenium	0.002	2.58	13.9	3/6	0.002	0.10	0.25	0/3	1.0	0
Silver	0.02	1.36	4.47	3/5	0.01	0.08	0.25	0/4	5.0	0
Thallium	0.0455	24.88	120	2/5	0.25	0.75	1.25	0/2	-	-
Vanadium	0.05	2.27	10	4/6	0.05	0.17	0.25	1/3	-	-
Zinc	0.6	5,794	53,000	10/10	6.47	71.49	167	5/5	-	-
Cyanide	36.00	36.00	36.00	1/1	-	-	-	0/0	-	-
Sulfide	1.20	1.20	1.20	1/1	-	-	-	0/0	-	-
Sulfate	2.50	363	964	6/7	41.00	74.00	107	2/2	-	-
Fluoride	80.00	3,934	25,900	7/7	155	304	453	2/2	-	-
Phosphate	25.00	1,833	9,070	6/6	591	662	732	2/2	-	-
Silica	63.00	63.00	63.00	1/1	-	-	-	0/0	-	-
Chloride	38.00	364	1,250	9/9	69	152	234	2/2	-	-
TSS	0.78	12652	50000	4/4	-	-	-	0/0	-	-
pH *	3.00	5.09	7.10	7/7					2<pH>12	0
Organics (TOC)	20.00	39.67	76.20	3/3					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - FURNACE OFFGAS SOLIDS - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	98.20	4,290	11,500	4/4	4.60	11.22	24.10	3/3	-	-
Antimony	0.43	9.68	25.50	2/3	0.050	0.76	1.32	2/3	-	-
Arsenic	0.050	12.78	25.50	0/2	0.020	0.56	1.30	5/7	5.0	0
Barium	0.84	34.18	96.70	3/3	0.050	0.14	0.25	2/4	100.0	0
Beryllium	0.022	1.29	2.55	1/2	0.005	0.015	0.025	0/2	-	-
Boron	39.000	185.50	332.00	2/2	24.000	24.000	24.000	1/1	-	-
Cadmium	0.45	60.74	200	4/4	0.011	8.05	27.00	7/7	1.0	4
Chromium	1.61	14.04	25.50	2/3	0.050	0.33	0.90	6/8	5.0	0
Cobalt	0.05	12.78	25.50	0/2	0.050	0.15	0.25	0/2	-	-
Copper	0.05	37.64	116	2/4	0.050	0.15	0.25	0/2	-	-
Iron	16.80	7,744	20,000	5/5	1.81	6.67	13.00	3/3	-	-
Lead	2.57	136	368	3/3	0.45	0.90	1.40	4/4	5.0	0
Magnesium	84.00	687	1,373	4/4	3.39	5.84	7.10	3/3	-	-
Manganese	2.79	337	1,170	4/4	0.25	0.74	1.55	2/3	-	-
Mercury	0.00010	0.00010	0.00010	0/1	0.00010	0.00010	0.00010	0/1	0.2	0
Molybdenum	0.050	12.78	25.50	0/2	0.05	0.15	0.25	0/2	-	-
Nickel	0.050	14.14	29.00	2/4	0.10	0.17	0.25	2/3	-	-
Selenium	0.050	12.78	25.50	0/2	0.010	0.07	0.25	3/5	1.0	0
Silver	0.050	12.78	25.50	0/2	0.020	0.12	0.25	4/6	5.0	0
Thallium	0.25	43.65	128	1/3	0.25	0.75	1.25	0/2	-	-
Vanadium	0.64	12.71	25.50	2/3	0.05	0.30	0.60	1/3	-	-
Zinc	5.70	13,489	61,665	5/5	6.07	116	267	3/3	-	-
Cyanide	52.00	52.00	52.00	1/1	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	173	8,802	17,616	4/4	-	-	-	0/0	-	-
Fluoride	941	1,221	1,500	2/2	-	-	-	0/0	-	-
Phosphate	13.38	240,007	480,000	2/2	-	-	-	0/0	-	-
Silica	50,000	125,000	200,000	2/2	-	-	-	0/0	-	-
Chloride	510	38,564	150,000	4/4	-	-	-	0/0	-	-
TSS	988,200	988,200	988,200	1/1	-	-	-	0/0	-	-
pH *	5.00	5.40	5.80	2/2					2<pH>12	0
Organics (TOC)	20.00	384,940	1,140,000	3/3					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PRECIPITATOR SLURRY - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	28	28	28	1/1	0.31	0.31	0.31	1/1	-	-
Arsenic	5	5	5	1/1	0.1	0.1	0.1	1/1	5.0	0
Barium	18	18	18	1/1	1	1	1	1/1	100.0	0
Beryllium	0.2	0.2	0.2	1/1	0.01	0.01	0.01	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	1300	1300	1300	1/1	0.022	0.022	0.022	1/1	1.0	0
Chromium	60	60	60	1/1	0.237	0.237	0.237	1/1	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	130	130	130	1/1	0.11	0.11	0.11	1/1	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	1	1	1	1/1	0.0005	0.0005	0.0005	1/1	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	11	11	11	1/1	0.08	0.08	0.08	1/1	-	-
Selenium	8	8	8	1/1	0.2	0.2	0.2	1/1	1.0	0
Silver	1	1	1	1/1	0.02	0.02	0.02	1/1	5.0	0
Thallium	650	650	650	1/1	0.2	0.2	0.2	1/1	-	-
Vanadium	60	60	60	1/1	0.3	0.3	0.3	1/1	-	-
Zinc	11000	11000	11000	1/1	69.9	69.9	69.9	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	200000	200000	200000	1/1	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - FURNACE SCRUBBER BLOWDOWN - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	3.70	2,360	18,000	8/8	0.25	4.23	11.40	5/6	-	-
Antimony	0.016	1.31	4.80	2/8	0.05	0.53	1.60	3/7	-	-
Arsenic	0.016	1.46	8.70	4/8	0.00125	0.14	0.54	3/6	5.0	0
Barium	0.050	41.94	280.00	4/7	0.050	0.43	1.20	4/7	100.0	0
Beryllium	0.0020	0.17	0.93	3/7	0.0025	0.01	0.03	1/6	-	-
Boron	25.00	25.00	25.00	1/1	19	19.00	19.00	1/1	-	-
Cadmium	0.0010	2.37	9.60	10/13	0.0050	0.40	2.07	4/7	1.0	2
Chromium	0.0005	110	940	7/10	0.005	0.34	0.90	4/7	5.0	0
Cobalt	0.0030	38.81	260	3/7	0.03	0.08	0.25	0/5	-	-
Copper	0.0005	46.66	310	3/7	0.005	0.07	0.25	1/5	-	-
Iron	0.030	10,382	63,000	8/8	0.0375	3.88	6.86	5/6	-	-
Lead	0.004	25.69	150	8/8	0.125	0.31	0.42	2/6	5.0	0
Magnesium	5.40	174	1,300	10/10	0.17	6.10	10.70	5/6	-	-
Manganese	0.50	3,464	26,000	7/8	0.25	2.03	6.50	5/6	-	-
Mercury	0.00010	0.019	0.10	2/8	0.0001	0.0001	0.0002	1/6	0.2	0
Molybdenum	0.029	11.06	71.00	4/7	0.010	0.074	0.25	0/5	-	-
Nickel	0.009	68.89	530	5/8	0.015	0.079	0.25	2/6	-	-
Selenium	0.003	0.12	0.50	3/7	0.0025	0.071	0.25	1/6	1.0	0
Silver	0.0010	0.48	1.60	1/7	0.01	0.074	0.25	1/6	5.0	0
Thallium	0.040	1.52	4.50	1/8	0.25	0.53	1.25	1/6	-	-
Vanadium	0.015	83.25	710	7/9	0.015	0.25	0.79	3/7	-	-
Zinc	0.023	79.11	211	12/12	0.55	44.38	130	7/7	-	-
Cyanide	0.900	0.90	0.90	1/1	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	18.10	3,167	18,600	8/8	6.00	7.00	8.00	2/2	-	-
Fluoride	51.60	2,481	20,200	9/9	2.41	5.66	8.91	2/2	-	-
Phosphate	6.40	959	3,700	7/7	2.17	4.02	5.87	2/2	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	0.38	177	420	10/11	0.27	0.47	0.67	2/2	-	-
TSS	0.49	2,667	8,000	4/4	-	-	-	0/0	-	-
pH *	1.10	4.38	6.61	10/10					2<pH>12	1
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT SLUDGE/SOLIDS - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	54500	54,500	54,500	1/1	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	233	233	233	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	1143	1,143	1,143	1/1	-	-	-	0/0	1.0	0
Chromium	-	-	-	0/0	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	17400	17,400	17,400	1/1	-	-	-	0/0	-	-
Lead	188	188	188	1/1	-	-	-	0/0	5.0	0
Magnesium	2775	2,775	2,775	1/1	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	10625	10,625	10,625	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	1507	1,507	1,507	1/1	-	-	-	0/0	-	-
Fluoride	150	2,575	5,000	2/2	-	-	-	0/0	-	-
Phosphate	200	200	200	1/1	-	-	-	0/0	-	-
Silica	50000	162,200	274,400	2/2	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	4	7.1	11.3	3/3					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT LIQUIDS - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.424	0.42	0.42	1/1	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	0.643	0.64	0.64	1/1	-	-	-	0/0	-	-
Cadmium	2.86	2.86	2.86	1/1	-	-	-	0/0	1.0	0
Chromium	0.014	0.04	0.07	2/2	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	-	-	-	0/0	-	-	-	0/0	5.0	0
Magnesium	54.5	54.50	54.50	1/1	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.00012	0.00012	0.00012	1/1	-	-	-	0/0	0.2	0
Molybdenum	0.084	0.084	0.084	1/1	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	0.045	0.045	0.045	1/1	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	0.21	0.37	0.53	2/2	-	-	-	0/0	-	-
Zinc	0.29	2.11	3.94	2/2	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	118	118	118	1/1	-	-	-	0/0	-	-
Fluoride	122	122	122	1/1	-	-	-	0/0	-	-
Phosphate	100	490	1,000	3/3	-	-	-	0/0	-	-
Silica	47.70	47.70	47.70	1/1	-	-	-	0/0	-	-
Chloride	38.00	111	183	2/2	-	-	-	0/0	-	-
TSS	240	240	240	1/1	-	-	-	0/0	-	-
pH *	4.00	5.33	6.80	4/4					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT LIQUID EFFLUENT - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	1.00	1.00	1.00	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	177	177	177	1/1	-	-	-	0/0	1.0	0
Chromium	-	-	-	0/0	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	-	-	-	0/0	-	-	-	0/0	5.0	0
Magnesium	190	190	190	1/1	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	536	536	536	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	1,533	1,533	1,533	1/1	-	-	-	0/0	-	-
Fluoride	22.80	22.80	22.80	1/1	-	-	-	0/0	-	-
Phosphate	100	100	100	1/1	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	2,308	2,308	2,308	1/1	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	4.00	4.85	5.70	2/2					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - AFM RINSATE - ELEMENTAL PHOSPHOROUS

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	0.2	0.2	0.2	1/1	-	-
Arsenic	1	1	1	1/1	0.14	0.14	0.14	1/1	5.0	0
Barium	-	-	-	0/0	1	1	1	1/1	100.0	0
Beryllium	-	-	-	0/0	0.01	0.01	0.01	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	4	4	4	1/1	4.12	4.12	4.12	1/1	1.0	1
Chromium	1	1	1	1/1	0.278	0.278	0.278	1/1	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	-	-	-	0/0	0.19	0.19	0.19	1/1	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	0.0005	0.0005	0.0005	1/1	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	0.08	0.08	0.08	1/1	-	-
Selenium	1	1	1	1/1	1.03	1.03	1.03	1/1	1.0	1
Silver	-	-	-	0/0	0.02	0.02	0.02	1/1	5.0	0
Thallium	-	-	-	0/0	0.03	0.03	0.03	1/1	-	-
Vanadium	-	-	-	0/0	0.19	0.19	0.19	1/1	-	-
Zinc	-	-	-	0/0	37.2	37.2	37.2	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	20000	20000	20000	1/1	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

FLUORSPAR AND HYDROFLUORIC ACID

A. Commodity Summary

In 1994, approximately 73 percent of the reported fluorspar (CaF_2) consumed in the United States was used in the production of hydrofluoric acid. About 10 percent of the fluorspar was used as a fluxing agent in steelmaking, and in iron and steel foundries. The remaining 17 percent was consumed in aluminum fluoride manufacture, primary aluminum production, glass manufacture, enamels, welding-rod coatings, and other miscellaneous end uses or products.[1] Fluorspar is sold in three grades: metallurgical (minimum 85 percent CaF_2), ceramic (85-96 percent CaF_2), and acid (minimum 97 percent CaF_2).[2] While there are seven active domestic fluorspar mines, the majority of fluorspar used in the U.S. is imported.[3]

Hydrofluoric acid is an aqueous solution of hydrogen fluoride produced by a reaction of fluorspar and sulfuric acid. Hydrofluoric acid is the feedstock used to produce almost all of the organic and inorganic fluorine-bearing chemicals. Hydrofluoric acid also is used in aluminum and uranium processing.[4] As of 1989, three facilities actively produced hydrofluoric acid. Although several other facilities produce hydrofluoric acid as an intermediate product during the formulation of commercial chemicals or compounds, these facilities are not included as part of the primary hydrofluoric acid industry. The names and locations of the three hydrofluoric acid production facilities are shown in Exhibit 1.

EXHIBIT 1

SUMMARY OF HYDROFLUORIC ACID PRODUCERS (IN 1989)

Facility Name	Location
Allied Signal	Geismar, LA
E.I. duPont	La Porte, TX
Attochemical, N.A.	Calvert City, KY

B. General Process Description

1. Discussion of the Typical Production Processes

Hydrofluoric acid is produced by reacting acid-grade fluorspar and sulfuric acid in a kiln, and cooling and purifying the product. This process is described in detail below.

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[1] M.M. Miller, "Fluorspar," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 58.

[2] M.M. Miller, "Fluorspar," from Minerals Yearbook. Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 487.

[3] U.S. Bureau of Mines, Randol Mining Directory 1994/1995, Randol International Ltd., Golden, CO, 1994, p. 165.

[4] M.M. Miller, 1994, Op. Cit., p. 58.

2. Generalized Flow Diagram

Before fluorspar can be used to make hydrofluoric acid, the raw ore must be physically concentrated and purified. Ceramic and acid grades of fluorspar are concentrated (not shown) by crushing and grinding fluorspar, and purified by froth flotation. First the fluorspar is crushed and ground. Then lead and zinc sulfides are preferentially floated away from the fluorspar. The easily floating fluorspar is removed and sent to the cleaner circuit. The tailings are discarded and the middling product is reground and passed through a cleaner circuit. The flotation process yields acid grade concentrate, and sometimes lower grade concentrates, which are sold either as ceramic or metallurgical grade fluorspar. Metallurgical grade fluorspar is produced by hand sorting, crushing and screening, and gravity concentration.[5]

Hydrofluoric acid is produced from acid-grade fluorspar (CaF_2) which reacts with sulfuric acid in a heated retort kiln to produce hydrogen fluoride gas, as shown in Exhibit 2. The acid grade fluorspar typically contains at least 97 percent calcium fluoride, as well as silica, calcium carbonate, carbon, sulfur, phosphorus pentoxide, chloride, mixed metal oxides, and a trace amount of arsenic. The sulfuric acid generally is between 93 and 99 percent pure. Both sulfuric acid and oleum (SO_3) are commonly used.[6] The residue remaining after retorting is calcium sulfate anhydrite, commonly known as fluorogypsum, which is a RCRA special waste. This solid is slurried in process water as it exits the kiln and is transported either to the waste management units[7] or, at the duPont plant, to a production operation for further processing for sale as a byproduct.[8] The process wastewater, the second RCRA special waste generated by this sector, is stored/treated in on-site surface impoundments and then either reused in the process operations or discharged.

The crude product gas is handled differently by the various manufacturers, but cooling and scrubbing are always involved. Exhibit 2 shows the gas being cooled, purified by scrubbing, and condensed. The crude product may be diluted and sold as an approximately 70 percent hydrofluoric acid solution, or distilled to remove any remaining water and impurities, and sold as anhydrous hydrogen fluoride, a colorless fuming liquid. The wastes from the refrigerated condenser go to an acid scrubber. The sulfuric acid used in this process unit is then sent to the acid feed, to react with the fresh fluorspar. The waste stream from the acid scrubber is sent to a water scrubber which generates fluorosilicic acid and gases. The fluorosilicic acid may be recovered or disposed.

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

No new novel processes have been utilized, however, a possible process under investigation involves extracting fluorine as fluorosilicic acid from phosphate rock during the production of phosphoric acid. Also under investigation is the production of calcium fluoride from calcium silicon hexafluoride ($CaSiF_6$) produced by the reaction of fluorosilicic acid and phosphate rock.[9]

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[5] M.M. Miller, 1992, Op. Cit., pp. 488-89.

[6] "Fluorspar," from Kirk Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. XI, 1994, p. 364.

[7] Allied Signal, Inc., 1989, Public comments from Allied Signal, Inc. addressing the 1989 Proposed Reinterpretation of the Mining Waste Exclusion (Docket No. MW2P00020); November 8, 1989; pg. 1.

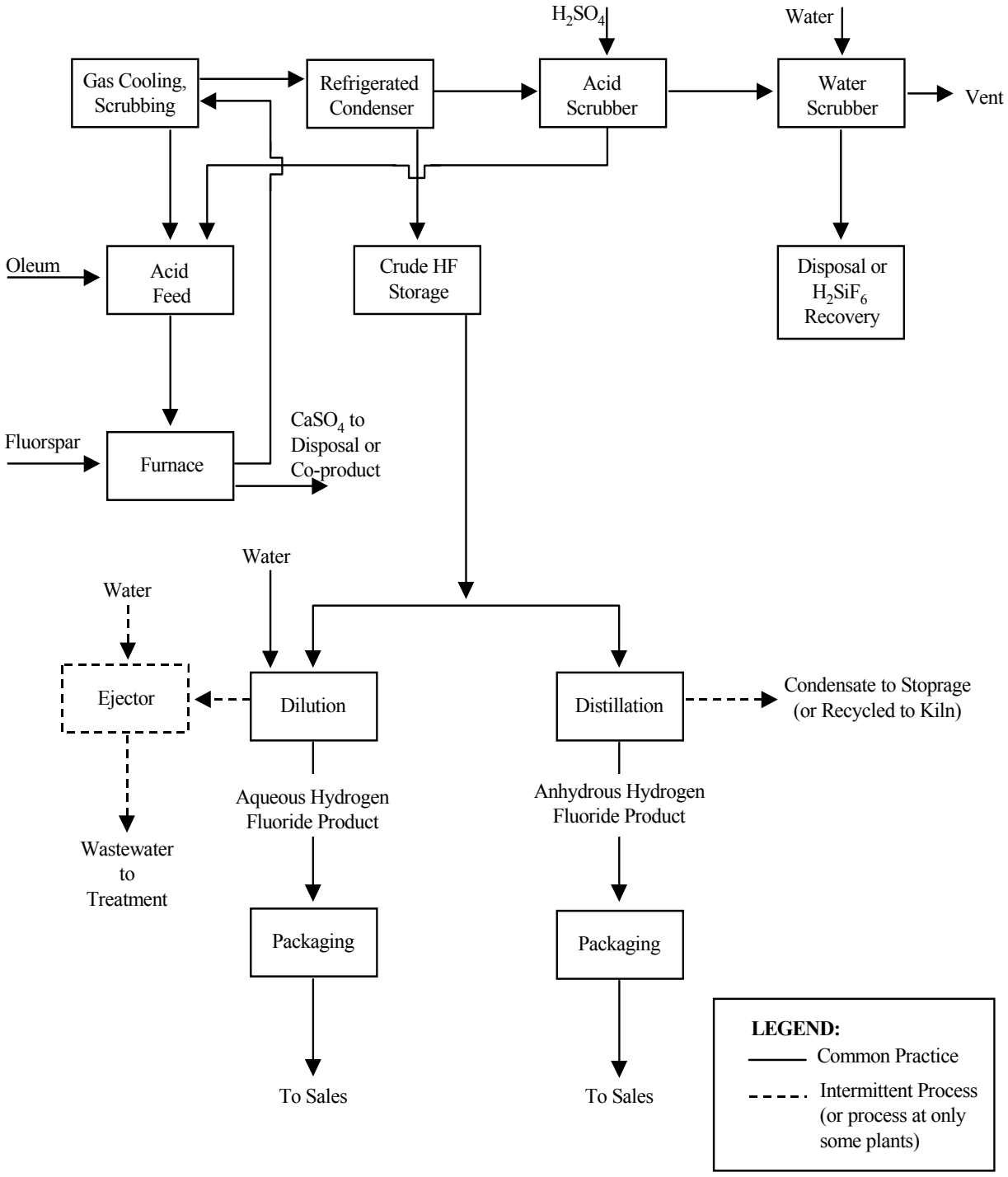
[8] At the duPont facility, lime is added when the fluorogypsum is quenched in order to enhance the chemical characteristics of the material for construction applications.

[9] "Fluorspar," 1994, Op. Cit., pp. 367-68.

EXHIBIT 2

HYDROFLUORIC ACID PRODUCTION

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1994, p. 367 and Development Document, Section 12, Hydrofluoric Acid Industry.)



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.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs when the beneficiated fluorspar is mixed with concentrated acid in the furnace/kiln where an intense exothermic chemical reaction occurs and signficantly alters the chemical structure of the fluorspar. 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

1. Extraction and Beneficiation Wastes

Gangue, lead and zinc sulfides, spent flotation reagents, and tailings are likely to be generated by the beneficiation of fluorspar. The lead and zinc sulfides may be processed further to recover the lead and zinc. No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

2. Mineral Processing Wastes

The hydrofluoric acid production process generates several waste streams. Two of these waste streams, fluorogypsum and process wastewater, were classified as RCRA special wastes, and were studied in the July 1990 Report to Congress on Special Wastes from Mineral Processing.

Fluorogypsum. This waste is a solid material consisting primarily of fine particles of calcium sulfate, usually less than 0.02 mm in diameter, that is slurried for transport from the kilns to waste management units. Using available data on the composition of fluorogypsum, EPA evaluated whether the waste exhibits any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. Based on analyses of four samples from two facilities (Geismar and Calvert City) and professional judgment, the

Agency does not believe the fluorogypsum exhibits any of these characteristics. All eight of the inorganic constituents with EP toxicity regulatory levels were measured in concentrations (using the EP leach test) that were at least two orders of magnitude below the regulatory levels.[10] According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 894,000 metric tons of fluorogypsum are produced annually in the United States.[11] The La Porte, TX plant sells its fluorogypsum for use as a filler for a road base, railroad subbase, and paving material.[12]

Process wastewater. This waste is an aqueous liquid, the chemical constituents of which include fluoride, calcium, and sulfate, with smaller amounts of iron and silicon, as well as many trace metals. Using available data on the composition of hydrofluoric acid process wastewater, EPA evaluated whether the wastewater exhibits any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. Based on available information and professional judgment, the Agency does not believe the wastewater is reactive, ignitable, or EP toxic. All eight of the inorganic constituents with EP toxicity regulatory levels were measured in concentrations (using the EP leach test) that were at most 0.6 times the regulatory levels. Some wastewater samples, however, exhibit the characteristic of corrosivity. Analyses of the pH of hydrofluoric acid process wastewater at the Geismar and Calvert City facilities indicate that the wastewater is corrosive in all of the nine samples analyzed, sometimes with pH values as extreme as 1.00 (for comparison, pH levels below 2.0 are operationally defined as corrosive wastes).[13] According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 13.6 million metric tons of process wastewater are produced annually in the United States.[14]

Sludges. 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.

Off-Spec Fluorosilicic acid (H_2SiF_6). This waste is recovered from the water scrubber, and can be used in water fluoridation after it is recovered. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 0 metric tons/yr, 15,000 metric tons/yr, and 44,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of corrosivity. This waste stream is partially recycled and classified as a by-product.

APC Dusts. 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.

D. Non-uniquely AssociatedWastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

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[10] From the response of Allied Signal, Inc. and Pennwalt Corp. to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities", conducted in 1989.

[11] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, August 1992, p. I-5.

[12] From the response of E.I. duPont to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities," conducted in 1989.

[13] From the response of Allied Signal, Inc. and Pennwalt Corp. to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities", conducted in 1989.

[14] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-5.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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GEM STONES

A. Commodity Summary

The gem stone industry in the United States is extremely small and relies on foreign trade to meet most of its source requirements. The United States has no known large resources of precious gem stones (i.e., diamonds, rubies, sapphires, and emeralds) and reserves are generally limited to semiprecious stones. Several semiprecious gem stone deposits are mined in the United States. In 1992, 91% of the total U.S. gem stone production (by value) was made up by the following states: Arizona, Nevada, Oregon, Maine, California, and Montana. In 1994, domestic natural gem stone production was approximately $51.6 million.[1]

Most gem stone mining appears to be done by hobbyists and amateurs in Mitchell County, NC; Judith Basin County, MT; San Diego County, CA; Oxford County, ME; and Gila County, AZ where gems such as turquoise, tourmaline, kunzite, emerald, and sapphire are found.

Gem stones are formed in nature in one of three ways: (1) from metamorphic processes, (2) by precipitating from aqueous solutions, and (3) by crystallizing from magmas. There are three major compositional groups of gem stones: silicate minerals comprise one-third; alumino-silicates comprise one-fifth; and oxides comprise one-seventh of gem minerals. The remaining groups are sulfides, phosphates, borosilicates, and carbonates.

Some semi-precious stones are produced as by-products of other mining operations. For example, beryl, tourmaline, spodumene, and gem quartz may be coproducts of mica, feldspar, quartz, or other pegmatite minerals. Diamonds may be recovered from gold dredges, turquoise from copper mines, agate and petrified wood from gravel pits, and gem garnet from abrasive garnet mines and mills.

Gem stones are used primarily for decoration. There are, however, some industrial applications for gem stone material. For instance, industrial processes requiring clean homogeneous stones use low-quality diamond. Tourmaline is used in laboratories to demonstrate the polarization of light, to measure the compressibility of fluids, and to measure high pressures. Agate is made into mortar and pestle sets, knife edges for balances, textile rollers, and spatulas. Gem stones are used as jewel bearings in timing devices, gauges, meters, and other applications requiring precision elements.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Gem stone production includes three steps, (1) mining, (2) processing, and (2) enhancement. These steps are discussed in greater detail below.

2. General Process Flow

Mining

Gem stone mining operations vary according to size and complexity. Small shallow deposits are generally mined by a few people with prybars, picks, shovels, and buckets. Drilling, blasting, and timbering may or may not be employed. Mechanized hauling and hoisting are done only at the largest mines.

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[1] Gordon Austin, "Gemstones," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 64-65.

Processing

In small operations, gem stone ores are broken, crushed, and concentrated by hand picking, washing, screening, or jigging. In larger operations, mechanized processes are employed. For instance, diamond processing involves standard gravity methods, grease belts, electrostatic separation, skin-flotation, magnetic separation, separation by x-ray luminescence, and separation by optical sorting.

Enhancement

Gem materials are cut in four main operations: sawing, grinding, sanding, and polishing. An initial cut is made with a diamond saw or blade to obtain a slice of desired thickness. Grinding of the stone may be done with impregnated-diamond, silicon carbide, aluminum oxide wheels, or coated abrasive disks. Multiple grinding steps ranging from 80 mesh through 600 mesh abrasives are used. Disk and belt sanders use abrasives bonded to cloth or waterproof reinforced paper. Leather laps or hard felt are used with a polishing agent to obtain the final polish.

Polishing agents such as fine diamond compound, tin oxide, tripoli, chromium oxide, cerium oxide, alumina, and rouge are typically used. These polished irregular shapes can then be further polished by tumbling them in a rubber lined drum and using a grinding and polishing medium with or without water.

Finally, many gem stones are further treated to enhance their appearance. Several different chemical and physical processes may be used, including bleaching, oiling, waxing, staining, dyeing, plastic and color impregnation by diffusion or dyeing, surface modification with color coating, lasering, glossing, heat treatment to change color, and irradiation by electromagnetic spectrum and by energetic particles to change color. Interference filters, foil backings, surface decoration, and inscribing are used to alter the surface of gems. The most common method of gem enhancement is heat treatment which can change color, structure, and clarity. A newer method of gem enhancement is diffusion treatment. This involves a chemical heat treatment in a bath of chemicals containing iron and titanium.[2]

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

Synthesis of materials that can replace rare crystalline materials has been encouraged by industry. Synthetic gem stones may be used in electronics and semiconductors or as frequency controllers, polarizers, transducers, radiation detectors, infrared optics, bearings, strain gages, amplifiers, lasers, lenses, crucibles, and more.[3]

4. Beneficiation/Processing Boundaries

Based on a review of the process, there are no mineral processing operations involved in the production of gem stones.

C. Process Waste Streams

Existing data and engineering judgement suggest that the wastes listed below from gem stone production do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

1. Extraction/Beneficiation Wastes

The extraction of gem bearing material in mines creates **overburden**. However, land disturbance due to

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[2] Gordon T. Austin, "Gemstones," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 501-519.

[3] Jean W. Pressler, "Gemstones," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 305-315.

gem stone extraction is minimal since the number of underground mines in operation is minimal.[4] Additional miscellaneous wastes include **spent chemical agents** used to color the gem stones, **spent polishing media**, and **waste minerals**.

2. Mineral Processing Wastes

No wastes are identified.

D. Non-uniquely AssociatedWastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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[4] Ibid.

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Pressler, Jean. "Gemstones." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 305- 315.

GERMANIUM

A. Commodity Summary

Germanium is recovered either as a minor byproduct of the refining of base metal ores, or as a constituent of coal deposits.[1] Germanium has a metallic grayish appearance and is hard and brittle. It is a semiconductor with electrical properties between those of metal and an insulator.[2] The Bureau of Mines estimated domestic consumption at 25,000 kilograms during 1994.[3] The domestic germanium industry is composed of three germanium refineries, one each in New York, Pennsylvania, and Oklahoma and a mining operation located in Tennessee.[4] Additional information is provided on a recovery operation in Utah. Exhibit 1 presents the names and locations of the facilities involved in the production of germanium.

EXHIBIT 1

SUMMARY OF GERMANIUM PROCESSING FACILITIES

Facility Name	Location	Type of Operations
Atomergic Chem	Plainview, NY	Refining
Cabot	Revere, PA	Refining
Eagle-Picher	Quapaw, OK	Refining
Jersey Miniere	Clarksville, TN	Mining
Musto Exploration	St. George, UT	Mining and Refining

Germanium is available commercially as a tetrachloride and a high purity oxide, and is commonly found in the form of zone-refined ingots, single crystal bars, castings, doped semiconductors, and optical materials.[5] Some of the major end uses for germanium include infrared optics, fiber-optics systems, detectors, and semiconductors.[6]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Germanium is recovered as a by-product of other metals, mostly copper, zinc, and lead. The process described in detail below refers to the recovery of germanium from residues at zinc ore processing facilities. Exhibits 2 through 4 present process flow diagrams for the production of germanium.

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[1] Thomas O. Llewellyn, "Germanium," from Minerals Yearbook Volume 1. Metals and Minerals, 1992, p. 531.

[2] Ibid., p. 531.

[3] Thomas O. Llewllyn, "Germanium," from Minerals Commodity Summaries, U.S. Bureau of Mines, 1995, p. 66.

[4] Ibid.

[5] Thomas O. Llewellyn, 1992, Op. Cit. p. 531.

[6] Thomas O. Llewellyn, 1994, Op. Cit., p. 70.

EXHIBIT 2

RECOVERY OF GERMANIUM DURING ZINC ORE PROCESSING

(Adapted from: 1988 Final Draft Summary Report on Mineral Industry Processing Wastes, 1988, pp. 3-93 - 3-99.)

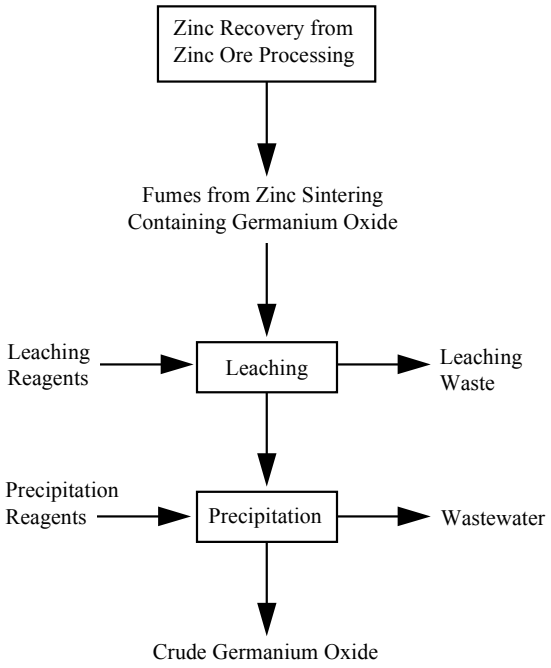


EXHIBIT 3

PRIMARY AND SECONDARY GERMANIUM PRODUCTION PROCESS

(Adapted from: Development Document for Effluent Limitations Guidelines and Standards for Nonferrous Metals Manufacturing Point Source Category, 1989, pp. 5231 - 5352.)

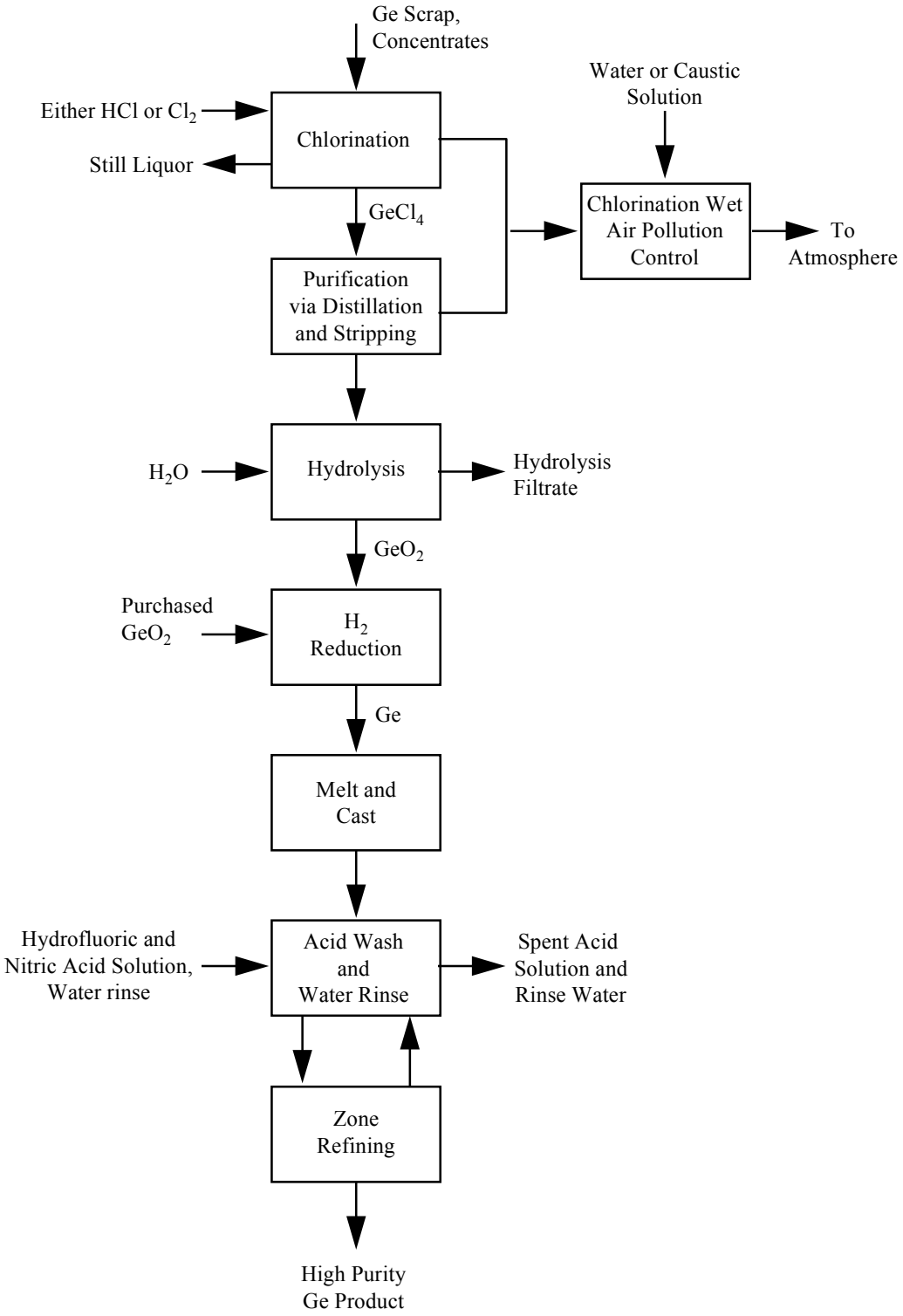
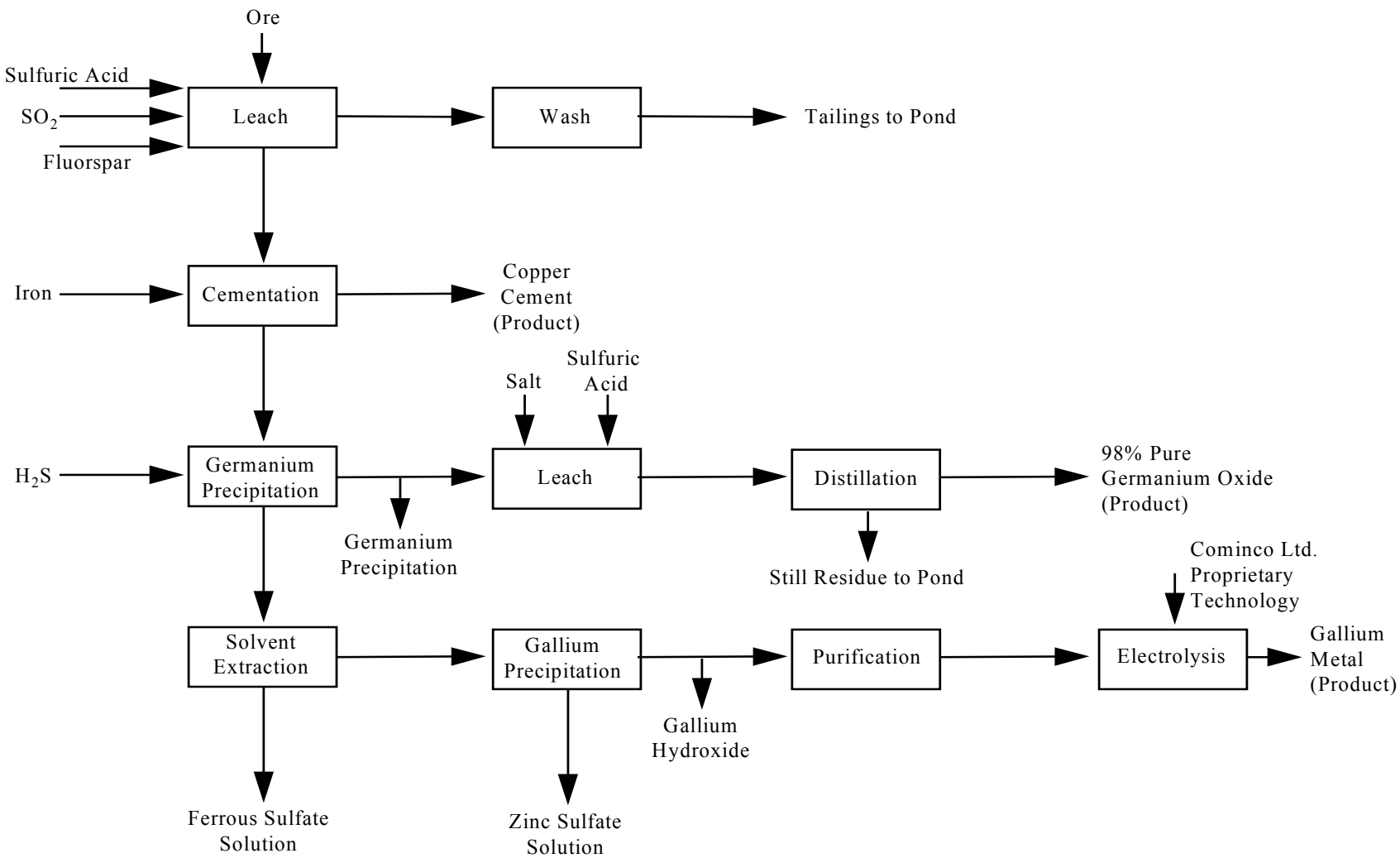


EXHIBIT 4

PROCESS FLOW SHEET FOR GALLIUM AND GERMANIUM PRODUCTION

(Adapted from: 1988 Final Draft Summary Report on Mineral Industry Processing Wastes, 1988, pp. 3-93 - 3-99.)



2. Generalized Process Flow Diagram

As shown in Exhibit 2, germanium-bearing residues from zinc ore processing facilities are a main source for germanium metal. In general, the ore is roasted and sintered. The sintering fumes, which contain oxidized germanium are then collected and leached with sulfuric acid, yielding a solution that contains germanium. Germanium can then be selectively precipitated from the solution through the addition of zinc dust. The remaining solids can be recycled to maximize the recovery of germanium.[7]

Most germanium, regardless of the process by which it was recovered from ore, is refined using chlorination. As shown in Exhibit 3, germanium concentrates are chlorinated with concentrated hydrochloric acid or chlorine gas to produce germanium tetrachloride ($GeCl_4$) in solution.[8] Chlorine is usually added to the primary distillation or subsequent fractionation, or both, to suppress the volatility of arsenic.[9] Solid impurities and still liquor are separated and discarded as waste or processed further, while the filtrates and other wash water are sent for further germanium recovery.[10]

The resultant purified germanium tetrachloride is then hydrolyzed with deionized water to produce a solid germanium dioxide (GeO_2). The germanium dioxide is removed by filtration, dried, and reduced to germanium metal with hydrogen at approximately 760 ºC. The metal can then be melted and cast into first reduction or as-reduced bars.[11]

An alternative process, shown in Exhibit 4, is used at the Musto Exploration site in Utah to recover germanium. Fluorspar and ore are leached with sulfuric acid and sulfur dioxide. The fluorspar forms hydrofluoric acid which then helps leach both germanium and gallium. Copper can be removed from the leachate by cementation on iron and can then be sold as a byproduct. Hydrogen sulfide is used to precipitate the germanium. Following this precipitation, the remaining liquid is sent for further gallium recovery. The recovered germanium is refined via leaching and distillation. Any still residues are discarded.[12]

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

None Identified.

4. Beneficiation/Processing Boundary

Since germanium is recovered as a by-product of other metals, all of the wastes generated during germanium recovery are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the reports for copper, zinc, and lead presented elsewhere in this background document.

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[7] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for Nonferrous Metals Manufacturing Point Source Category, Vol. X, Office of Water Regulations Standard, May 1989, p. 5256.

[8] Ibid., p. 5256.

[9] "Germanium," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed, Vol XI, 1994, p. 796.

[10] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 5256.

[11] "Germanium," 1994, Op. Cit. p. 796.

[12] U.S. Environmental Protection Agency, "Germanium," from 1988 Final Draft Summary Report on Mineral Industry Processing Wastes, Office of Solid Waste, 1988, p. 3-96.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Not applicable.

2. Mineral Processing Wastes

Exhibit 3 identifies the following wastes from the recovery of primary and secondary germanium and gallium recovery. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate low, medium, and high annual waste generation rates.

Waste Still Liquor. As shown in Exhibit 3, plants which chlorinate germanium raw materials generate an acidic still liquor containing arsenic, nickel, zinc and germanium, and suspended solids.[13] Low, medium, and high annual waste generation rates were estimated as 10 metric tons/yr, 210 metric tons/yr, and 400 metric tons/yr. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (arsenic, cadmium, chromium, lead, selenium, and silver) and ignitability. Waste characterization sampling data for this waste stream is included as Attachment 1.

Chlorinator Wet Air Pollution Control Sludge. Plants chlorinating germanium use a wet scrubbing system to control HCl and H_2 fumes. Waste from the scrubbing system contains cadmium, lead, nickel, germanium, suspended solids, and an alkaline pH.[14] Low, medium, and high annual waste generation rates were estimated as 10 metric tons/yr, 210 metric tons/yr, and 400 metric tons/yr. We used best engineering judgment to determine that this waste stream may be partially recycled and may exhibit the characteristic of toxicity (arsenic, cadmium, chromium, lead, selenium, and silver). This waste is classified as a sludge. Waste characterization sampling data for this waste stream is included as Attachment 1.

Hydrolysis Filtrate. As shown in Exhibit 3, germanium tetrachloride is hydrolyzed to germanium dioxide by adding deionized water. Germanium dioxide solids are separated from the liquid phase by filtration, and the filtrate may be discharged. The filtrate contains nickel and germanium.[15] Low, medium, and high annual waste generation rates were estimated as 10 metric tons/yr, 210 metric tons/yr, and 400 metric tons/yr. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (arsenic, cadmium, chromium, lead, selenium, and silver). Waste characterization sampling data for this waste stream is included as Attachment 1.

Waste Acid Wash and Rinse Water. Germanium ingots or bars are washed with a HF-HNO_3 mixture and then rinsed with water to remove residual acid from the bar. The discharged spent acid and rinse water contain treatable concentrations of lead, germanium, and fluoride.[16] Low, medium, and high annual waste generation rates were estimated as 400 metric tons/yr, 2,200 metric tons/yr, and 4,000 metric tons/yr. We used best engineering judgment to determine that this waste stream may be partially recycled and may exhibit the characteristics of toxicity (arsenic, cadmium, chromium, lead, selenium, and silver) and corrosivity. This waste is classified as a spent material. Waste characterization sampling data for this waste stream is included as Attachment 1.

Exhibits 2 through 4 also identify the following mineral processing wastes associated with the production of germanium. No information on waste generation or management is available for these wastestreams.

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[13] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 5273.

[14] Ibid., p. 5273.

[15] Ibid.

[16] Ibid.

Roaster off-gases. Off-gases containing sulfur dioxide are generated during roasting and sent to an acid plant for treatment.

Leach Residues. Ferrous residues are removed and sent to disposal. Residues containing copper and cadmium are sent to further treatment and distribution. This waste stream has a reported annual waste generation rate of 10 metric tons/yr. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (cadmium and lead).

Germanium-Oxides Fumes. As shown in Exhibit 2, fumes containing germanium oxide are generated during sintering. From these fumes, scrubbing water or solids as well as air pollution control dusts may also be generated.

Spent Acid/Leachate. Spent acid is generated by leaching the germanium oxide fumes from the zinc sintering. The spent acid likely contains arsenic and other heavy metals, including lead and zinc. Low, medium, and high annual waste generation rates were estimated as 400 metric tons/yr, 2,200 metric tons/yr, and 4,000 metric tons/yr. We used best engineering judgment to determine that this waste stream may be partially recycled and may exhibit the characteristics of toxicity (arsenic and lead) and corrosivity. This waste is classified as a spent material.

Wastewater. Some wastewater will result from the precipitation step. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

As shown in Exhibit 4, tailings are generated as a result of the initial leaching at the Musto Exploration process. Still residues are generated as a result of further refining operations at Musto Exploration and sent to ponds for further treatment.[17]

D. Non-uniquely AssociatedWastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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[17] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-96.

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ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTE ACID WASH AND RINSE WATER - GERMANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Min.	Avg.	Max.	# Detects	Level	In Excess
Aluminum	350	350	350	1/1	-	-	-	0/0	-	-
Antimony	0.04	0.04	0.04	1/1	-	-	-	0/0	-	-
Arsenic	0.39	0.39	0.39	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.05	0.05	0.05	1/1	-	-	-	0/0	1.0	0
Chromium	0.50	0.50	0.50	1/1	-	-	-	0/0	5.0	0
Cobalt	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Copper	0.10	0.10	0.10	1/1	-	-	-	0/0	-	-
Iron	2.90	2.9	2.9	1/1	-	-	-	0/0	-	-
Lead	0.78	0.78	0.78	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	0.09	0.09	0.09	1/1	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Nickel	0.20	0.20	0.20	1/1	-	-	-	0/0	-	-
Selenium	0.01	0.01	0.01	1/1	-	-	-	0/0	1.0	0
Silver	0.07	0.07	0.07	1/1	-	-	-	0/0	5.0	0
Thallium	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Vanadium	1.00	1.00	1.00	1/1	-	-	-	0/0	-	-
Zinc	0.06	0.06	0.06	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - HYDROLYSIS FILTRATE - GERMANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Min.	Avg.	Max.	# Detects	Level	In Excess
Aluminum	0.78	0.78	0.78	1/1	-	-	-	0/0	-	-
Antimony	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Arsenic	0.20	0.20	0.20	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.05	0.05	0.05	1/1	-	-	-	0/0	1.0	0
Chromium	0.50	0.50	0.50	1/1	-	-	-	0/0	5.0	0
Cobalt	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Copper	0.10	0.10	0.10	1/1	-	-	-	0/0	-	-
Iron	0.37	0.4	0.4	1/1	-	-	-	0/0	-	-
Lead	0.20	0.20	0.20	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	0.52	0.52	0.52	1/1	-	-	-	0/0	-	-
Nickel	1.00	1.00	1.00	1/1	-	-	-	0/0	-	-
Selenium	0.12	0.12	0.12	1/1	-	-	-	0/0	1.0	0
Silver	0.00	0.00	0.00	1/1	-	-	-	0/0	5.0	0
Thallium	0.02	0.02	0.02	1/1	-	-	-	0/0	-	-
Vanadium	1.00	1.00	1.00	1/1	-	-	-	0/0	-	-
Zinc	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTE STILL LIQOUR - GERMANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Min.	Avg.	Max.	# Detects	Level	In Excess
Aluminum	1.50	1.50	1.50	1/1	-	-	-	0/0	-	-
Antimony	0.03	0.03	0.03	1/1	-	-	-	0/0	-	-
Arsenic	1.70	1.70	1.70	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.23	0.23	0.23	1/1	-	-	-	0/0	1.0	0
Chromium	0.50	0.50	0.50	1/1	-	-	-	0/0	5.0	0
Cobalt	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Copper	0.16	0.16	0.16	1/1	-	-	-	0/0	-	-
Iron	1.80	1.8	1.8	1/1	-	-	-	0/0	-	-
Lead	0.20	0.20	0.20	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	2.20	2.20	2.20	1/1	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Nickel	2.00	2.00	2.00	1/1	-	-	-	0/0	-	-
Selenium	0.09	0.09	0.09	1/1	-	-	-	0/0	1.0	0
Silver	0.00	0.00	0.00	1/1	-	-	-	0/0	5.0	0
Thallium	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Vanadium	1.00	1.00	1.00	1/1	-	-	-	0/0	-	-
Zinc	150.00	150.00	150.00	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - CHLORINATOR WET APC - GERMANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Min.	Avg.	Max.	# Detects	Level	In Excess
Aluminum	4.10	4.10	4.10	1/1	-	-	-	0/0	-	-
Antimony	0.02	0.02	0.02	1/1	-	-	-	0/0	-	-
Arsenic	0.10	0.10	0.10	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.46	0.46	0.46	1/1	-	-	-	0/0	1.0	0
Chromium	0.50	0.50	0.50	1/1	-	-	-	0/0	5.0	0
Cobalt	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Copper	0.20	0.20	0.20	1/1	-	-	-	0/0	-	-
Iron	11.00	11.0	11.0	1/1	-	-	-	0/0	-	-
Lead	0.45	0.45	0.45	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	0.25	0.25	0.25	1/1	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	0.50	0.50	0.50	1/1	-	-	-	0/0	-	-
Nickel	1.80	1.80	1.80	1/1	-	-	-	0/0	-	-
Selenium	0.04	0.04	0.04	1/1	-	-	-	0/0	1.0	0
Silver	0.00	0.00	0.00	1/1	-	-	-	0/0	5.0	0
Thallium	0.02	0.02	0.02	1/1	-	-	-	0/0	-	-
Vanadium	1.00	1.00	1.00	1/1	-	-	-	0/0	-	-
Zinc	0.17	0.17	0.17	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

GOLD AND SILVER

A. Commodity Summary

Gold and silver are discussed together in this report since most of the processes used to recover one will also recover the other. In addition, both metals are often found together in nature. A mine is generally classified as a gold or silver mine based on which metal recovered yields the greatest economic value to the operator. Exhibit 1 presents the names and locations of known gold and silver smelters and refineries. Exhibit 2 presents the names and locations of the 25 leading gold-producing mines in the United States.

EXHIBIT 1

SUMMARY OF KNOWN GOLD AND SILVER SMELTERS AND REFINERIES

Facility Name	Facility Location
ASARCO, Inc.	Amarillo, TX Omaha, NE
AURIC-CHLOR, Inc.	Rapid City, SD
David Fell & Company, Inc.	City of Commerce, CA
Drew Resources Corp.	Berkeley, CA
Eastern Smelting & Refining Corp.	Lynn, MA
Englehard Industries West, Inc.	Anaheim, CA
GD Resources, Inc.	Sparks, NV
Handy & Harman	Attleboro, MA South Windsor, CT
Johnson Matthey	Salt Lake City, UT
Metalor USA Refining Corp.	North Attleboro, MA
Multimetco, Inc.	Anniston, AL
Nevada Gold Refining Corp.	Reno, NV
Sunshine Mining Co.	Kellogg, ID
Williams Advanced Materials	Buffalo, NY

Source: Randol Mining Directory, 1994, pp. 741-743.

EXHIBIT 2

TWENTY-FIVE LEADING GOLD-PRODUCING MINES IN THE UNITED STATES (IN ORDER OF OUTPUT)

Mine	Location	Source of Gold
Nevada Mines Operations, Newmont Gold Company	Elko and Eureka, NV	Gold ore
Gold Strike, Barrick Mercur Gold Mines, Inc.	Eureka, NV	Gold ore
Bingham Canyon, Kennecott-Utah Copper Corp.	Salt Lake, UT	Copper ore
Jerritt Canyon (Enfield Bell), Freeport-McMoran Gold Company	Elko, NV	Gold ore
Smoky Valley Common Operation, Round Mountain Gold Corp.	Nye, NV	Gold ore
Homestake, Homestake Mining Company	Lawrence, SD	Gold ore
McCoy and Cove, Echo Bay Mining Company	Lander, NV	Gold ore
McLaughlin, Homestake Mining Company	Napa, CA	Gold ore
Chimney Creek, Gold Fields Mining Company	Humboldt, NV	Gold ore
Fortitude and Surprise, Battle Mountain Gold Company	Lander, NV	Gold ore
Bulldog, Bond Gold, Bullfrog, Inc.	Nye, NV	Gold ore
Mesquite, Goldfields Mining Company	Imperial, CA	Gold ore
Getchell, FMG, Inc.	Humboldt, NV	Gold ore
Sleeper, Amax Gold, Inc.	Humboldt, NV	Gold ore
Cannon, Asamera Minerals (U.S.), Inc.	Chelan, WA	Gold ore
Ridgeway, Ridgeway Mining Company	Fairfield, SC	Gold ore
Jamestown, Sonora Mining Corp.	Tuolumne, CA	Gold ore
Paradise Peak, FMC Gold Company	Nye, NV	Gold ore
Rabbit Creek, Rabbit Creek Mining, Inc.	Humboldt, NV	Gold ore
Barney's Canyon, Kennecott Corp.	Salt Lake City, UT	Copper ore
Continental, Montana Resources	Silver Bow, MT	Gold ore
Zortman-Landusky, Pegasus Gold, Inc.	Phillips, MT	Gold ore
Golden Sunlight, Golden Sunlight Mines, Inc.	Jefferson, MT	Gold ore
Wind Mountain, Amax Gold, Inc.	Washoe, NV	Gold ore
Foley Ridge & Amie Creek, Wharf Resources	Lawrence, SD	Gold ore

Source: Mining Industry Profile Gold, 1993, pp. 5.

The United States is the second largest gold producing nation in the world. Gold lode and placer mines are located mostly in western states and Alaska while production in Nevada and California accounts for 70 percent of domestic production. The 1994 mine production value was over $4.1 billion. Uses of gold include jewelry and arts, 71 percent; industrial (electronic), 22 percent; and dental, 7 percent.[1] The 1994 silver production was valued at $240 million. Nearly three-fourths of the 1994 silver mine production was in Nevada, Idaho, Arizona, and Montana. Approximately 50 percent of the refined silver consumed domestically during 1993 was used in the manufacture of photographic products; 20 percent in electrical and electronic products; 10 percent in electroplated ware, sterlingware, and jewelry; and 20 percent in other uses.[2]

Silver occurs as native metal, but is usually found in sulfur-bearing minerals. About two-thirds of the world silver reserves and resources are contained in copper, lead, and zinc deposits. Ores in which silver or gold is the main component account for the remaining one-third of total world reserves and resources. The chief silver minerals found in domestic reserves are native silver, argentite, ceragyrite, polybasite, proustite, pyrargyrite, and tetrahedrite. Other ore minerals of silver are the tellurides, stromeyerite, and pearceite. Gold occurs mainly as native metal, alloyed with silver and/or other metals, and as tellurides. A naturally occurring alloy of gold and silver is known as electrum. Other gold minerals are rare. Gold is commonly associated with the sulfides of antimony, arsenic, copper, iron, and silver.[3]

B. Generalized Process Description

Precious metals may be recovered from the ore or from refining processes of base metals such as copper and lead. Because these are distinct and separate recovery methods, they are discussed separately in this report. Section 1 describes precious metal recovery from ore, and Section 2 describes precious metal recovery from refinery slimes. Section 3 is a discussion of precious metal refining operations.

SECTION 1: PRECIOUS METAL RECOVERY FROM ORES

1. Discussion of Typical Production Processes

Most domestic gold comes from surface lode mines. Silver is mined using open pit and underground methods. Several processes may be used to recover gold and silver from their ores. These include gravity separation, amalgamation, froth flotation, and cyanidation. Several processes may be combined at any given plant. These processes are discussed in more detail below.

2. Generalized Process Flow Diagram

Gravity Separation

Gravity separation relies on density differences to separate desired materials from host rock. Devices used include gold pans, sluices, shaking tables, and jigs. Gravity separation is used at most placer mines and at some lode or vein deposits.[4]

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[1] John Lucas, "Gold," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1994, pp. 72-73.

[2] Robert Reese, "Silver," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 154-155.

[3] John M. Lucas, "Gold," from Minerals Yearbook Volume 1 Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 535-561.

[4] U.S. Environmental Protection Agency, "Gold and Silver," from, 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, Office of Solid Waste, 1988, pp. 3-100- 3-115.

Amalgamation

Fine gold in placer deposits is often not separable from the ore minerals by density alone. The fine concentrate stream from a gravity separator, called "black sand" because of its color, often contains several dense minerals as well as fine gold. This fine gold may be recovered by amalgamation which involves the dissolution of gold or silver in mercury. The resulting alloy, amalgam, is relatively soft and will adhere readily to other pieces of amalgam or to mercury.[5]

Historically, amalgamation was widely used in the United States for recovery of gold and silver from their ores. Although this method is still practiced in other parts of the world, amalgamation most likely occurs domestically on a very limited scale.

Ore Preparation

Extracted ore must be milled to prepare it for further recovery activities. Uniformly sized particles may be obtained by crushing, grinding, and wet or dry classification. The degree of milling performed on the ore depends on the gold concentration of the ore, mineralogy and hardness of the ore, the mill's capacity, and the next planned step for recovery. Milled ore is pumped to the next operation unit in the form of a slurry. Fugitive dust generated during crushing and grinding activities is usually collected by air pollution control devices and recirculated into the beneficiation circuit. Most mills use water sprays to control dust from milling activities.[6]

After milling, sulfide ores may be subjected to oxidation by chlorination, bio-oxidation, roasting, or autoclaving. Chlorination is not commonly used to oxidize sulfide ores because of high equipment maintenance costs caused by the corrosive nature of the oxidizing agent. Bio-oxidation of sulfide ores employs bacteria to oxidize the sulfur-bearing minerals. Roasting of sulfide ores involves heating the ores in air to convert them to oxide ores and break up their physical structure, allowing leaching solutions to penetrate and dissolve the gold. Roasting oxidizes the sulfur in the ore, generating sulfur dioxide that can be captured and converted to sulfuric acid. Roasting temperatures are dependent on the mineralogy of the ore, but range as high as several hundred degrees Celsius. Roasting of carbonaceous ores oxidizes the carbon to prevent interference with leaching, which, in time, improves gold recovery efficiency. Autoclaving (pressure oxidation) is a relatively new technique that operates at lower temperatures than roasting. Autoclaving uses pressurized steam to start the reaction and oxygen to oxidize sulfur-bearing minerals. Heat released from the oxidation of sulfur sustains the reaction. The Getchell and Barrick Goldstrike Mines in Nevada, the McLaughlin Mine in California, and the Barrick Mercur Mine in Utah are currently using pressure oxidation (autoclave) technology, totally or in part, to beneficiate sulfide or carbonaceous gold ores.[7]

Agglomeration

Because ores with a high proportion of small particles may retard the percolation of the lixiviate, agglomeration is used to increase particle size. This operation includes mixing the crushed ore with portland cement and/or lime, wetting the ore evenly with cyanide solution to start leaching before the heap is built, and mechanically tumbling the ore mixture so fine particles adhere to larger particles.

Cyanidation - Leaching

Cyanidation leaching is the primary means of recovery of fine gold and silver. In this process, solutions of sodium or potassium cyanide are brought into contact with an ore which may or may not require extensive preparation prior to leaching. Gold and silver are dissolved by cyanide in high pH solutions in the presence of

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[5] Ibid.

[6] U.S. Environmental Protection Agency, Technical Resource Document, Extraction and Beneficiation of Ores and Minerals, Vol. II, July 1994.

[7] Ibid.

oxygen. There are three general methods of contacting ores with leach solutions: (1) heap leaching, (2) vat leaching, and (3) agitation leaching. Cyanidation heap leaching and agitation leaching account for most gold and silver recovery.[8,9] These leaching methods are discussed in detail below.

(1) Cyanidation - Heap Leaching

Heap leaching, shown in Exhibit 3, is the least expensive process and is used most often to treat low value ores. In 1993, heap leaching accounted for 39 percent of gold production.[10] In many cases, heaps are constructed on lined pads and ore is sent directly from the mine with little or no preparation. However, at about half of the heap leaching operations, ore is crushed and agglomerated prior to placement on the heap to increase permeability of the heap and maintain the high pH (optimally 10.5) needed for leaching to occur.

Two types of pads used in gold heap leaching are permanent heap construction on a pad from which the leached ore is not removed, and on-off pads, which allow the spent ore to be removed from the pad following the leach cycle and fresh ore to be placed on the pad. Permanent heaps are typically built in lifts. Each lift typically is composed of a 5- to 30-foot layer of ore, though lifts may be higher at times.[11] On-off pads are not commonly used in the industry.

After the ore is piled on a leaching pad, the leaching solution is applied to the top of the pile by sprinklers. The solution generally has a concentration of 0.5 to 1 pound of sodium cyanide per ton of solution, though one major gold producer reports that the leaching solution is generally in the range of 0.25 pounds of sodium cyanide per ton of solution.[12,13] The precious metals are dissolved as the solution trickles through the pile, and the metal bearing solution is collected on the impervious pad and pumped to the recovery circuit. Following rejuvenation, which involves removing the metals, the solution is returned for reuse. The leaching process continues until no more precious metal is extracted. Typical operations will involve leaching for several months on each heap. The process is relatively inexpensive and can be operated for less than two dollars per ton of ore. However, as much as half of the gold and silver may not be extracted either because the leach liquor never contacts the precious metal or because the metal bearing solution is trapped in blind channels. At one facility, at least 60 percent (and often much higher[14] percentages) of the gold contained in leach-grade ore is recovered through heap leaching.[15] Waste streams from this process include spent ore and leaching solutions as well as residual leach liquor in the pile.

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[8] Personal communication between ICF Incorporated and Robert G. Reese, U.S. Bureau of Mines, September 23, 1994.

[9] Newmont Gold Company. Comments submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[10] Personal communication between ICF Incorporated and John M. Lucas, U.S. Bureau of Mines, September 15, 1994.

[11] Newmont Gold Company. Op. Cit.

[12] U.S. Environmental Protection Agency, Technical Resource Document, Treatment of Cyanide Heap Leaches and Tailings, Office of Solid Waste Special Waste Branch, 1994, pp. 2-4.

[13] Newmont Gold Company. Op. Cit.

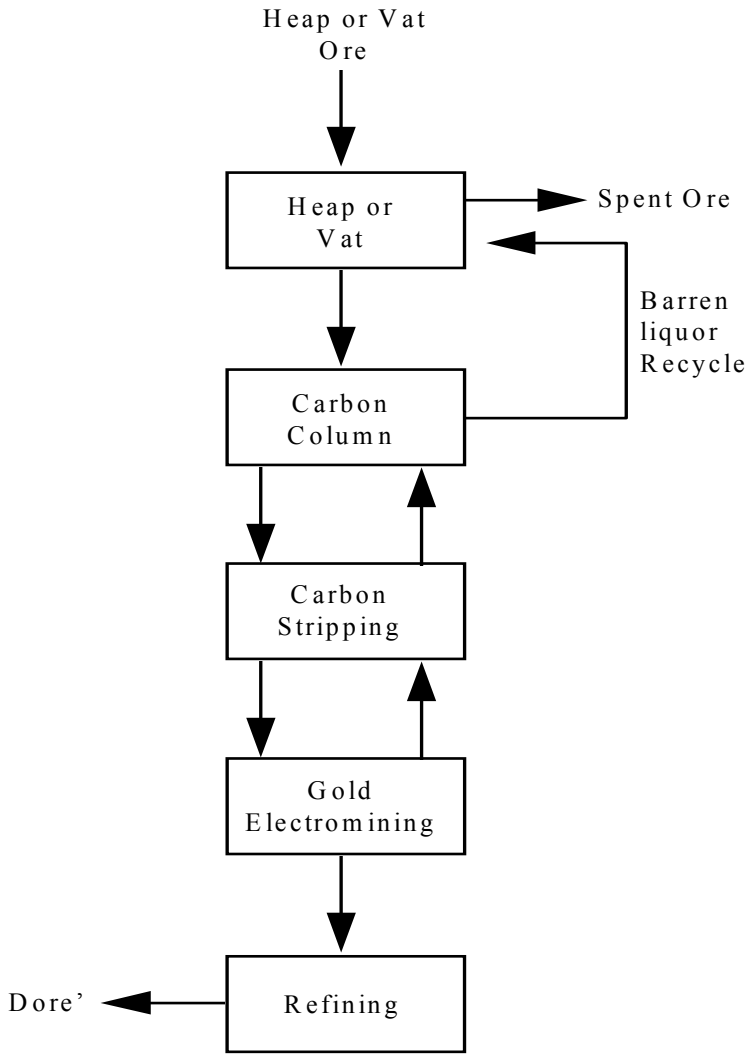
[14] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-100 - 30-115.

[15] Ibid.

EXHIBIT 3

GOLD-SILVER LEACHING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-100 - 3-115.)



(2) Cyanidation - Vat Leaching

Vat leaching, shown in Exhibit 3, is used when greater solution control than that afforded by heap leaching is necessary. In this system, prepared ore is placed in a vat or tank and flooded with leach liquor. The solution is continuously cycled through, draining from the bottom of the vat, proceeding to gold recovery, rejuvenation, and returning to the top of the vat. The process is more expensive than heap leaching because the material must be removed from the vat at the end of the leaching process. While the primary advantage of vat leaching is better solution contact, channelization and stagnant pockets of solution still occur (almost as severely as in heap leaching) when solution is drained from the vat. However, some of the trapped solution is recovered when the solids are removed from the vat. Wastes from this process include spent ore and leaching solutions.[16]

(3) Cyanidation - Agitation Leaching

Agitation leaching is the most commonly used leaching process in gold beneficiation operations in the United States.[17] High value ores are treated by agitation leaching, shown in Exhibit 4, to maximize the recovery of metal values. The ore is crushed and ground in water to form a slurry. Cyanide is usually added at the grinding mill to begin the leaching process, and more cyanide may be added to the leaching tanks. Ores may be leached anywhere from 24 to 72 or more hours. Silver ores tend to require longer leaching times. The method of recovering the precious metal from solution determines how the solution is separated from the solids. If the Merrill-Crowe or carbon-in-column metal recovery process is used, the leach liquor will be washed out of the solids, usually by a combination of counter-current decantation and filtration washing with water. This produces a concentrated wash solution and recovers the maximum pregnant liquor from the solids. The resultant slurry will contain very little cyanide or gold and would not be expected to exhibit any hazardous characteristics. The carbon-in-leach and carbon-in-pulp beneficiation processes are the most commonly used metal recovery processes used in gold beneficiation operations.[18] If carbon-in-leach or carbon-in-pulp metal recovery is practiced, the slurry may be discarded without washing. The carbon should remove all of the precious metals, and the solution is recovered from the tailings treatment and recycled back to the process.[19]

Cyanidation - Metal Recovery

In leaching operations, after dissolving the metal, the leach solution is separated from the ore, and the gold and silver are removed from solution in one of two ways: (1) the Merrill-Crowe process, or (2) activated carbon loading followed by activated carbon stripping.[20] The primary difference between recovery methods is whether the metal is removed by precipitation with zinc or by adsorption on activated carbon. Zinc cyanide is more soluble than gold or silver cyanide and if pregnant liquor is contacted with metallic zinc the zinc will go into solution and the gold and silver will precipitate.[21] The two different recovery methods are described below.

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[16] U.S. Environmental Protection Agency, 1988, Op. Cit., 3-100 - 3-115.

[17] Newmont Gold Company and National Mining Association. Comments submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[18] Ibid.

[19] U.S. Environmental Protection Agency, 1988, Op. Cit., 3-100-3-115.

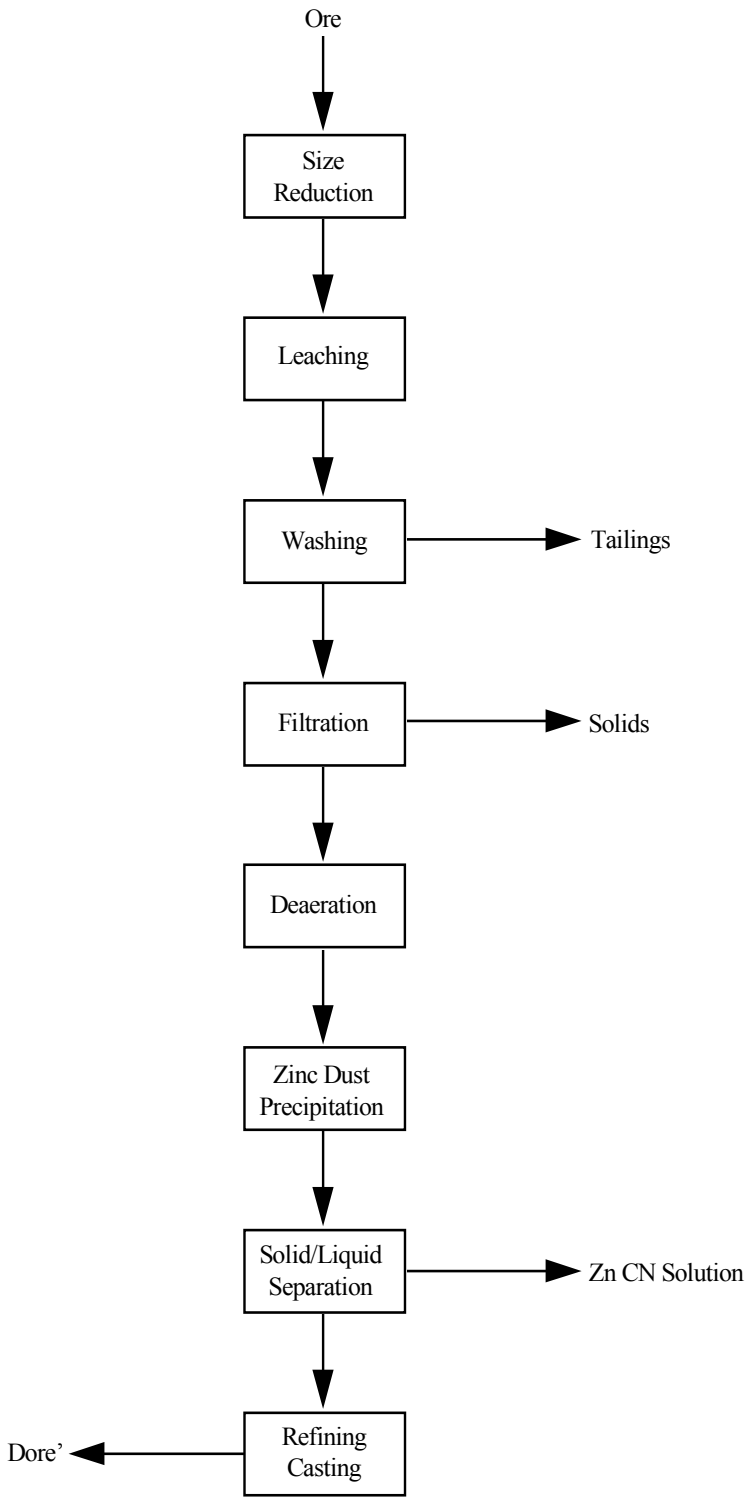
[20] Newmont Gold Company and National Mining Association. Op. Cit.

[21] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-100 - 3-115.

EXHIBIT 4

AGITATION LEACHING WITH MERRILL-CROWE RECOVERY

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-100 - 3-115.)



(1) Cyanidation - Metal Recovery - Merrill-Crowe

In the Merrill-Crowe process, the pregnant leaching solution is filtered for clarity, then vacuum deaerated to remove oxygen and decrease precious metal solubility. The deaerated solution is then mixed with fine zinc powder to precipitate the precious metals. The solids, including the precious metals, are removed from the solution by filtration, and the solution is sent back to the leaching circuit. The solids are melted and cast into bars. If silver and gold are present, the bars are called doré. In most cases, the metal is then sent to an off-site refinery. Most operations using zinc precipitation in the United States use some variation of the Merrill-Crowe process.[22]

(2) Cyanidation - Metal Recovery - Activated Carbon Loading/Activated Carbon Stripping

Precious metal leach solutions can be brought into contact with activated carbon by carbon-in-column, carbon-in-pulp, and carbon-in-leach processes.

Carbon-in-column systems are used at heap and vat leach operations and in other situations where the leaching solution is separated from the solids being leached prior to precious metal recovery. The leaching solution is passed through a series of columns containing beds of activated carbon. The gold and silver are adsorbed as cyanide complexes on the surface of the carbon. After passing through the columns, the solution is returned to the leaching circuit. When the carbon in a column is loaded with precious metals, the column is switched to a stripping circuit.[23]

In many agitation plants, the gold is recovered from the leached material before the solution is separated from the solids. In the *carbon-in-pulp* system, the leached pulp passes from the last stage of the leaching circuit into another series of agitation tanks. Each tank contains activated carbon granules. The slurry flows from tank to tank in series while the carbon is retained by screens. When the carbon in the first tank is fully loaded with precious metals, it is removed and sent to the stripping and reactivation circuit; the carbon in the other tanks is moved ahead one stage, and new carbon is added to the last stage. The carbon moves counter-current to the leached slurry and the leached slurry is finally sent to the tailings area for dewatering.[24] A process flow diagram of carbon-in-pulp metal recovery is shown in Exhibit 5.

Carbon-in-leach is similar to carbon-in-pulp except that the carbon is in the leaching tanks instead of in a separate recovery circuit. One advantage of carbon-in-leach over carbon-in-pulp is that some cyanide is released when gold adsorbs on carbon, making it available for more leaching. Another advantage is that fewer agitation tanks are necessary since the separate recovery circuit is eliminated. However, the agitation is more aggressive in the leach circuit causing more attrition of the carbon than in the carbon-in-pulp. Thus, the finely abraded carbon and its load of precious metals may be lost, reducing recovery and increasing costs due to increased carbon replacement.[25] A process flow diagram of carbon-in-leach metal recovery is presented in Exhibit 5.

Gold stripping from loaded activated carbon is usually done with a hot, concentrated alkaline cyanide solution, sometimes including alcohol. These conditions favor the desorbtion of the precious metals into the stripping solution. The solution then goes into an electrowinning cell where the precious metals are plated out, generally onto a steel wool cathode. The solution is recycled to the stripping stage and the cathode is sent on to

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[22] Ibid.

[23] Ibid.

[24] Ibid.

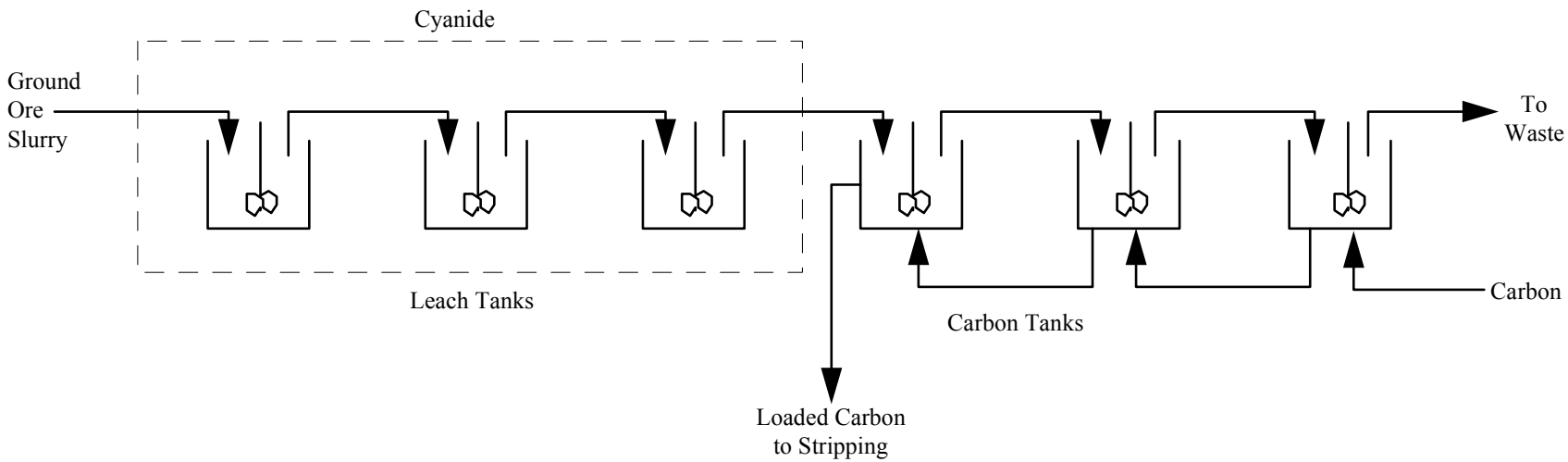
[25] Ibid.

EXHIBIT 5

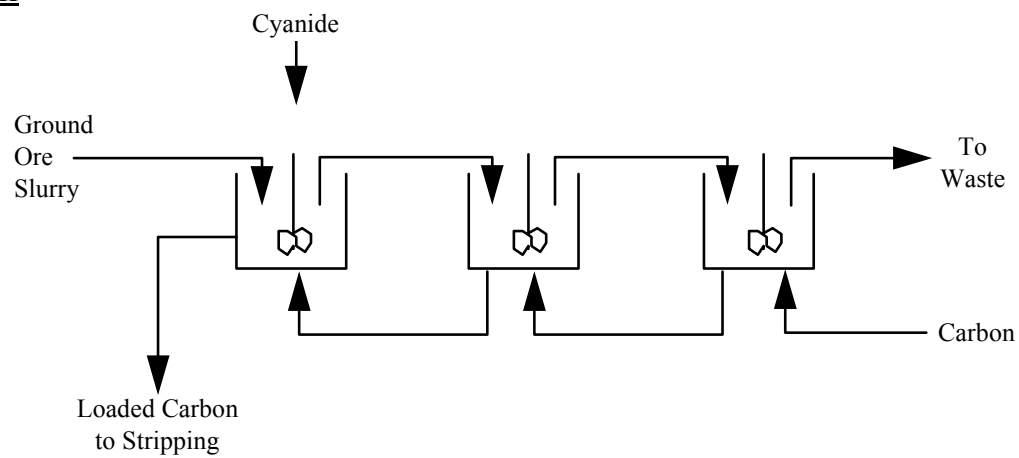
CARBON-IN-PULP AND CARBON-IN-LEACH METAL RECOVERY

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-100 - 3-115.)

CARBON-IN-PULP



CARBON-IN-LEACH



refining. Some operations refine the steel wool on site to make doré while others ship it directly to commercial refineries. The primary waste from carbon stripping is the spent stripping solution.[26]

The Anglo-American Research Laboratory (AARL) elution method is an alternative stripping process being used by at least one facility. In the first step of the AARL method, the loaded carbon is rinsed with a dilute (i.e., three percent) hydrochloric acid solution and then flushed with water to render the gold more amenable to separation from the carbon. The rinse waters resulting from this process are recycled by pipe to the carbon-in-leach circuit to recover any loaded carbon that is flushed out by the acid wash (loaded carbon typically contains 150 ounces of gold per ton). Following the acid wash/water rinse stage, desorption occurs. The loaded carbon is soaked in a concentrated solution composed of six percent sodium hydroxide and three percent sodium cyanide. This soaking loosens the bond between the carbon and gold. A fresh water rinse then picks up the gold. The resulting pregnant gold-bearing solution is pumped to the electrowinning circuit.[27]

Carbon Regeneration

After stripping, the carbon is reactivated on- or off-site and recirculated to the adsorption circuit. Carbon used in adsorption/desorbtion can be reactivated numerous times. The regeneration technique varies with mining operations, but generally involves an acid wash before or after extraction of the gold-cyanide complex, followed by reactivation in a kiln. The activated carbon is washed with dilute acid solution (pH of 1 or 2) to dissolve carbonate impurities and metal-cyanide complexes that adhere to the carbon along with the gold. This technique may be employed either immediately before or after the gold-cyanide complex is removed. Acid washing before the gold is removed enhances gold recovery. The Barrick Mercur Mine in Utah, the Barrick Goldstrike Mine in Nevada, and the Ridgeway Gold Mine in South Carolina are examples of facilities using acid prewash techniques. The Golden Sunlight Mine in Montana and the Battle Mountain Mine in Nevada use acid postwash techniques.[28]

The specific acid used for carbon washing is determined by the types of impurities need to be removed. Usually, a hydrochloric acid solution is circulated through 3.6 metric tons of carbon for approximately 16 to 20 hours. Nitric acid also is used in these types of operations, but is thought to be less efficient than hydrochloric acid in removing impurities. The resulting spent acid wash solutions may be neutralized with a high pH tailings slurry, dilute sodium hydroxide solution, or water rinse. When the spent acid wash solution reaches a stable pH of 10, it is sent to a tailing impoundment. Metallic elements may also be precipitated with sodium sulfide to remove them from the carbon.[29]

The carbon is screened to remove fines and thermally reactivated in a rotary kiln at about 730 ˚C for 20 minutes. The reactivated carbon is subsequently rescreened and reintroduced into the recovery system. Generally, less than 10 percent of the carbon is lost during the process because of particle abrasion.[30] Recirculating the carbon material gradually decreases performance in subsequent absorption and reactivation series. Carbon adsorption efficiency is closely monitored, and fresh carbon is added to maintain efficiency at design levels.[31]

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[26] Ibid.

[27] Newmont Gold Company. Op. Cit.

[28] U.S. Environmental Protection Agency, July 1994, Op. Cit., pp. 1-12.

[29] Ibid.

[30] Newmont Gold Company. Op. Cit.

[31] U.S. Environmental Protection Agency, July 1994, Op. Cit., pp. 1-12.

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

None identified.

4. Beneficiation/Processing Boundaries

EPA has determined that all of the activities discussed in Section 1 are classified as beneficiation activities.

SECTION 2: PRECIOUS METAL RECOVERY FROM REFINERY SLIMES

1. Discussion of Typical Production Processes

Gold and silver also are recovered from the refining processes for base metals, primarily lead and copper. Smelting operations remove iron, sulfur, and other impurities from the ore and produce copper anodes for electrolytic refining. In refining operations, the anodes produced from smelting are purified electrolytically to produce copper cathodes. The refinery slimes from these operations are processed for precious metals recovery, as portrayed in Exhibit 6. The recovery of precious metals in lead refineries is a normal part of the operation called "desilverizing."

2. Generalized Process Flow Diagram

A major source of precious metals from the copper industry is electrolytic cell slimes. The slimes are periodically removed from the cells in the refinery for treatment. The first stage of treatment removes the copper in the slimes by acid leaching, either as is or after roasting. The decopperized slimes are then placed in a furnace and melted with a soda-silica flux. The siliceous slag formed in this melting is removed, and air is blown through the molten material. Lime is added, and a high lead content slag is formed which is combined with the siliceous slag and returned to the copper anode casting furnace. Next, fused soda ash is added to the furnace and air is again blown through the melt, forming a soda slag which is removed and treated to recover selenium and tellurium. The remaining doré in the furnace is removed and sent to refining to recover the precious metals.[32] See the selenium and tellurium commodity reviews for a more detailed discussion of product recovery.

The desilverizing process takes advantage of the solubility of precious metals in molten zinc which is greater than their solubility in molten lead. Lead from previous stages of refining is brought in contact with a zinc bath, either in a continuous operation or in batches. The zinc absorbs the precious metals from the lead, and the lead is then passed onto a dezincing operation. The zinc bath is used until it contains 5,000 to 6,000 troy ounces of precious metal per ton of zinc. The zinc bath is then retorted to recover zinc by distillation. The zinc is returned to the desilverizing process, and the "retort metal" is treated by cupellation to produce doré bullion. In the cupellation,step, the base metals in the retort metal are oxidized with air and removed from the precious metals. The oxides are all treated for the recovery of their various precious metals. The doré is then sent to refining.[33]

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

None identified.

4. Beneficiation/Processing Boundaries

Because the slimes from which gold is recovered are mineral processing wastes generated in the recovery of other metals, all of the wastes generated during gold recovery from refinery slimes are, therefore, mineral processing wastes as well.

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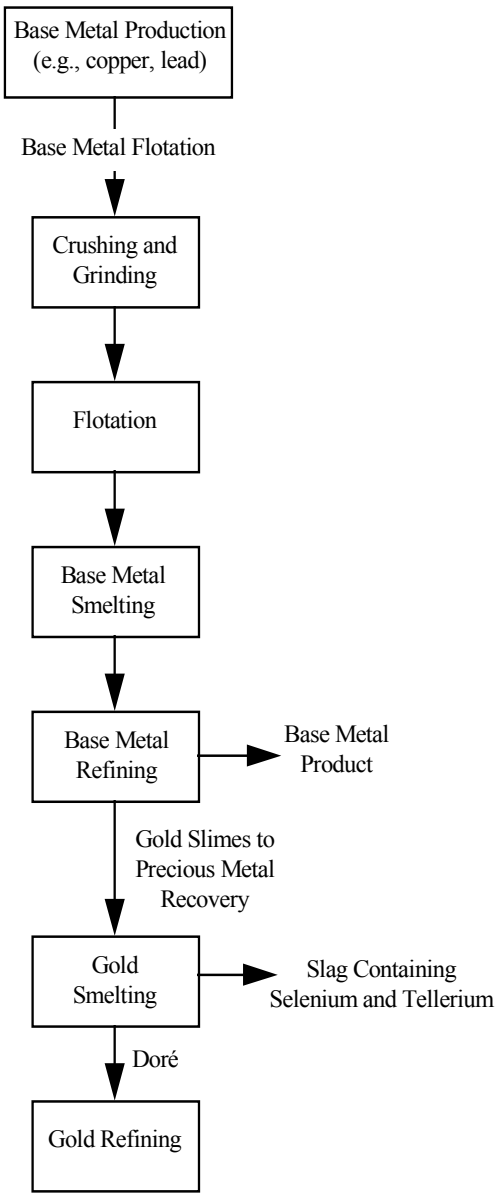
[32] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-100 - 3-115.

[33] Ibid.

EXHIBIT 6

OVERVIEW OF GOLD PRODUCTION FROM BASE METALS

(Adapted from: Technical Resource Document, Extraction and Beneficiation of Ores and Minerals, July 1994, pp. 1-12.)



SECTION 3: PRECIOUS METAL REFINING

1. Discussion of Typical Production Processes

The refining process used for gold and silver depends on the composition of the material in the feed. The most basic operation is "parting" which is the separation of gold and silver. Parting can be done electrolytically or by acid leaching. In either case, the silver is removed from the gold. Further treatments may be necessary to remove other contaminants. These treatments have the potential to produce wastes with hazardous characteristics, primarily corrosivity, since strong acids are used.[34]

2. Generalized Process Flow Diagram

Like several other gold refineries, the Newmont facility in Nevada electrowins its gold cyanide solution onto steel wool cathodes after carbon stripping. The barren cyanide solution is returned to the leach circuit for gold recovery. Sludge from the bottom of the electrowinning cell is filtered and sent to the retort for mercury recovery. The gold/steel wool cathode is placed in a vat containing a sulfuric acid solution. The solution dissolves the steel wool from the gold and silver, leaving a solid gold and silver residue. The waste sulfuric acid and steel wool solution is discharged to the tailings slurry. The gold and sislver solids are filtered under vacuum through diatomaceous earth. The gold and silver filter cake is then sent to the retort furnace where it is subjected to 1,200 °F for 14 hours. After retorting, a flux of silica and borax is added, and the gold and silver mixture is smelted in an induction furnace. It is from this induction furnace that gold doré bars are poured. Within days of generation, the slag generated from this smelting is sent to a ball mill for crushing and grinding and is then leached in tanks with sodium cyanide. The resulting gold rich slurry is conveyed to the cyanidation/leaching circuit where it is processed with primary gold-bearing slurries. In some cases, portions of the slag are recycled directly back into the induction furnaces for gold recovery. The gold slag may have between 3 and 4 ounces per ton of recoverable gold.[35] The slag from one facility reportedly averages 150 ounces of gold per ton.[36]

Silver Chloride Reduction

Silver metal is produced from silver chloride by a dissolution and cementation process. The silver chloride is dissolved in a dilute solution of ammonium hydroxide and recovered by cementation. The silver is replaced in solution, causing the silver ions to be reduced and precipitated from solution as silver metal.

Mercury Recovery

Many gold-bearing ores from the western United States contain small quantities of mercury. The presence of mercury decreases the gold-loading capacity of the activated carbon. During cyanidation of mercury-bearing gold-silver ores, significant amounts of mercury are extracted. Addition of calcium sulfide to the cyanide leach slurry precipitates the solubilized mercury and also some silver.[37] Primary mercury is also produced from gold-bearing ores by roasting or calcining. These processes are described in more detail in the chapter on mercury. Exhibit 7 presents an overall process flow sheet for gold production from ores.

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[34] Ibid.

[35] U.S. Environmental Protection Agency, Trip report for Newmont Gold Corporation, South Operations Facilities, Carlin Nevada, May 17, 1995.

[36] Newmont Gold Company. Op. Cit.

[37] Simpson, W.W., W.L. Staker, and R.G. Sandberg, Calcium Sulfide Precipitation of Mercury From Gold-Silver Cyanide-Leach Slurries, U.S. Department of Interior, 1986.

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

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.

EPA determined that for recovering gold and silver from precious metal refining, the beneficiation/ processing line occurs between electrowinning and retorting because this is where a significant chemical change occurs. 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 during the production of gold and silver, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Mining

Mine water is a waste stream generated from gold and silver production. This waste consists of all water that collects in mine workings, both surface and underground, as a result of inflow from rain or surface water and ground water seepage. If necessary, the water is pumped to allow access to the ore body or to keep the mine dry. This water may be pumped from sumps within the mine pit or from interceptor wells. Mine water may be used and recycled to the beneficiation circuit, pumped to tailings ponds, or discharged to surface water. Quantity and chemical composition of mine water varies from site to site.[38]

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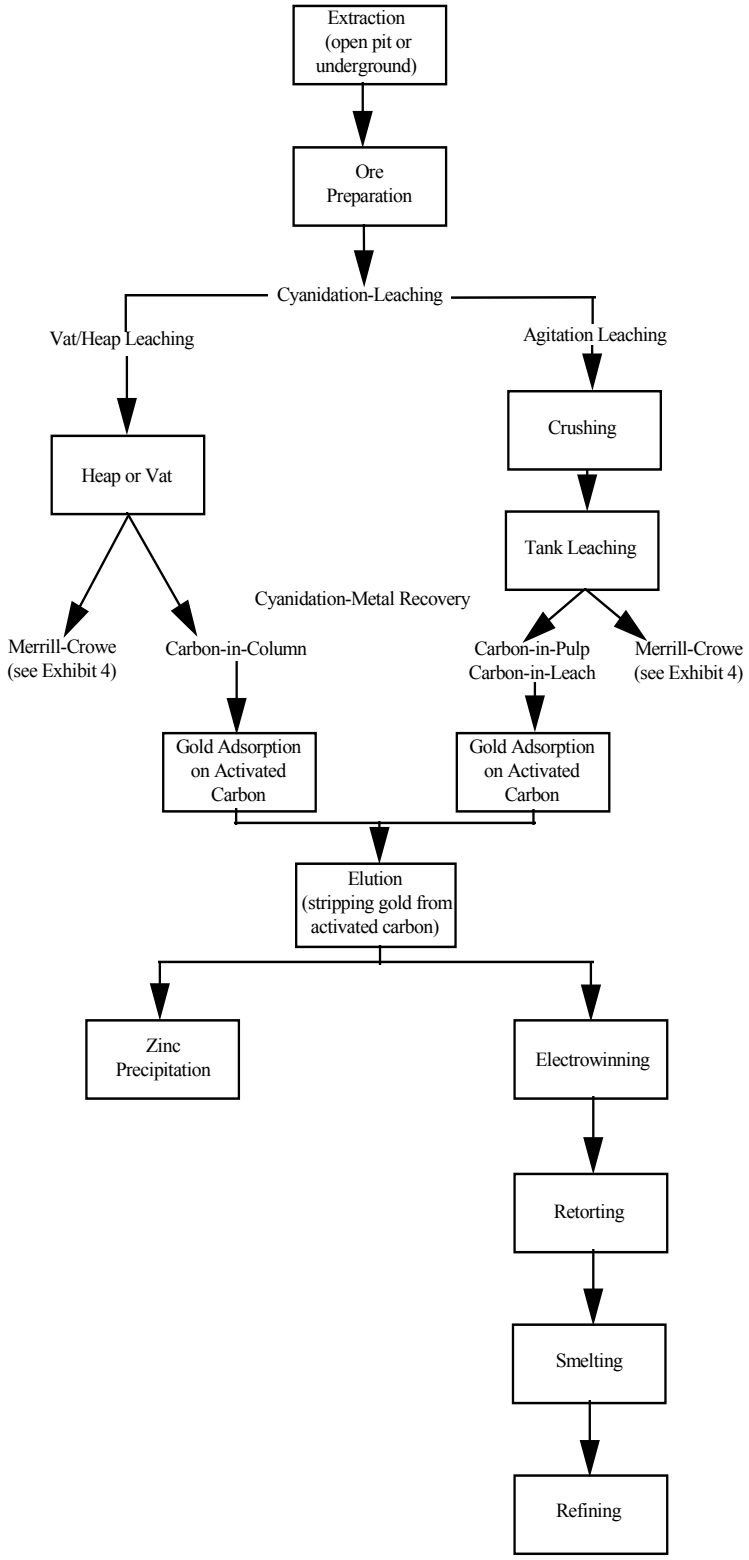
[38] U.S. Environmental Protection Agency, Mining Industry Profile, Gold, Office of Solid Waste, Special Waste Branch, 1993, pp. 41-45.

EXHIBIT 7

OVERVIEW OF GOLD PRODUCTION FROM ORES

(Adapted from: Technical Resource Document, Extraction and Beneficiation of Ores and Minerals, July 1994, pp. 1-12.)



Waste Rock. Overburden and mine development is referred to by the industry as waste rock. This waste is generally disposed of in waste rock piles or dumps. An estimated 25 million metric tons of overburden and mine development rock was generated in 1980 and 39 million metric tons in 1982. At surface mines, 71 percent of all material handled is discarded as waste. At underground mines, 20 percent is discarded as waste. The quantity and composition of the waste rock varies by site. Depending on the composition of the ore body, this waste may contain sulfides or oxides.

Amalgamation

Waste rock, clay, and sand may be disposed of in a tailings pond.

Black sand may contain residual mercury and be disposed of in a tailings pond.

Mercury bearing solution may be sent to mercury recovery or a tailings pond.

Ore Preparation

Sulfur dioxide may be routed to an acid plant and converted to sulfuric acid. This may be sold to other mines or used on-site for carbon washing and regeneration. At least one facility, Newmont's operation in Nevada, generates sulfuric acid,.[39]

Cyanidation

Spent Ore. The ore from leaching may contain residual cyanide. The ore in continuous or valley fill heaps is stacked in lifts and left in place for subsequent leaching, detoxification, and closure. Ore removed from on-off heap leaching pads is permanently disposed at waste or spent ore disposal sites. Typically, detoxification of the spent ore involves rinsing with water until the cyanide concentration in the effluent is below a specific standard set by the State regulatory agency. The heap may then be reclaimed with wastes in place. Spent ore from vat leaching exists in the form of a slurry composed of gangue and process water bearing cyanide and cyanide-metal complexes. The spent ore may be treated to neutralize cyanide prior to disposal. The slurry is typically disposed of in a tailings impoundment with some of the liquid component being recirculated to the tank leach as make-up water.[40]

Spent Leaching Solution. During the leaching operations, most of the barren cyanide solution is recycled to leaching activitie. On rare occasions, however, the build-up of metal impurities may interfere with the dissolution and precipitation of gold and, therefore, require a portion of the solution volume to be bled off and disposed. These solutions may contain free cyanide and metallo-cyanide complexes of copper, iron, nickel, and zinc, as well as other impurities, such as arsenic and antimony, mobilized during the leaching. Management practices for these solutions are unclear; however, they have been discharged to tailings impoundments.[41]

Merrill-Crowe

Filter cake resulting from zinc precipitation consists primarily of fine gangue material and may contain gold-cyanide complex, zinc, free cyanide, and lime. The filter may be washed with water, which is disposed of as part of the waste. The waste is typically sent to tailings impoundments or piles.

Spent leaching solution from zinc precipitation is often returned to the leaching process.

Metal Recovery - Activated Carbon Stripping

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[39] Newmont Gold Company. Op. Cit.

[40] U.S. Environmental Protection Agency, 1994, Op. Cit., pp. 1-12.

[41] Ibid.

Tailings in slurry form, composed of gangue (including sulfide materials and dissolved base metals) and process water bearing cyanide and cyanide-metal complexes, are generated from carbon-in-pulp and carbon-in-leach processes. The characteristics of this waste vary depending on the ore, cyanide concentration, and water source (fresh or recycled). The characteristics of the gangue are dependent on the ore source. The slurry is typically disposed of in a tailings impoundment with some of the liquid component being recirculated to the tank leach or other water consumptive system.[42]

Waste sulfuric acid from elution is exempt under the Bevill Amendment because it is generated in a beneficiation activity that is uniquely associated with mineral processing. This waste may be corrosive.

Waste steel wool solution may be corrosive.

Acid wash from carbon regeneration may be corrosive.

2. Mineral Processing Wastes

Smelting and Refining

Slag. Slag is typically generated at gold mining and milling operations.[43] At one facility, metal-bearing slag is broken off the molten dore and then placed into barrels inside the refinery building. The slag is then processed for gold recovery, normally within several days of its generation. Specifically, the slag is ground and then leached in tanks with sodium cyanide. The gold-rich slurry that results is then conveyed, by pipe, to the primary gold-bearing slurries in the mill for mixing. The facility also reports that in the past, slag also was processed by placing it directly back into the induction furnaces for gold recovery. Assays performed by Newmont Gold during 1995 and 1997 show that slag generated at its Nevada Mines Complex typically contains between 100 and 700 ounces of gold per ton. Tests also indicate that the slag may exhibit the characteristic of toxicity for cadmium.[44] No published information regarding waste generation rate or characteristics was found, though one facility reportedly generates approximately 38 to 57 tons of slag per year.[45, 46] This facility also indicated that it takes weeks to accumulate enough slag to constitute a large enough batch for cost effective metals recovery. The total industry generation rate for slag is thus probably less than 500 metric tons per year. One facility also indicated that slag may possess the characteristic of toxicity for cadmium.[47] The slag is not stored or processed on the land, nor does it enter the outside environment. Slag is believed to be fully recycled and was formerly classified as a byproduct.

WWTP Sludge. WWTP sludge is typically generated at gold refineries.[48] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 360,000 metric tons/yr, and 720,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for silver. This waste may be recycled and was formerly classified as a sludge.

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[42] Ibid.

[43] Precious Metals Producers. January 25, 1996. Op. Cit.

[44] Newmont Gold Company. May 12, 1997. Op. Cit.

[45] Newmont Gold Company. January 25, 1996. Op. Cit.

[46] Newmont Gold Company. May 12, 1997. Op. Cit.

[47] Ibid.

[48] Precious Metals Producers. Op. Cit.

Spent Furnace Dust. Spent furnace dust is typically generated at gold mining and milling operations.[49] As part of the smelting process, gold-bearing dust is generated in the induction furnaces. This dust is conveyed by pipe to a baghouse located in the refinery building and collected in barrels. The barrels of baghouse dust are never stored outdoors. At the Nevada Mines Complex, sealed barrels of baghouse dust are accumulated for up to four months before being shipped off-site for smelting. At other facilities, smelting of baghouse dust may be done in the on-site induction furnace. Assays performed by Newmont Gold in 1995 and 1996 show that the baghouse dust from its Nevada Mines Complex contains approximately 2,200 ounces of gold per ton and that the dust may exhibit the characteristic of toxicity for cadmium and selenium. This facility generated approximately 1,550 ounces of gold in 1996 by smelting baghouse dust, generating revenues of over $600,000.[50] Thus, the facility generated less than one ton of baghouse dust in 1996, suggesting an industry-wide generation rate of less than 9 tons per year. The dust is entirely recycled and was formerly classified as a byproduct. At one facility, several months are required to accumulate sufficient baghouse dust to constitute a large enough batch to ship off-site for smelting.[51] We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for silver. At one facility, the dust exhibits the characteristic of toxicity for cadmium and selenium. The dust is not land stored and never enters the outside environment.[52,53] This waste is recycled and was formerly classified as a byproduct.

Retort Cooling Water. The retorting process at Newmont Gold's Nevada Mines Complex generates mercury-, silver- and gold-bearing gases. Water is used to cool and condense those gases. Through this process, the cooling water becomes contaminated with gold, silver, and mercury. This water is conveyed by pipe to the main beneficiation circuit to allow recovery of the metals and reuse of the water.[54]

Wastewater is typically generated at gold refineries and is generated from numerous sources, including the smelter air pollution control (APC), silver chloride reduction, electrolytic cell wet APC, and electrolyte preparation wet APC.[55] Wastewater from electrolyte preparation wet APC, electrolytic cell wet APC, and smelter wet APC may contain toxic metals, suspended solids, oil, and grease. This waste may be recycled.[56] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 440,000 metric tons/yr, 870,000 metric tons/yr, and 1,700,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for arsenic, silver, cadmium, chromium, and lead. This waste was formerly classified as a sludge.

Refining Wastes. The most basic refining operation for the separation of gold and silver is "parting" which can be done electrolytically or by acid leaching. Further treatments are sometimes necessary to remove additional contaminants. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 360,000 metric tons/yr, and 720,000 metric tons/yr, respectively. We used best

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[49] Ibid.

[50] Newmont Gold Company. May 12, 1997. Op. Cit.

[51] Ibid.

[52] Newmont Gold Company. January 25, 1996. Op. Cit.

[53] Newmont Gold Company. May 12, 1997. Op. Cit.

[54] Ibid.

[55] Precious Metals Producers. Op. Cit.

[56] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Vol. V, 1989, pp. 2185-2186.

engineering judgment to determine that this waste may exhibit the characteristics of toxicity for silver and corrosivity. This waste is recycled to extraction/beneficiation units.

D. Non-uniquely Associated Wastes

Ancilary hazardous wastes also 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.

E. Summary of Comments Received by EPA

New Factual Information

Three commenters submitted comments in response to the January 25, 1996 Supplemental Proposed Rule (COMM43, COMM57, COMM58), and one commenter submitted comments in response to the May 12, 1997 Second Supplemental Proposed Rule (Newmont Gold Company). All four commenters provided new factual information that has been incorporated into the gold and silver sector report.

Sector-specific Issues

Three commenters addressed sector-specific issues.

- Three commenters stated that the retorting step is, in fact, a beneficiation activity (COMM43, COMM57, COMM58). EPA has clarified in the report that the beneficiation/mineral processing boundary for gold recovery from ores is between electrowinning and retorting. Therefore, retorting is a mineral processing activity.

- One commenter stated that slag and spent furnace dust are not wastes because they are destined for reclamation (COMM57). EPA recognizes that these materials contain high concentrations of precious metals and that they are reclaimed. However, they are still considered to be wastes, and no change was made to the report.

- One commenter expressed confusion over the status of acid washing solution (COMM43), while another commenter stated that EPA incorrectly classified acid washing during the elution process as non-uniquely associated with mineral processing (COMM57). The Agency clarified in the report that the use of an acid solution to dissolve the steel wool from the gold/steel wool cathode is a beneficiation activity that is uniquely associated with mining or mineral processing. Acid wash solution from carbon regeneration activities after the gold is stripped, however, is not uniquely associated and, therefore, is not exempt under the Bevill Amendment.

- One commenter requested that EPA clarify the status of sulfuric acid (COMM43). The report was modified to indicate that waste sulfuric acid from elution is exempt under the Bevill Amendment because it is generated in a beneficiation activity that is uniquely associated with mining or mineral processing.

- One commenter noted an inconsistency in that spent carbon is identified as a beneficiation waste whereas carbon fines are not uniquely associated with mineral processing (COMM43). One commenter stated that spent carbon is routinely regenerated and reused and, therefore, is not a waste (COMM43). Another commenter stated that carbon fines generated at on-site carbon regeneration kilns as well as other secondary materials generated during carbon regeneration are uniquely associated with mineral processing (COMM57). Spent carbon after the gold has been stripped is, in fact, a waste. The Agency clarified that spent carbon from cyanidation is a non-uniquely associated waste because spent carbon results from carbon regeneration which is a non-uniquely associated operation because many industries

routinely regenerate carbon and generate wastes such as carbon fines. Therefore, carbon regeneration and the resulting wastes are non-uniquely associated with mining or mineral processing.

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IODINE

A. Commodity Summary

Iodine compounds are found in seawater, seaweed, marine organisms, and brines. Iodine and its compounds are generally marketed in the form of crude iodine, resublimed iodine, calcium iodate, calcium iodide, potassium iodide, sodium iodide, and numerous organic compounds.[1] Final uses of iodine include animal feed supplements, catalysts, inks and colorants, pharmaceuticals, photographic chemicals and film, sanitary and industrial disinfectants, and stabilizers.

Japan and Chile are the largest producers of iodine in the world and account for 99% of the U.S. iodine imports. All domestic iodine production is from iodine-rich natural brines in the deep subsurface of the Anadarko basin of northwestern Oklahoma. Oklahoma production began in 1977 and at present, three companies operate a total of four facilities (three major plants and one miniplant) for the recovery of iodine. The U.S. Bureau of Mines estimates that domestic production was 2,000,000 kilograms in 1994.[2] Exhibit 1 presents the names and locations of the facilities involved in the production of iodine.

EXHIBIT 1

SUMMARY OF IODINE PROCESSING FACILITIES

Facility Name	Location
Asahi Glass Company of Japan	Woodward, OK
Iochem Corporation of Japan	Vici, OK
North American Brine Resources (miniplant)	Dover, OK
North American Brine Resources (major plant)	Woodward, OK

B. Generalized Process Description

1. Discussion of Typical Production Processes

All three facilities (Asahi Glass Company of Japan, Iochem Corporation of Japan, and North America Brine Resources) obtain iodine-rich brines from the Morrowan sandstones. Asahi Glass Company operates 22 production wells and 10 injection wells ranging in depth from 2,130 to 2,290 meters. The Iochem facility has nine production wells and four injection wells ranging in depth from 3,000 to 3,183 meters. The North American Brine Resources facility operates two production wells and three injection wells drilled to about 1,800 meters.

North American Brine Resources also operates a mini facility near Dover, OK. At the Dover facility, North American Brine Resources recovers iodine from oil-field brines collected from a number of oil and gas wells in nearby parts of northwestern Oklahoma.

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[1] Kenneth S. Johnson, "Iodine," from Industrial Minerals and Rocks, 6th edition, Society for Mining, Metallurgy, and Exploration, 1994, pp. 583-587.

[2] Phyllis Lyday, "Iodine," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 82-83.

Brines are separated from hydrocarbons by using the blowing-out process. Iochem Corporation and North American's Woodward facility both use this process.[3] Exhibit 2 presents a typical process flow diagram for the production of iodine from brines by the blowing-out process.

2. Generalized Process Flow Diagram

Exhibit 2 displays the blowing-out process. In the first stage of this process, hydrogen sulfide gas (contained in the brine) is removed. This gas is reacted to form sulfur compounds which are sent to a hazardous waste disposal facility. The second stage of processing is chlorine oxidation to convert iodide to iodine. The iodine is then removed from the brine by air vapor stripping (air-blowout). The waste brine is treated with lime to adjust pH and is reinjected into Class IV disposal wells. The iodine vapor is absorbed by a solution of hydriodic and sulfuric acids. Sulfur dioxide is added to reduce the absorbed iodine to hydriodic acid. Most of the solution is recirculated to the absorption tower, but a bleed stream is sent to a reactor for iodine recovery. In the reactor, chlorine is added to oxidize and liberate the iodine which precipitates and settles out of solution. The settled iodine is filtered to remove waste liquor and melted under a layer of concentrated sulfuric acid. The melted iodine is then solidified either as flakes or ingots.[4]

Iodine is also recovered from oil well brines. In a settling tank, the iodine containing brine settles to the bottom and the oil rises to the top. The oil is skimmed off and processed with other oil from nearby wells. The brine is sent through a chlorinator which frees the iodine. It is then absorbed onto charcoal which is back-flushed with potassium or sodium hydroxide when full. This solution is treated with hydrochloric acid which results in a 90% crude iodine product. The spent brine is reinjected and the potassium/sodium hydroxide is recycled.[5]

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

While domestic iodine production employs the chlorine-oxidation air-blowout method for recovery of iodine, three other brine clarification processes exist. In one process, silver iodide is precipitated by the addition of a silver nitrate solution. The silver iodide is filtered and treated with scrap iron to form metallic silver and a solution of ferrous iodide. The silver is redissolved in nitric acid and recycled, and the solution is treated with chlorine to liberate the iodine. In a second process, chlorine is added after clarification to liberate the iodine as a free element in solution. Passing the solution over bales of copper wire precipitates insoluble cuprous iodides. At intervals, the bales are agitated with water to separate the adhering iodide; the bales are then recycled. The cuprous iodide suspended in the water is filtered, dried, and sold. The third process uses ion-exchange resins on brines which have been oxidized to liberate iodine. The liberated iodine, which is in the form of polyiodide, is absorbed on an anion-exchange resin. When the ion-exchange resin is saturated, it is discharged from the bottom of the column and then transferred to the elutriation column. Iodine is elutriated with a caustic solution followed by sodium chloride. The regenerated resin is returned to the absorption column. The iodine-rich elutriant is acidified and oxidized to precipitate iodine. The crude iodine is then separated in a centrifuge and purified with hot sulfuric acid or refined by sublimation.[6]

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[3] Phyllis A. Lyday, "Iodine," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 609-612.

[4] U.S. Environmental Protection Agency, "Iodine," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-109 - 2-112.

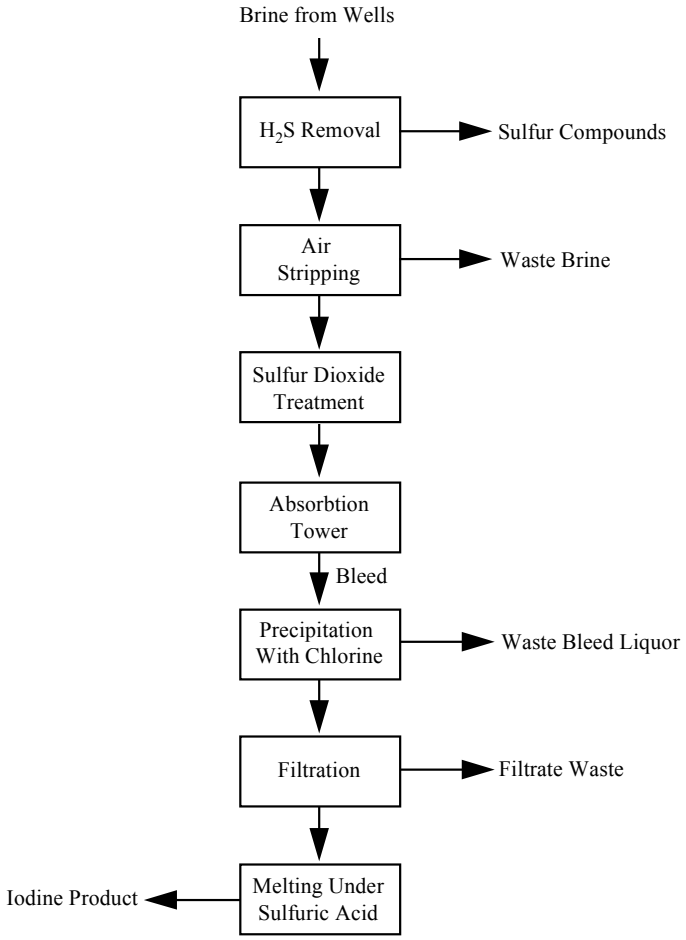
[5] Personal Communication between ICF Incorporated and Phyllis Lyday, U.S. Bureau of Mines. October 11, 1994.

[6] "Iodine and Iodine Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., 1981, Vol. XIII, pp. 655-656.

EXHIBIT 2

THE BLOWING-OUT PROCESS

(Adapted from; 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-109 - 2-112.)



The Chilean nitrate industry employs another method for iodine recovery. Iodine is extracted from caliche as sodium iodate, along with sodium nitrate. The iodate accumulates in mother liquors during crystallization of the nitrate. Part is drawn off and treated with sodium bisulfite solution. Fresh mother liquor is added to the solution to liberate the iodine. The precipitated iodine is filtered in bag filters and the iodine-free mother liquor is returned to the nitrate leaching cycle after neutralization with soda ash. The iodine cake is washed, pressed, broken up, and sublimed in retorts. The product is then crushed and packaged.[7]

4. Beneficiation/Processing Boundaries

Based on a review of the process, there are no mineral processing operations involved in the production of iodine.

C. Process Waste Streams

Existing data and engineering judgement suggest that the wastes listed below from iodine production do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

1. Extraction/Beneficiation Wastes

Sulfur compounds from hydrogen sulfide removal are sent to a hazardous waste disposal facility.

Waste brine. Waste brine contains 6,800 kkg of spent brine solids per kkg of product iodine. Waste brine is processed for other solids recovery and then either used in chlor-alkali manufacture or returned to the source. Bromine, calcium chloride and magnesium hydroxide may be recovered from these spent brines.[8]

Precipitation with Chlorine

Waste bleed liquor.

Filtration

Filtrate wastes may be recycled.

Sludge.

Waste Acid.

2. Mineral Processing Wastes

None are identified.

D. Non-uniquely AssociatedWastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

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[7] Ibid.

[8] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Volume II, 1980, Chapter 9.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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U.S. Environmental Protection Agency. "Iodine." From 1988 Draft Report Summary Report of Mineral Industry Processing Wastes. 1988. pp. 2-109 - 2-112.

U.S. Environmental Protection Agency. Multi-Media Assessment of the Inorganic Chemicals Industry. Vol. 2. 1980. Chapter 9.

IRON AND STEEL

A. Commodity Summary

The iron and steel industry, including primary and secondary producers, is composed of 79 companies that produce raw steel at 116 locations. Iron is generally produced from iron ore (taconite) in a primary mineral production process, while steel is produced using both primary and secondary processes. Primary production refers to those operations where the feedstock is composed of at least 50 percent ore (or ore that has been beneficiated). Electric arc furnaces use a high percentage of scrap steel as the feedstock in their operations and are therefore classified as secondary production and not considered primary minerals processing. Although the electric arc furnace process is described in this section, some of the wastes generated from this operation are currently regulated under RCRA Subtitle C. Specifically, electric arc furnace dust (K061) is a listed hazardous waste.

The annual aggregate raw steel production capacity is 99 million metric tons; 1993 production is reported to be 87 million metric tons. According to the U.S. Bureau of Mines, the iron and steel producers and ferrous foundries produced goods valued at $55 billion. Currently, pig iron (i.e., molten iron from iron blast furnaces) is produced at 15 companies operating integrated steel mills, with approximately 58 blast furnaces (of which 41 or 42 are in continuous operation). Integrated companies accounted for approximately 67% of steel production, including output of their electric arc furnaces (which are classified as secondary production).[1]

Pig iron production in 1994 is estimated at 49 million metric tons. Pig iron is sent to either basic oxygen furnaces or electric arc furnaces for further processing at steel facilities. Basic oxygen furnaces (BOFs) and electric arc furnaces (EAFs) account for 61 percent and 39 percent of steel production, respectively. Continuously cast steel accounted for 89 percent of steel production. Lastly, open hearth furnaces (OHFs) have been phased out and were not used domestically to produce steel in 1993.[2] Exhibit 1 presents the names and locations of facilities involved in the primary production of iron and steel.

EXHIBIT 1

SUMMARY OF PRIMARY IRON AND STEEL PRODUCERS IN 1989

Facility Name	Location	Type of Operations
Acme	Riverdale, IL	Iron; BOF Steel
Alleghany Ludlum	Brackenridge	Iron; BOF Steel
Armco Steel Co., L.P.	Middletown, OH	Iron; BOF Steel
Armco Steel Co., L.P.	Ashland, KY	Iron; BOF Steel
Bethlehem Steel	Sparrows Point, MD	Iron; BOF Steel
Bethlehem Steel	Bethlehem, PA	Iron; BOF Steel
Bethlehem Steel	Chesterton, IN	Iron; BOF,OHF Steel
Geneva Steel	Orem, UT	Iron; OHF Steel
Gulf States Steel	Gadsden, AL	Iron; BOF Steel

[1] Gerald Houck, "Iron and Steel," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 86.

[2] Ibid.

EXHIBIT 1 (continued)

SUMMARY OF PRIMARY IRON AND STEEL PRODUCERS IN 1989

Facility Name	Location	Type of Operations
Inland Steel	E. Chicago, IN	Iron; BOF Steel
LTV	E. Cleveland, OH	Iron; BOF Steel
LTV	W. Cleveland, OH	Iron; BOF Steel
LTV	Indiana Harbor, IN	Iron; BOF Steel
McLouth Steel	Trenton, MI	Iron; BOF Steel
National Steel	Granite City, IL	Iron; BOF Steel
National Steel	Escore, MI	Iron; BOF Steel
Rouge Steel	Dearborn, MI	Iron; BOF Steel
Sharon Steel	Farrell, PA	Iron; BOF Steel (shut down in November 1992)[a]
Shenango	Pittsburgh, PA	Iron
US Steel	Braddock, PA	Iron; BOF Steel
US Steel	Gary, IN	Iron; BOF Steel
US Steel	Fairless Hills, PA	Iron; OHF Steel
US Steel	Fairfield, AL	Iron; BOF Steel
US Steel/Kobe	Lorain, OH	Iron; BOF Steel
Warren Steel	Warren, OH	Iron; BOF Steel
Weirton Steel	Weirton, WV	Iron; BOF Steel
Wheeling-Pittsburgh Steel	Steubenville, OH	Iron; BOF Steel
Wheeling-Pittsburgh Steel	Mingo Junction, OH	Iron; BOF Steel

[a] Gerald Houck, "Iron and Steel." from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 649.

On a tonnage basis, about nine-tenths of all metal consumed in the United States is iron or steel. Iron and steel are used in the manufacture of transportation vehicles, machinery, pipes and tanks, cans and containers, and the construction of large buildings, roadway superstructures, and bridges.[3] According to the U.S. Bureau of Mines in 1993, steel consumption was divided amongst the following uses: warehouse and steel service centers, 26%;

[3] Gerald Houck, "Iron and Steel," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 412.

transportation (mainly for automotive production), 16%; construction 15%, cans and containers, 5%; and other uses, 38%.[4]

B. Generalized Process Description

1. Discussion of Typical Production Processes

The production of steel products from iron ore involves two separate steps: ironmaking and steelmaking. Each of these is described in detail below. Iron blast furnaces produce molten iron (pig iron) that can be cast (molded) into products; however, the majority of pig iron is used as the mineral feedstock for steel production. Steel furnaces produce a molten steel that can be cast, forged, rolled, or alloyed in the production of a variety of materials.

Ironmaking

Iron is produced either by blast furnaces or by one of several direct reduction processes; blast furnaces, however, account for over 98 percent of total domestic iron production.[5] The modern blast furnace consists of a refractory-lined steel shaft in which a charge is continuously added to the top through a gas seal. The charge consists primarily of iron ore, sinter, or pellets; coke; and limestone or dolomite. Iron and steel scrap may be added in small amounts. Near the bottom of the furnace, preheated air is blown in. Coke is combusted in the furnace to produce carbon monoxide which reduces the iron ore to iron. Silica and alumina in the ore and coke ash are fluxed with limestone to form a slag that absorbs much of the sulfur from the charge. Molten iron and slag are intermittently tapped from the hearth at the bottom. The slag is drawn off and processed. The product, pig iron, is removed and typically cooled, then transported to a steel mill operation for further processing in either an electric arc furnace or a basic oxygen furnace, as depicted in Exhibit 2. As shown in Exhibit 2, the iron can also be directly reduced before it is sent for further processing.

Recent changes in the process include modifications in the fluxing practices. Flux is often introduced through fluxed sinter or fluxed pellets rather than by direct charging. The use of external desulfurization of hot metals prior to steel making has also increased.[6]

Steelmaking

All contemporary steelmaking processes convert pig iron, scrap, or direct-reduced iron, or mixtures of these, into steel by a refining process that lowers the carbon and silicon content and removes impurities (mainly phosphorus and sulfur). Three major furnace types can be used for making steel:

- open hearth furnaces, no longer used for domestic steel production;
- basic oxygen furnaces, with 62 percent of the total; and
- electric arc furnaces, accounting for the remaining 38 percent.

The latter predominantly uses scrap (i.e., non-mineral material) as feedstock and is classified as a secondary process. The open-hearth process was prevalent in the United States between 1908 and 1969, but it is no

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[4] Gerald Houck, 1994, Op. Cit., p. 90.

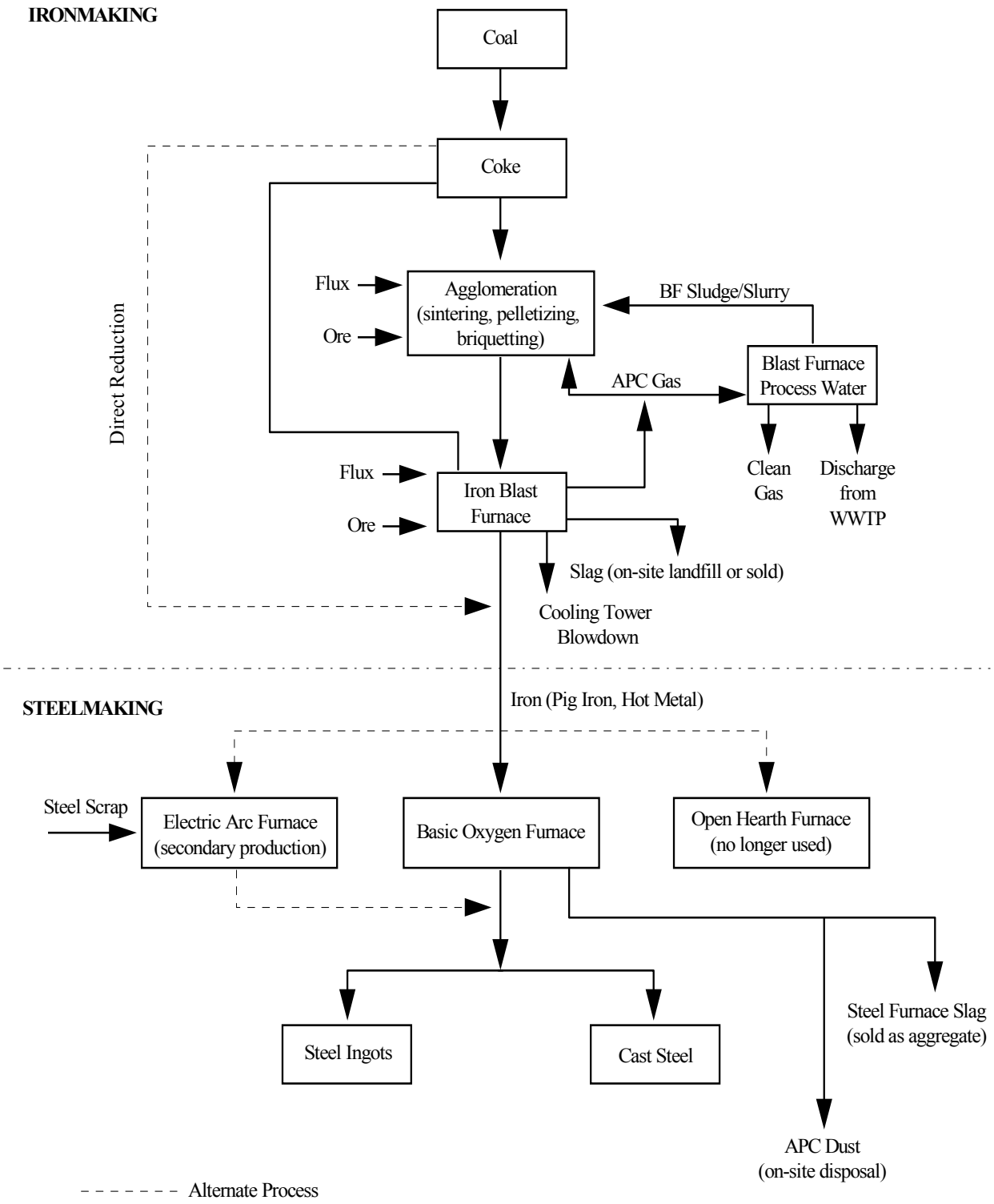
[5] American Iron and Steel Institute, "Annual Statistical Report," 1984, p. 78.

[6] Harold R. Kokal and Madhu G. Ranade, "Fluxes for Metallurgy," from Industrial Minerals and Rocks, 1994, pp. 668-669.

EXHIBIT 2

IRONMAKING AND STEELMAKING PROCESSES

(Adapted from: USS Lorain flow diagram.)



longer in use domestically. The basic oxygen process has supplanted it as the predominant primary steel-making process, making up approximately 95 percent of domestic primary steel production in 1987.[7]

Modern steelmaking also includes treatment of steel in ladles. This use of ladles (1) improves the cleanliness of the steelmaking process, (2) increases throughput in steel vessels, and (3) allows for shape control of inclusions in continuous casting operations.[8]

2. Generalized Process Flow Diagram

A general flow diagram for the production of raw steel from iron ore is presented in Exhibit 2. In general, the process involves (1) beneficiation of the iron ore, (2) either direct-reduction or reduction in an iron blast furnace, (3) processing in steelmaking furnaces, and (4) casting.

Ironmaking

Beneficiation of the Iron Ore: Sintering, Pelletizing, or Briquetting

There are a variety of beneficiation methods that can be used to prepare iron ores, depending on the iron content in the ores. Some ores contain greater than 60 percent iron and require only crushing and blending to prepare them for further processing. In other cases, operations including screening and concentrating are necessary to prepare the raw materials. The characteristics of the iron-bearing ores vary geographically. Specifically, magnetite is the main iron-bearing ore in the Lake Superior district and in the northeastern United States, while hematite and hematite magnetite mixtures tend to be found in ores in Alabama and the Southwest.

When magnetite occurs in lower grade deposits, the ore is ground, and the concentrate is separated magnetically from the gangue with the ore in a water suspension. Ore containing hematite can be high in clay content and requires washing to remove the clay and concentrate the iron. Low grade ores that can not be separated magnetically may also need to be concentrated via washing, jigging, heavy media separation, or flotation.[9]

Ores that will be sent to blast furnaces for ironmaking need to be permeable to allow for an adequate flow of gas through the system. Additionally, concentrates in raw ores that are very fine need to be agglomerated before they can be used as feed stock for the blast furnaces. The three major processes used for agglomeration include:

- sintering;
- pelletizing; and
- briquetting.

Sintering. Sintering involves mixing the iron-bearing material such as ore fines, flue dust, or concentrate with fuel (e.g., coke breeze or anthracite).[10] The mixture is then spread on surface beds which are ignited by gas burners. The heating process fuses the fine particles, and the resulting product is lumpy material known as sinter. The sinter is sized and the fines are recycled. Sintering operations are used to recycle wastes from other iron and steel manufacturing processes.

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[7] Frederick J. Schottman, "Iron an Steel," from Minerals Yearbook Volume I. Metals and Minerals, U.S. Bureau of Mines, 1989, p. 511.

[8] Harold R. Kokal and Madhu G. Ranade, 1994, Op. Cit., pp. 668-9.

[9] U.S. Environmental Protection Agency, "Iron and Steel," from 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes, Office of Solid Waste, 1988, p. 3-128.

[10] Ibid.

Pelletizing. Pelletizing involves forming pellets from the raw ore or concentrates, then hardening the pellets by heating. Solid fuel can be combined with the concentrate to promote the heating necessary to harden the pellet. Common binders added to strengthen the pellets include limestone, dolomite, soda ash, bentonite, and organic compounds. After the pellets are sized, any remaining fraction of materials are recycled back through the sintering process.

Briquetting. Briquetting, another form of agglomeration, involves heating the ore and pressing it into briquettes while the materials are still hot. Once the briquettes are cooled, they are sent directly to the blast furnaces.

Reduction of the Iron Ore

There are two basic methods for reducing iron ore:

- direct reduction; and
- reduction in a blast furnace.

Direct Reduction. Direct reduction involves the reduction of iron ore that is in the solid state - at less than 1000 ºC.[11] The solid primary metal produced by direct reduction of iron ores (DRI) can be used to supply electric arc furnaces.

Blast Furnace. During ironmaking, agglomerated iron ore is combined with prepared limestone, silica, and coke and placed into a blast furnace. Heated air is blown into the furnace and causes the limestone and silica to form a fluid slag which combines with other impurities. The slag can be separated from the molten iron and sent to a slag reprocessing unit. Generally, the molten iron from the blast furnace is transferred directly to the steelmaking furnaces.

A number of integrated steelwork facilities in the United States have increased their use of fluxed pellets, which are more easily reducible. The fluxed pellets are produced by adding limestone ($CaCO_3$) and/or dolomite [$(Ca,Mg)CO_3$] to the iron ore concentrate during the balling stage. Flux is added until the ratio of calcium and magnesium oxide to silicon dioxide and aluminum oxide ($(CaO+MgO)/(SiO2+Al_2O_3)$) in the pellet is above 0.6. The most common ratio documented is approximately 1.0.[12]

Steelmaking

Processing in Steelmaking Furnaces

There are three basic methods of steel production:

- open hearth furnaces (no longer in use domestically);
- basic oxygen furnaces; and
- electric arc furnaces (secondary production).

Open Hearth Furnace (no longer used). During the open-hearth process, a relatively shallow bath of metal was heated by a flame that passed over the bath from the burners at one end of the furnace while the hot gases resulting from combustion were pulled out the other end. The heat from the exhaust gas was retained in the exhaust system's brick liners, which were known as checker-brick regenerators. Periodically the direction of the flame was reversed and air was drawn through what had been the exhaust system; the hot checker-bricks preheated the air before it was used for combustion in the furnace. Impurities were oxidized during the process and fluxes formed a slag; this slag was drawn off and processed or discarded.

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[11] J. Astier, "Present Status of Direct Reduction and Smelting Reduction," from Steel Times, October 1992, pp. 453-458.

[12] William S. Kirk, "Iron Ore," from Minerals Yearbook Volume 1. Metals and Minerals, 1992, p. 618.

Basic Oxygen Furnace. The basic oxygen process uses a jet of pure oxygen that is injected into the molten metal by a lance of regulated height in a basic refractory-lined converter. Excess carbon, silicon, and other reactive elements are oxidized during the controlled blows, and fluxes are added to form a slag. This slag, one of the RCRA special wastes, is drawn off and processed or discarded.

The first step in the BOF process is charging the furnace. Hot metal (molten iron from the blast furnace) which accounts for most of the metallic charge is added to the furnace by ladles. Once the furnace has been charged, a water-cooled oxygen lance is lowered into the furnace and high purity oxygen is blown in the top of the furnace. One modification to this process is the Q-BOP in which the oxygen and other gases are blown in from the bottom of the furnace instead of the top. In the bottom blown process, oxygen is introduced through a number of tuyeres, consisting of two concentric pipes in the bottom of the converter.[13]

In the furnace, oxygen combines with the carbon and other unwanted elements to oxidize the impurities in the molten charge, and thereby converting the molten charge to steel. The lime and other fluxes help remove the oxidized impurities as a layer of slag. The refined steel is then poured into ladles. At this point, any alloys can be added to the steel to obtain the desired strength and characteristics required in the final product.

Electric Arc Furnace (secondary production). Electric arc furnaces are generally used for scrap processing and have traditionally been used to produce alloy, stainless, tool, and specialty steels. Scrap steel is the principal metallic charge to electric furnaces. Direct reduction of iron ore also produces pellets with high enough iron content to be used. Limestone and other fluxes are charged after the scrap becomes molten. As in the blast furnace operation, the impurities in the steel form a floating layer of slag that can be poured off. The molten steel is then poured into ladles and sent to be cast.

In all steelmaking operations, gases from the furnace must be cleaned in order to meet air pollution control requirements. Facilities may use dry collection (e.g., bag houses, filters, or electrostatic precipitators) or wet scrubbers or, as is most often practiced, both types of controls. Large volumes of dust and scrubber sludge are collected for either further processing or disposal. Some of these air pollution control residuals are RCRA special wastes.

The molten steel, from whichever type of furnace is used, flows into ladles and is sent for further processing at rolling mills to form the finished products.

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

- **Dezincing and Detoxification of Electric Arc Furnace Steelmaking Dust via Ammonium Carbonate Leaching.** The use of ammoniacal ammonium carbonate (AAC) leaching for the treatment of carbon steel making EAF dust has been investigated on a laboratory scale. The tests were performed using dust samples from three European steel companies. The dusts were found to be toxic due to the leachability of silver, mercury, lead, and cadmium. After treatment, the toxicity tests indicated leachates below past and current EPA toxicity threshold limits.[14]

- **Recovery of Manganese from Steel Plant Slag by Carbamate Leaching**. The U.S. Bureau of Mines investigated the feasibility of using ammonium carbamate leaching to recover manganese from steel plant slag. It was found that treatment of the slag with hydrogen prior to the leaching increased the

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[13] Association of Iron and Steel Engineers, The Making, Shaping and Treating of Steel, 1985, pp. 539-652.

[14] R.L. Nyirenda et al, "Dezincing and Detoxification of Electric Arc Furnace Steelmaking Dust via Ammonium Carbonate Leaching," The Minerals, Metals, & Mining Society, 1993, pp. 894-906.

amount of manganese recovered. Results indicated that the method cannot be applied satisfactorily to all steelmaking slags.[15]

- **Glassification[16] of Electric Arc Furnace Dust.** A new process has been developed to treat hazardous materials, including electric arc furnace dust, slag, and spent refractories. The process, known as Glassification, utilizes electric arc furnace dust from both the steel and nonferrous metals industries to produce glass products.[17]

- **Treatment of Steel Plant Wastes by Magnetic Cyclones.** Steel plants generate sludges containing high concentrations of iron which display ferromagnetic properties. Methods of treating these wastes to take advantage of these properties using magnetic cyclones have been evaluated. The results indicated that the cycloning process creates an underflow with a high solids content and a clean water overflow.[18]

4. Beneficiation/Processing Boundary

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.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between agglomeration (sintering, pelletizing, and briquetting) and reduction of iron ore in a blast furnace. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is

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[15] S.N. McIntosh and E.G. Baglin, "Recovery of Manganese from Steel Plant Slag by Carbamate Leaching," U.S. Bureau of Mines, 1992.

[16] Glassification is a registered trademark.

[17] R.B. Ek and J.E. Schlobohm, "Glassification of Electric Arc Furnace Dust," from Iron and Steel Engineer, April 1993, pp. 82-84.

[18] John L. Watson and Suren Mishra, "The Treatment of Steel Plant Wastes by Magnetic Cyclones," Conference Paper from Symposium on Emerging Process Technologies for a Cleaner Environment, Phoenix, AZ, February 24-27 1992.

here where a significant chemical change to the iron ore occurs. 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 the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Waste characterization data, waste generation data, and waste management data are not available for all of the wastes identified as generated from the production of iron and steel.

Tailings. Wastes from magnetic separation include tailings consisting mostly of silicate rock. The magnetite ore from lower grade deposits is ground, and the concentrate is separated magnetically from the gangue with the ore in a water suspension. These wastes are typically managed in tailing impoundments.

Wastewater and Waste Solids. Ore containing hematite can be high in clay content and require washing to remove the clay and concentrate the iron. The wastewater and waste solids generated from washing ores containing clay are not expected to be hazardous. No information is available on management practices for these wastes.[19]

2. Mineral Processing Wastes

Ferrous metal production operations generate four RCRA special mineral processing wastes that are exempt from RCRA Subtitle C: iron blast furnace slag, iron blast furnace air pollution control dust/sludge, steel furnace slag, and steel furnace air pollution control dust/sludge. The Agency did not evaluate the four RCRA special mineral processing wastes further. Besides these RCRA special wastes, the only other types of wastes generated appear to be various types of wastewater, including cooling water, wash water, and scrubber water.

Iron Blast Furnace Slag. In 1988, iron blast furnace slag was reported as generated at 26 of the 28 ferrous metal production facilities in the United States surveyed by the U.S. Environmental Protection Agency in 1989 -- all 24 integrated iron/steel facilities and two additional blast furnace operations.

Blast furnace slag contains oxides of silicon, aluminum, calcium, and magnesium, along with other trace elements. There are three types of blast furnace slag: air-cooled, granulated, and expanded. Air cooled slag comprises approximately ninety percent of all blast furnace slag produced. The physical characteristics of the slags are in large part determined by the methods used to cool the molten slag. In the surveys, all facilities characterized their slags as solid, though slag is molten at the point of generation.[20]

The primary management practice for iron blast furnace slag is processing (e.g., crushing, sizing) and sale for use as aggregate. In 1990, only one facility disposed its slag in an adjacent water body in order to build up a land area that was intended for use managing other waste materials as part of an Army Corp of Engineers approved fill project.[21]

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[19] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-128.

[20] U.S. Environmental Protection Agency, "Chapter 8," from Report to Congress on Special Wastes from Mineral Processing, Vol II, Office of Solid Waste, July 1990.

[21] Ibid.

Iron Blast Furnace Air Pollution Control (APC) Dust/Sludge. In 1988, iron blast furnace APC dust/sludge was generated at 26 of the 28 ferrous metal facilities in the United States submitting surveys, including all 24 integrated iron/steel facilities and the two additional blast furnace operations.

Air pollution control (APC) devices treat the top gases emitted from iron blast furnaces. The air pollution control devices generate either dusts or sludges. APC dust/sludge is composed primarily of iron, calcium, silicon, magnesium, manganese, and aluminum.[22]

The two primary waste management practices at the iron facilities regarding APC dust/sludge are disposal in on-site units and the return of the material to the production process via the sinter plant operation or blast furnace.[23]

Steel Furnace Slag. In 1988, steel furnace slag was generated at 26 of the 28 ferrous facilities in the United States that submitted surveys, including all 24 integrated iron/steel facilities and the two additional steel production operations. Steel slag is composed primarily of calcium silicates and ferrites combined with fused oxides of iron, aluminum, manganese, calcium, and magnesium. At the point of generation, the slag is in a molten form. The molten slag is air cooled and is broken into varying sizes once processing (e.g., crushing) begins.[24]

The primary management practice for steel slag is processing (e.g., granulating, crushing, sizing) and sale for use as aggregate, though several facilities dispose or stockpile their steel slag.

Steel Furnace Air Pollution Control (APC) Dust/Sludge. Steel furnace APC dust/sludge was generated at 26 of the 28 domestic ferrous metal production facilities surveyed in 1989, including all 24 integrated iron/steel facilities and the two additional steel production facilities. Steel APC dust/sludge consists mostly of iron, with smaller amounts of silicon, calcium, and other metals.

Waste management practices were reported for only ten of the 26 facilities in 1989. Eight of the ten reportedly dispose the APC dust/sludge on-site; the remaining two return the material to the production process via the sinter plant operation.

Wastewater. Wastewater is generated from a number of sources during both the ironmaking and the steelmaking processes. In addition to process wastewaters, wastewater streams also are generated from non-contact operations (i.e., cooling tower water, cooling tower blowdown) and from non-process operations including maintenance and utility requirements. However, the primary source of wastewater from ironmaking is water used for the cleaning and cooling of gases. Most plants either recirculate or recycle their cooling process wastewater to reduce the total pollutant load discharged from their facilities. The wastewaters from the blast furnace process contain suspended particulate matter and cyanide, phenol, and ammonia. All of these pollutants are limited by NPDES permit requirements. Other wastewaters contain toxic metals (predominantly zinc) and organic pollutants which come from the raw materials or form during the reduction process.

Many of the pollutants in the process wastewaters are the result of compounds found in the charges and fluxes added to the furnace. In both iron and ferromanganese blast furnaces operations, ammonia is present in the exit gases and as a result is also present in the process wastewater. The ammonia is formed from the various nitrogen compounds that are removed from the coke charge during blast furnace operations. Fluoride is also present in the wastewater as a result of fluoride compounds, primarily calcium chloride from the limestone flux. Manganese is present in wastewaters from ferromanganese production and other elements may be present depending on the various ores and alloys used in production. Lastly, cyanide is generated as a result of the reaction of nitrogen, in the blast air, with carbon from the coke charge in the reducing atmosphere of the blast furnace.

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[22] Ibid.

[23] Ibid.

[24] Ibid.

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

D. Non-uniquely Associated Wastes

Wastes associated with the coke making process, stainless steel production, and steel finishings are considered to be non-uniquely associated. In addition, 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 naphtha), 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, and some waste oil and other lubricants. Other ancillary wastes associated with the coke making process, stainless steel production, and the spent pickling liquors resulting from steel finishing at some integrated steel mills are currently classified as listed and/or characteristic wastes and regulated under RCRA Subtitle C requirements.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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