

US EPA ARCHIVE DOCUMENT

## MOLYBDENUM, FERROMOLYBDENUM, AND AMMONIUM MOLYBDATE

### A. Commodity Summary

Almost all molybdenum is recovered from low-grade deposits of the mineral molybdenite, naturally occurring molybdenum disulfide ( $\text{MoS}_2$ ), mined either from a primary deposit, or as a byproduct of copper processing.<sup>1</sup> In 1993, one mine extracted molybdenum ore, and nine mines recovered molybdenum as a byproduct. Two plants converted molybdenite concentrate to molybdic oxide, which was used to produce ferromolybdenum, metal powder, and other molybdenum compounds.<sup>2</sup> Exhibit 1 presents the names and locations of molybdenum mines and processing facilities.

### EXHIBIT 1

#### SUMMARY OF MOLYBDENUM, MOLYBDIC OXIDE, AND FERROMOLYBDENUM PRODUCERS<sup>a</sup>

Facility Name	Location
Cyprus-Climax - Henderson	Empire, CO
Cyprus-Climax	Fort Madison, IA
Cyprus-Climax	Clear Water, MI
Cyprus-Climax - Green Valley	Tucson, AZ
Cyprus-Climax	Baghdad, AZ
Kennecott	Bingham Canyon, UT
Molycorp Inc.	Washington, PA
Montana Resources Inc.	Butte, MT
Phelps Dodge	Chino, NM
San Manuel	San Manuel, AZ
San Manuel	Morenci, AZ
Thompson Creek	Chalis, ID
Thompson Creek	Langeloth, PA

<sup>a</sup> - Personal Communication between ICF Incorporated and John W. Blossom, U.S. Bureau of Mines, October 1994.

Molybdenum metal is a refractory metal used as an alloying agent in steels, cast irons, and superalloys.<sup>3</sup> Ferromolybdenum is an alloy of iron and molybdenum used primarily as an alternative additive in producing alloy steels, cast irons, and nonferrous alloys. The two most common grades of ferromolybdenum are low carbon- and high carbon ferromolybdenum. Ammonium molybdate is an intermediate in manufacturing both molybdenum metal and molybdic oxide, although it can also be sold as a product. Purified  $\text{MoS}_2$  concentrate also is used as a lubricant.

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<sup>1</sup> J.W. Blossom, "Molybdenum," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 849.

<sup>2</sup> J.W. Blossom, "Molybdenum," Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 114.

<sup>3</sup> J.W. Blossom, 1992, Op. Cit., p. 847.

## B. Generalized Process Description

### 1. Discussion of Typical Production Processes

Molybdenum and molybdenum products, including ammonium molybdate, are made by roasting concentrated ore, followed by purification and/or reduction. Ferromolybdenum is typically produced by reaction of technical grade molybdic oxide and iron oxide with a conventional metallothermic process using silicon and/or aluminum as the reductant. These processes are described in greater detail below.

### 2. Generalized Process Flow Diagram

#### Molybdenum Metal and Ammonium Molybdate

Molybdenum metal and ammonium molybdate are made by roasting concentrated molybdenite ore, as shown in Exhibit 2. The concentration operations, which are not shown, include crushing, grinding, and flotation of either primary or copper ores. Molybdenite is recovered from either primary molybdenite or copper sulfide ore by flotation, after the ore has been crushed and ground to a suitable size. Several stages of grinding and re flotation concentrate the molybdenite in the primary ore to a 90 to 95 percent purity concentrate.<sup>4</sup> The remainder of the concentrate is primarily silica.<sup>5</sup> Copper, iron and lead are the impurities removed as tailings by this flotation process. Several sequential stages of flotation also are used for the copper ore, first to separate the gangue, and then the copper. The molybdenite concentration is usually 70 to 90 percent purity, when recovered from copper ores.<sup>6</sup>

Technical grade molybdic oxide, consisting of 90 to 95 percent MoO<sub>3</sub>, is produced by roasting molybdenite concentrate in a multiple hearth furnace at temperatures up to 650°C.<sup>7</sup> Molybdenum concentrates may be leached with nitric acid prior to roasting to reduce the alkali concentrations in the concentrates.<sup>8</sup> The roasting process removes sulfur and converts the sulfide to oxide. The flue gas contains products of combustion, SO<sub>2</sub>, and may contain rhenium or selenium. The SO<sub>2</sub> in the flue gas is converted to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).<sup>9</sup> More information on the processing of the flue gas, and the production of sulfuric acid can be found in the Rhenium and Selenium sections of this document.

Pure molybdic oxide can be produced from technical grade molybdic oxide through sublimation and condensation or by leaching. In sublimation, the technical grade oxide is heated to approximately 1,100°C in a muffle type furnace. The oxide is vaporized and carried in a stream of forced air through cooling ducts and

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<sup>4</sup> Ibid., p. 850.

<sup>5</sup> "Molybdenum and Molybdenum Alloys," from Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XV, 1981, p. 670.

<sup>6</sup> Blossom, J. W., 1992, Op. Cit., p. 850.

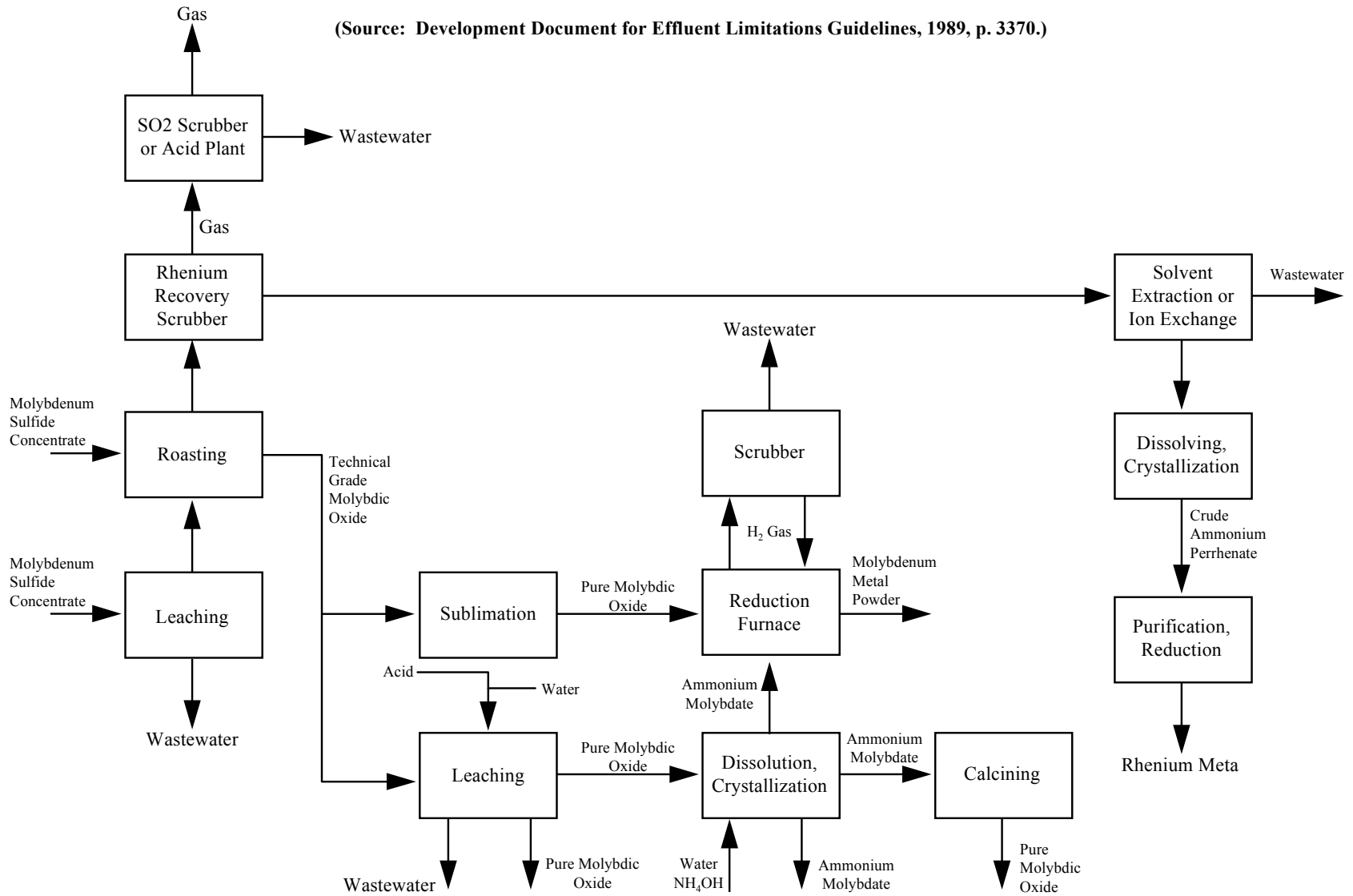
<sup>7</sup> Ibid., p. 848.

<sup>8</sup> U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Volume VI, Office of Water Regulations and Standards, May 1989, p. 3364.

<sup>9</sup> "Molybdenum and Molybdenum Alloys," 1981, Op. Cit., p. 670.

EXHIBIT 2  
 MOLYBDENUM PRODUCTION

(Source: Development Document for Effluent Limitations Guidelines, 1989, p. 3370.)



the condensed oxide particles are collected in a fabric filter. The purified oxide contains greater than 99.5 percent MoO<sub>3</sub>. Technical grade oxide may also be purified by leaching with a hydrochloric acid-ammonium chloride solution (not shown). The impurities are dissolved and separated from the solid molybdic oxide by filtration. The pure oxide may be sold as a product, reduced to molybdenum metal powder, or used to produce various molybdenum chemicals.<sup>10</sup>

Ammonium molybdate is formed by reacting technical grade molybdic oxide with ammonium hydroxide and crystallizing out the pure molybdate. The ammonium molybdate may be sold as product, calcined to form pure molybdic oxide, or reduced to form molybdenum metal powder.<sup>11</sup>

Hydrogen is used to reduce ammonium molybdate or pure molybdic oxide to molybdenum powder, at 500-1150°C, in a boat- or tube-type furnace. The metal powder is sintered and cast into ingots or bars.<sup>12</sup>

### Ferromolybdenum

Exhibit 3 illustrates the production of low carbon and high carbon ferromolybdenum. Low carbon ferromolybdenum is produced by mixing technical grade molybdic oxide, aluminum, ferrosilicon, iron oxide, limestone, lime, and fluorspar, and igniting the aluminum (not shown). A metal button and a slag are formed, allowed to solidify, and then are separated.<sup>13</sup> One firm added that when it produces low carbon ferromolybdenum no furnace is necessary, only a sand bed.<sup>14</sup> High carbon content ferromolybdenum is made by reducing technical grade molybdic oxide, calcium molybdate, or sodium molybdate with carbon in the presence of iron in an electric furnace (not shown). The impurities from a slag which is discarded.<sup>15</sup> Low carbon ferromolybdenum produced by the thermite process is more common than the high carbon alloy.

### **3. Identification of Novel or Distinct Processes**

One researcher has investigated the separation and recovery of critical metals (including molybdenum) from mixed and contaminated superalloy scrap.<sup>16</sup>

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<sup>10</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., p. 3364.

<sup>11</sup> Ibid.

<sup>12</sup> "Molybdenum and Molybdenum Alloys," 1981, Op. Cit., p. 674.

<sup>13</sup> U.S. Environmental Protection Agency, "Molybdenum," 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes, 1988, p. 3-154.

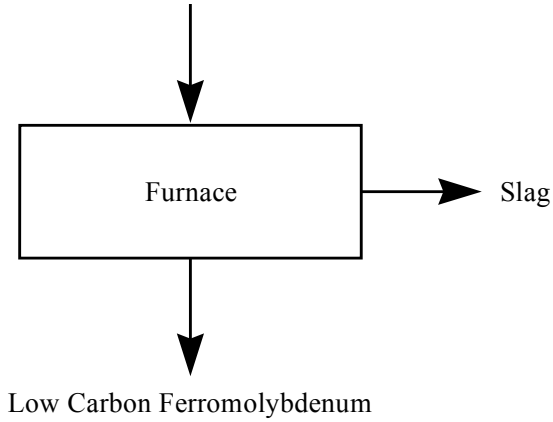
<sup>14</sup> Molycorp, Inc. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

<sup>15</sup> Ibid., p. 3-154.

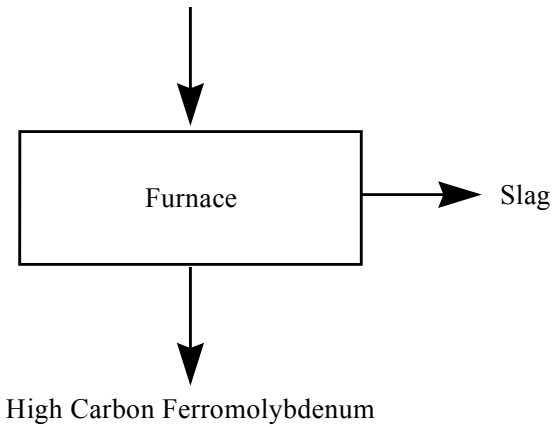
<sup>16</sup> Hundley, G.L., and D.L. Davis, "Recovery of Critical Metals from Superalloy Scrap by Matte Smelting and Hydrometallurgical Processing," U.S. Bureau of Mines Report of Investigations 9390, 1991, p. 1.

**EXHIBIT 3**  
**FERROMOLYBDENUM PRODUCTION**

Aluminum, Technical Grade Molybdic Oxide,  
Ferrosilicon, Iron Oxide, Limestone, Lime and Fluorspar



Technical Grade Oxide, Iron, Calcium or  
Sodium Molybdate, Carbon



#### 4. Extraction/Beneficiation 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. The idea that beneficiation wastes are earthen in character is only a guide, and not a standard. There may be instances where beneficiation operations produce a waste that is "not" earthen in character. In such instances, the operation is not considered a processing operation, because of the waste's non-earthen characteristics, and instead remains a beneficiation operation.

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.

##### Molybdenum Powder

EPA determined that for the production of molybdenum powder, the beneficiation/processing line occurs between the roasting and sublimation steps because leaching does not follow and because the molybdenum disulfide is chemically roasted to pure molybdc oxide.<sup>17</sup> 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.

##### Ammonium Molybdate and Pure Molybdc Oxide

Based on a review of the process, there are no mineral processing operations involved in the production of either ammonium molybdate or pure molybdc oxide.

##### Ferromolybdenum

EPA determined that for ferromolybdenum, the beneficiation/processing line occurs at the furnace where the technical grade molybdc oxide and other materials are charged and undergo thermal reduction to form

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<sup>17</sup> Molycorp, Inc. Op. Cit.

ferromolybdenum. One firm, Molycorp Inc., reported that in their operations furnaces were restricted to high carbon ferromolybdenum production.<sup>18</sup>

## C. Process Waste Streams

### 1. Extraction/Beneficiation Wastes

The following wastes may be generated by extraction and beneficiation operations: gangue, flotation tailings, spent flotation reagents, and wastewater.<sup>19,20</sup> The tailings from molybdenite concentration are not expected to exhibit any hazardous characteristics, although metal leaching and acid formation may take place.<sup>21</sup>

### 2. Mineral Processing Wastes

#### Ammonium Molybdate Refining

**Refining Wastes.** Available data do not indicate that ammonium molybdate refining wastes exhibit any hazardous characteristics.<sup>22</sup> Therefore, the Agency did not evaluate this material further.

#### Technical Grade Molybdic Oxide Production

**Liquid Residues.** Approximately 1,000 metric tons of liquid residues are generated annually in the United States. Available data indicate that this waste is potentially TC toxic. Potentially hazardous constituents include arsenic, cadmium, lead, and selenium.<sup>23</sup> The waste is not recycled. Liquids from the quench and scrubber towers/thickener contained the following constituents: arsenic - 60 ppm; cadmium - 1.2 ppm; chromium - 1.8 ppm; lead - 5.8 ppm; molybdenum - 100 ppm; and selenium - 32 ppm.<sup>24</sup> Additional data is provided in Attachment I. No other information on waste characteristics, or waste management was available in the sources listed in the bibliography.

**Treatment Solids.** Available data do not indicate that treatment solids exhibit any hazardous characteristics.<sup>25</sup> Silicon was found at a concentration of 10 percent in solids from the quench and scrubber towers/thickener.<sup>26</sup> Therefore, the Agency did not evaluate this material further.

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<sup>18</sup> Ibid.

<sup>19</sup> PEI Associates, Site Specific Data Summary Forms: Facilities Involved in the Extraction and Beneficiation of Ores and Minerals, Prepared for U.S. Environmental Protection Agency, Office of Research and Development, November 1986.

<sup>20</sup> Weiss, Norman L., Ed. "Molybdenum," SME Mineral Processing Handbook, Volume II, Society of Mining Engineers, 1985, pp. 16-1 - 16-36.

<sup>21</sup> U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-152.

<sup>22</sup> U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Volume I, Office of Solid Waste, August 1992, p. I-2.

<sup>23</sup> Ibid., p. I-6.

<sup>24</sup> Ibid., Vol. II, p. 28-11.

<sup>25</sup> Ibid., Vol. I, p. I-6.

<sup>26</sup> Ibid., Vol. II, p. 28-8.



**Solid Residues.** Available data do not indicate that solid residues exhibit any hazardous characteristics (see Attachment 1).<sup>27</sup> Therefore, the Agency did not evaluate this material further.

**Roaster Gas Blowdown Solids.** Approximately 100 metric tons of roaster gas blowdown solids are generated annually in the United States. Available data do not indicate that this waste exhibits any hazardous characteristics.<sup>28</sup> Therefore, the Agency did not evaluate this material further.

**Molybdc Oxide Refining Wastes.** Approximately 2,000 metric tons of molybdc oxide refining wastes are generated annually in the United States.<sup>29</sup> This waste is believed to not exhibit any hazardous characteristics<sup>30</sup> and has not been evaluated further by the Agency.

**Flue Dust/Gases.** The flue gases produced during the roasting of molybdenite concentrates could contain volatile metals in the flue dust, in addition to the SO<sub>2</sub>. These metals may include lead, zinc, tin and others.<sup>31</sup> Although no published information regarding waste generation rate 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 1,100 metric tons/yr, 250,000 metric tons/yr, and 500,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead. This waste typically is not recycled. However, Molycorp Inc. reported that flue dust is recycled at its Washington, PA facility. It also reported that in its operations there was no difference between flue dust/gases and roaster gas blowdown solids.<sup>32</sup>

#### Metal Refining

**Refining Wastes.** Available data do not indicate that metal refining wastes exhibit any hazardous characteristics.<sup>33</sup> Therefore, the Agency did not evaluate this material further.

**H<sub>2</sub> Reduction Furnace Scrubber Water.** Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste (see Attachment 1). Therefore, the Agency did not evaluate this material further.

#### Ferromolybdenum Production

**APC Dust/Sludge.** This waste is generated by the baghouse or other APC device receiving the fumes from the ferromolybdenum furnace. Available data do not indicate that APC dust/sludge exhibits any hazardous characteristics.<sup>34</sup> Therefore, the Agency did not evaluate this material further.

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<sup>27</sup> Ibid., Vol. II, p. I-6.

<sup>28</sup> Ibid.

<sup>29</sup> Ibid.

<sup>30</sup> Molycorp, Inc. Op. Cit.

<sup>31</sup> U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-153.

<sup>32</sup> Molycorp, Inc. Op. Cit.

<sup>33</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., Vol. I, p. I-6.

<sup>34</sup> Ibid., p. I-4.

**Slag.** This waste, formed in either the production of low carbon ferromolybdenum or high carbon ferromolybdenum, is not expected to exhibit any hazardous characteristics. The slag is usually discarded.<sup>35</sup> Therefore, the Agency did not evaluate this material further.

**D. Non-uniquely Associated Hazardous Wastes**

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents, and tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

**E. Summary of Comments Received by EPA**

**New Factual Information**

Two commenters provided new information on facility specific operations and processes (COMM40, COMM69). This new information has been incorporated into the Agency's sector report.

**Site-specific Issues**

None.

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<sup>35</sup> U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-154.

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**ATTACHMENT 1**

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SOLID RESIDUES - MOLYBDENUM OXIDE

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
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	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	100,000	100,000	100,000	1/1	-	-	-	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 - H2 REDUCTION FURNACE SCRUBBER WATER - MOLYBDENUM OXIDE

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.001	0.0090	0.024	3/3	-	-	-	0/0	-	-
Arsenic	0.002	0.0107	0.024	3/3	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.001	0.0023	0.005	3/3	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.001	0.0010	0.001	3/3	-	-	-	0/0	1.0	0
Chromium	0.001	0.0040	0.006	3/3	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.004	0.3947	0.64	3/3	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.001	0.0657	0.17	3/3	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0002	0.0002	3/3	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.024	1.1613	2.8	3/3	-	-	-	0/0	-	-
Selenium	0.001	0.0010	0.001	3/3	-	-	-	0/0	1.0	0
Silver	0.001	0.0053	0.014	3/3	-	-	-	0/0	5.0	0
Thallium	0.001	0.0010	0.001	3/3	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.51	0.5733	0.63	3/3	-	-	-	0/0	-	-
Cyanide	0.01	0.0100	0.01	3/3	-	-	-	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.





## PHOSPHORIC ACID

### A. Commodity Summary

Most phosphoric acid facilities are co-located with other manufacturing facilities.<sup>1</sup> The primary product from phosphoric acid facilities is commercial-grade wet process phosphoric acid, approximately 95 percent of which is used at co-located facilities to produce fertilizers and animal feed. Most of the remaining portion is used as a feedstock in chemical processing operations. Phosphoric acid producing facilities are listed in Exhibit 1.

### EXHIBIT 1

#### SUMMARY OF PHOSPHORIC ACID PRODUCING FACILITIES

Facility Name	Locations	Type of Operations	Potential Factors Related to Sensitive Environments
Agrico Chem	Pierce, FL Uncle Sam, LA Donaldsonville, LA	Wet Process Wet Process Wet Process	Uncertain Uncertain Uncertain
Albright & Wilson	Fernald, OH Charleston, SC	Furnace Furnace	Uncertain Uncertain
Arcadian	Geismar, LA	Wet Process	Located in 100-year floodplain, within 1 mile of wetland
Cargill	Riverview (Tampa), FL	Wet Process	Located in 100-year floodplain, located in wetland
Central Phosphates	Plant City, FL	Wet Process	Within 1 mile of wetland, located in area of karst terrain
CF Ind.	Bartow, FL	Wet Process	Uncertain
Chevron	Rock Springs, WY	Wet Process	Uncertain
Conserv	Nichols, FL	Wet Process	Within 1 mile of wetland
Farmland	Pierce (Bartow), FL	Wet Process	Within 1 mile of wetland
FMC	Carteret, NJ Lawrence, KS Newark, CA	Furnace Furnace Furnace	Uncertain Uncertain Uncertain
Gardinier, Inc.	Riverview, FL	Wet Process	Uncertain
Hydrate	Milwaukee, WI	Furnace	Uncertain
IMC	Mulberry, FL	Wet Process	Located within 1 mile of wetland

<sup>1</sup> U.S. Environmental Protection Agency, "Phosphoric Acid Production," from Report to Congress on Special Wastes from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, pp. 12-1 - 12-61.

**EXHIBIT 1 (continued)**

Facility Name	Locations	Type of Operations	Potential Factors Related to Sensitive Environments
JR Simplot	Pocatello, ID	Wet Process	Located in 100-year floodplain, located in fault zone
Mobil	Pasadena, TX	Wet Process	Located in 100-year floodplain
Monsanto	Trenton, MI Augusta, GA Carondelet, MO Long Beach, CA	Furnace Furnace Furnace Furnace	Uncertain Uncertain Uncertain Uncertain
Nu West	Soda Springs (Conda), ID	Wet Process	Uncertain
Nu South	Pascagoula, MS	Wet Process	
Occidental	Jeffersonville, IN Columbia, TN White Springs, FL  Dallas, TX	Furnace Furnace Wet Process  Furnace	Uncertain Uncertain Located within 1 mile of wetland Uncertain
Royster	Palmetto (Piney Pt.), FL  Mulberry, FL	Wet Process  Wet Process	Located within 6.5 miles of endangered species habitat, within 1 mile of wetland, located in area of karst terrain  Located within 1 mile of wetland
Seminole	Bartow, FL	Wet Process	Located in endangered species habitat, located in 100-year floodplain, within 1 mile of wetland
Stauffer	Morrisville, PA Nashville, TN Richmond, CA Chicago Heights, IL Chicago, IL	Furnace Furnace Furnace Furnace Furnace	Uncertain Uncertain Uncertain Uncertain Uncertain
Texasgulf	Aurora, NC	Wet Process	Located in 100-year floodplain, located in wetland
US Agri-Chemicals Corp (USAC)	Ft. Meade, FL	Wet Process	Within 1 mile of wetland Uncertain

## B. Generalized Process Description

There are two processes for producing phosphoric acid: (1) the wet process, and (2) the furnace process. Wet process acid, produced directly from phosphatic ores, is characterized by relatively high production volume, low cost, and low purity. It is used primarily in fertilizers. Furnace or thermal acid, manufactured from elemental phosphorus, is more expensive and considerably purer than wet-process acid. It also is produced in much smaller quantities, almost exclusively for applications requiring high purity.<sup>2</sup> As shown in Exhibit 1, there are 22 facilities that use the wet process and 18 that use the furnace process. There are significant differences in these processes and therefore, this report is divided into two sections. The wet process, as described in Section 1, is the main focus of this chapter. A brief discussion of the furnace process is provided in Section 2. (The furnace process uses a saleable mineral commodity as a primary raw material (elemental phosphorous) and as such, is completely outside the scope of the Mining Waste Exclusion.) Finally, Section 3 describes several related processes such as ammoniated fertilizer production, animal feed production, superphosphoric acid production, fluoride recovery, and sulfuric acid production.

### SECTION 1: The Wet Process

#### 1. Discussion of the Typical Production Processes

Wet process steps include digestion, filtration, and concentration. Phosphate rock is dissolved in phosphoric acid, to which sulfuric acid is added. The slurry from this operation is sent to filters where solids are collected, washed, and sent to phosphogypsum stacks. The acid is concentrated by evaporation. The wet process is described in more detail below.

#### 2. Generalized Process Flow Diagram

During digestion, the first step in phosphoric acid production, beneficiated phosphate rock is dissolved in phosphoric acid; sulfuric acid, which chemically digests the calcium phosphate, is added to this solution. The product of this operation is a slurry that consists of the phosphoric acid solution and a suspended solid, calcium sulfate, commonly known as phosphogypsum. The slurry is routed to a filtration operation where the suspended phosphogypsum is separated from the acid solution. The acid isolated during filtration is concentrated through evaporation to produce "merchant grade" (54 percent) phosphoric acid. The phosphogypsum is re-slurried, this time in recycled process wastewater, and sent to disposal in phosphogypsum stacks.<sup>3</sup> Exhibit 2 presents a process flow diagram of phosphoric acid production.<sup>4</sup>

Only five percent of raw product acid is purified. Purification of wet-process acid is accomplished by two primary methods: (1) solvent extraction, and (2) chemical precipitation. Exhibit 3 presents a typical flow diagram for solvent extraction purification of wet-process phosphoric acid. (Purification steps are outside the scope of mineral processing.) In the production of sodium phosphates using chemical precipitation, almost all wet-process acid impurities may be induced to precipitate as the acid is neutralized with sodium carbonate or sodium hydroxide. The main exception, sulfate, may be precipitated as calcium or barium sulfate. Most fluorine and silica can be removed with the sulfate filter cake as sodium fluorosilicate by the addition of sodium ion and control of the Si/F ratio in the process.<sup>5</sup>

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<sup>2</sup> "Phosphoric Acid and the Phosphides," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XVII, 1982, pp. 426-442.

<sup>3</sup> U.S. Environmental Protection Agency, 1990, Op. Cit., pp. 12-1 - 12-61.

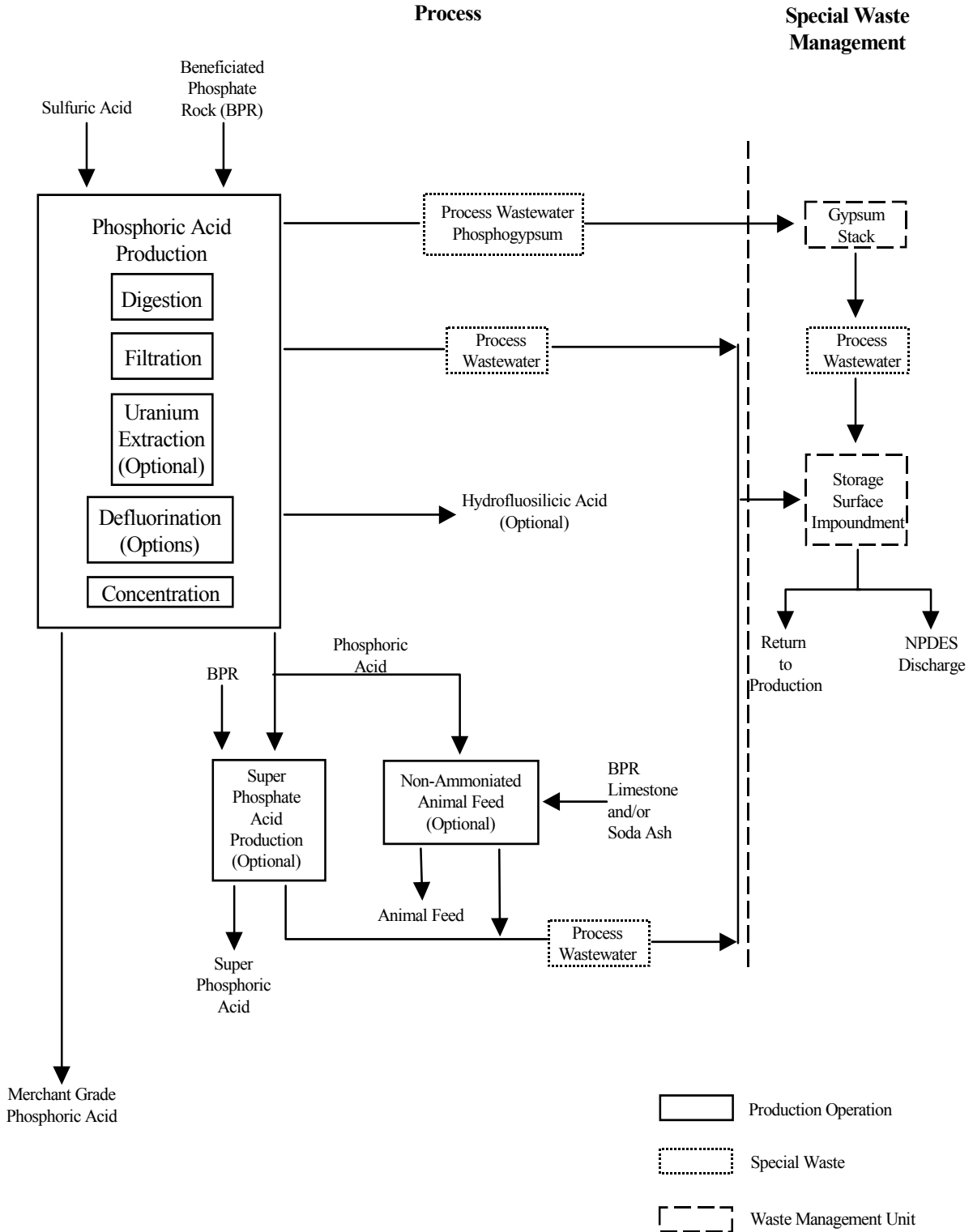
<sup>4</sup> Ibid.

<sup>5</sup> Kirk-Othmer Encyclopedia of Chemical Technology, 1982, Op. Cit., pp. 426-442.

**EXHIBIT 2**

**PHOSPHORIC ACID TREATMENT**

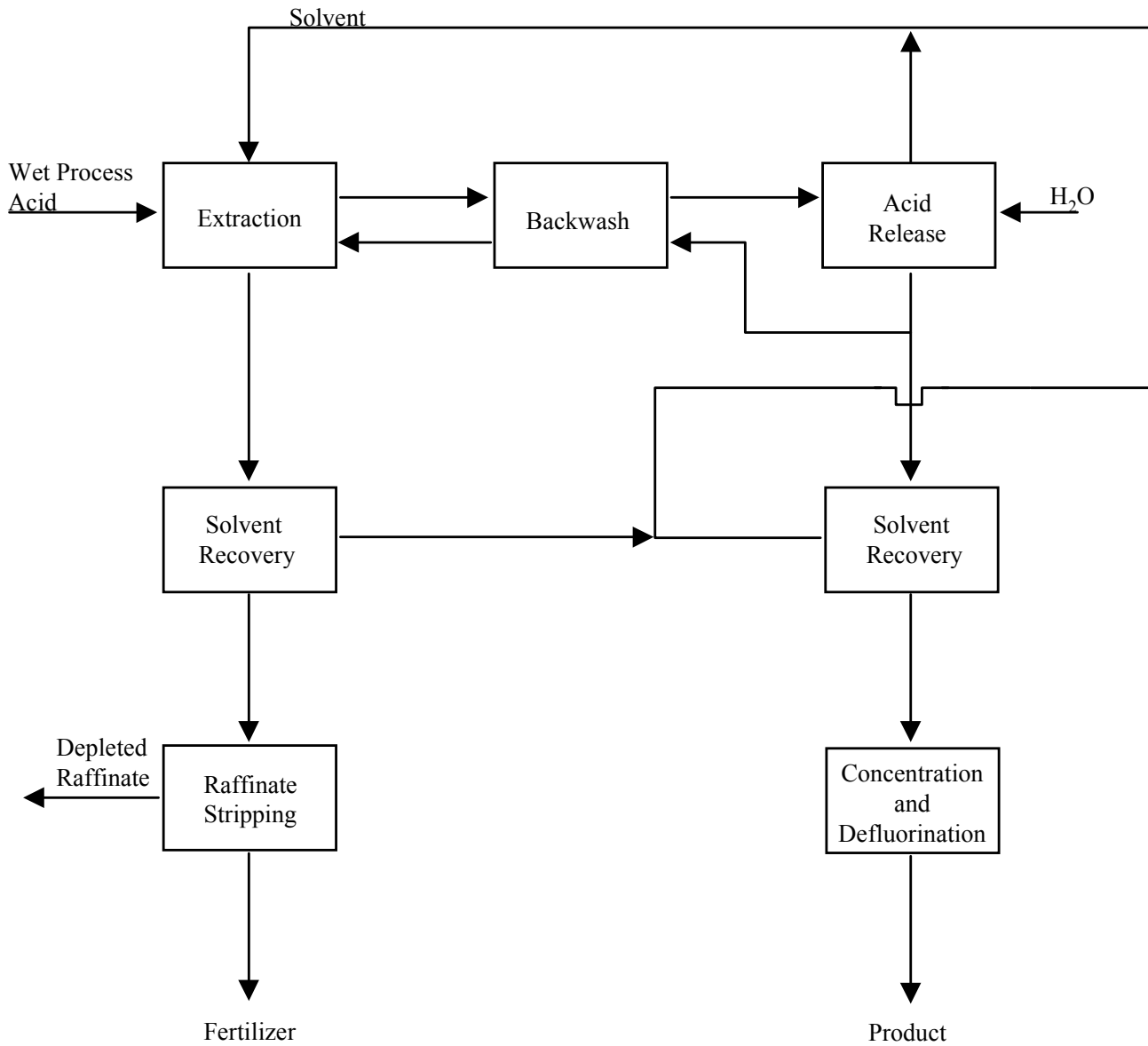
(Adapted from: Report to Congress on Special Wastes from Mineral Processing, July 1990, pp. 12-1 - 12-61.)



### EXHIBIT 3

#### SOLVENT EXTRACTION PURIFICATION OF WET PROCESS PHOSPHORIC ACID

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1982, pp. 426 - 442.)



In the double-neutralization process for wet process acid purification, sodium fluorosilicate is precipitated and removed by filtration at a pH of 3-4. Upon raising the pH to 7-9, insoluble phosphates of iron, aluminum, calcium, and magnesium form and separate. Iron can be precipitated as hydrous ferric oxide, reducing the phosphate loss in the second filter cake. Both the fluorosilicate and metal phosphate filter residues tend to be voluminous cakes that shrink when dewatered; recovery of soluble phosphates trapped within the cakes is difficult.<sup>6</sup>

The double-neutralization process is used in the production of high volume detergent-builder phosphates because the phosphate precursor solutions occur at pH 7-9. More acidic salts, however, require an additional filtration to eliminate discoloration caused by remaining traces of ferric oxide that precipitate at higher pH.<sup>7</sup>

The increasing cost differential between the sulfur used in manufacture of wet-process acid and the electricity needed for thermal acid has encouraged the development of new processes for purifying wet-process acid. These are based mostly on solvent extraction using organic solvents with low miscibility in water. Crude wet-process acid is typically concentrated and clarified prior to extraction to remove sludge-forming components and improve partition coefficients. Chemical precipitation of sulfate, silicate, and fluoride may also be used as a prepurification step preceding solvent extraction.<sup>8</sup>

Organic-phase extraction of  $H_3PO_4$  is accomplished in a series of countercurrent mixer-settlers, with extraction generally limited to 50-75 percent of the feed acid  $P_2O_5$  content. Higher extraction results in sludge precipitation in the settlers and in the depleted raffinate stream. Raffinate is stripped of residual solvent and used in fertilizer production.<sup>9</sup>

The acid is washed from the organic stream by water or aqueous alkali in another series of countercurrent mixer-settlers, stripped of residual solvent, and concentrated to the desired  $P_2O_5$  level. The solvent is recycled to the extraction section. Many variations of this basic scheme have been developed to improve extraction of phosphate and rejection of impurities to the raffinate stream, and numerous patents have been granted on solvent extraction processes.<sup>10</sup>

Processing phosphate rock to produce phosphate fertilizer is water-intensive. At larger wet process phosphoric acid plants, water use can reach 50,000 gallons per ton of phosphoric acid. At one phosphoric acid plant with a rated capacity of 4,500 tons per day, 155,000 gallons of water per minute are used. Water uses include phosphogypsum transport, phosphoric acid concentration, and phosphoric acid temperature control and cooling.<sup>11</sup>

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

None identified.

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<sup>6</sup> Ibid.

<sup>7</sup> Ibid.

<sup>8</sup> Ibid.

<sup>9</sup> Ibid.

<sup>10</sup> Ibid.

<sup>11</sup> The Fertilizer Institute. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1995.

#### 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 the production of phosphoric acid via the wet process, the beneficiation/processing line occurs between beneficiation of phosphate rock and digestion, because the beneficiated phosphate rock undergoes a complete acid digestion, which destroys the physical matrix of the rock to yield phosphoric acid and phosphogypsum. 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.

#### SECTION 2: The Furnace Process

##### 1. Discussion of the Typical Production Processes

In the furnace process, elemental phosphorus is burned to phosphorus pentoxide which is sent to hydration for the production of phosphoric acid. This entire operation uses a saleable mineral commodity as a primary raw material (elemental phosphorus) and therefore is completely outside the scope of the Mining Waste Exclusion.

##### 2. Generalized Process Flow Diagram

In the manufacture of phosphoric acid from elemental phosphorus, phosphorus is burned in excess air, the resulting phosphorus pentoxide is hydrated, the heats of combustion and hydration are removed, and the phosphoric acid mist is collected. There are three principal process unit types used to deal with the very high combustion-zone temperatures, the reactivity of hot phosphorus pentoxide, the corrosive nature of hot phosphoric acid, and the difficulty of collecting the very fine phosphoric acid mist. These process unit types are (1) wetted wall, (2) water-

cooled, and (3) air-cooled; depending on the method used to protect the combustion chamber wall.<sup>12</sup> Exhibit 4 presents process flow diagrams for the three furnace-grade phosphoric acid production process units.

In wetted-wall units, the walls of a tall circular, slightly tapered combustion chamber are protected by a high volume curtain of cooled acid flowing down inside the wall. Phosphorus is atomized by compressed air or steam into the top of the chamber and burned in additional combustion air supplied by a forced or induced draft fan. Acid sprays at either the bottom of the chamber or in a subsequent, separate spraying chamber complete the hydration of phosphorus pentoxide.<sup>13</sup>

When all the acid is to be converted into sodium phosphate salt, a variation of the wetted-wall acid plant is used. In this case, a relatively noncorrosive, neutral sodium phosphate solution is circulated in lieu of phosphoric acid. Phosphorus pentoxide absorption is rapid and over 95 percent is collected by the circulating stream. Alkali and make-up water are added through a tail scrubber as dilute caustic soda, soda ash, or sodium sesquicarbonate solution adjusted to maintain the system materials balance.<sup>14</sup>

Air-cooled plants are characterized by a large refractory-lined combustion chamber from which waste heat is removed by radiation and convection. The combustion chamber is constructed of carbon steel lined with a single layer of high alumina refractory brick.<sup>15</sup>

Hot combustion gases from both the air-cooled combustion chamber and the water-cooled combustion chamber are quenched and saturated with water in a hydrator. An absorber bed of carbon or graphite rings may be mounted above the hydrator in the same structure to obtain more complete absorption of  $P_2O_5$  and to assure that the gas stream is cooled to about 100°C. Weak acid from mist collection is sprayed on the absorber bed, and product acid at 75-85 percent  $H_3PO_4$  leaves the hydrator through a heat exchanger.<sup>16</sup>

The  $P_2O_5$  initially is hydrated and absorbed in the hot gas stream by direct contact with relatively strong acid. This is often followed by successive stages of scrubbing with progressively more dilute acid and finally, with incoming make-up water.<sup>17</sup>

Since most furnace grade phosphoric acid is used to make food-grade acid, the arsenic it contains must be removed in a purification step. The phosphoric acid is reacted with a small amount of hydrogen sulfide to precipitate arsenic sulfide which is removed by filtration.

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

None identified.

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<sup>12</sup> Kirk-Othmer Encyclopedia of Chemical Technology, 1982, Op. Cit., pp. 426-442.

<sup>13</sup> Ibid.

<sup>14</sup> Ibid.

<sup>15</sup> Ibid.

<sup>16</sup> Ibid.

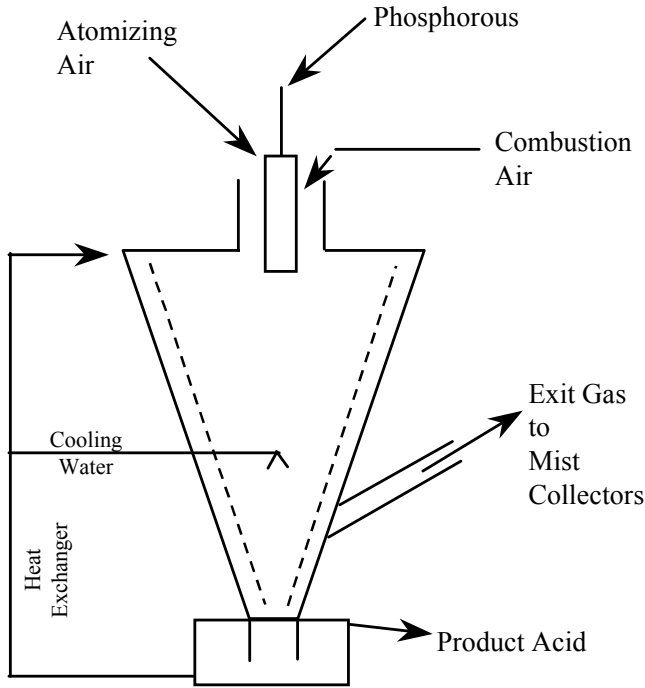
<sup>17</sup> Ibid.



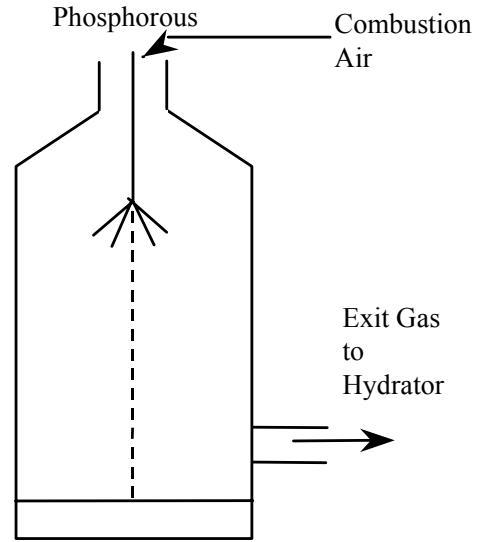
EXHIBIT 4

FURNACE-GRADE PHOSPHORIC ACID PROCESSES

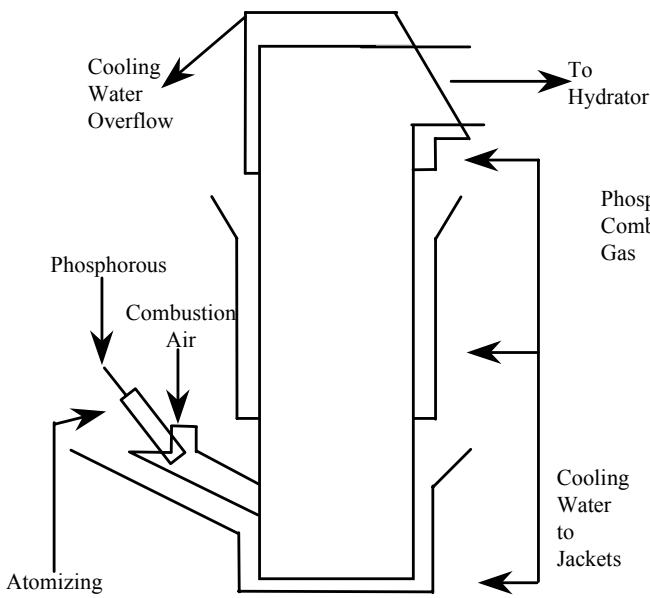
(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1982, pp. 426 - 442.)



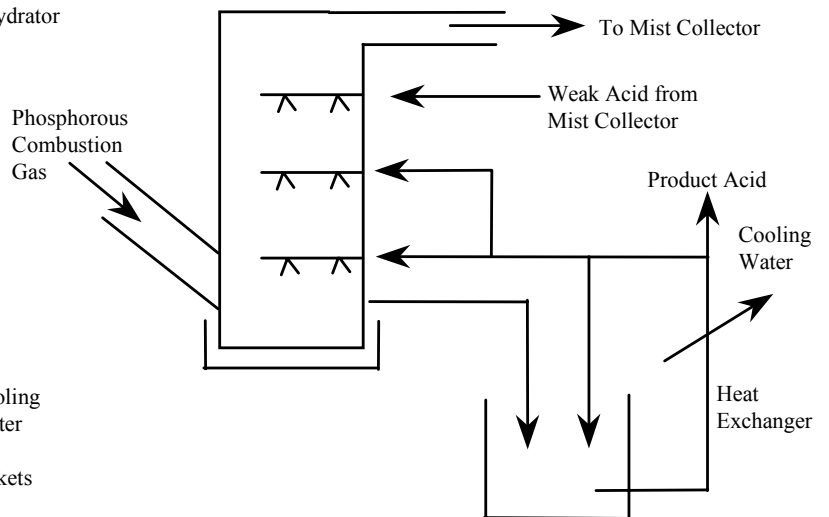
(a) Wetted-Wall Combustion Chamber



(b) Air-Cooled Combustion Chamber



(c) Water-Cooled Combustion Chamber



(d) Hydrator/Absorber

#### 4. Extraction/Beneficiation Boundaries

The furnace process uses a refined mineral commodity and as such, is completely outside the scope of the Mining Waste Exclusion.

##### SECTION 3: Ancillary Processes

Feed and fertilizer plants, as well as sulfuric acid plants, often are co-located with phosphoric acid facilities. This section describes production of many products related to phosphoric acid. Exhibit 5 presents an overview of phosphoric acid and related product manufacturing operations. All of these ancillary processes use a saleable commodity (merchant grade phosphoric acid) as the primary raw material and, therefore, are outside the scope of the Mining Waste Exclusion.

##### Fertilizer Operations

About 95 percent of commercial phosphoric acid is used to make ammoniated fertilizer and animal feed. Several facilities produce ammoniated fertilizers such as DAP (diammonium phosphate), MAP (monoammonium phosphate), and GTSP (granular triple superphosphate). MAP and DAP are generated by ammoniating phosphoric acid and GTSP manufacturing involves reacting phosphate rock and phosphoric acid.<sup>18</sup>

##### Animal Feed Production

Ammonia is reacted with defluorinated  $P_2O_5$  to produce the defluorinated ammonium phosphates Monofos and Duofos. Limestone is reacted with defluorinated  $P_2O_5$  to produce the defluorinated calcium phosphates Dynafos and Biofos. IMC in Mulberry, FL produces up to 2,500 tons per day of these products.<sup>19</sup>

##### Superphosphoric Acid Operations

Superphosphoric acid is produced from concentrated (54 percent) acid by heating it in a shell and tube heat exchanger, routing it to an evaporator to remove the remainder of the free water, and concentrating the acid to 70 percent. This product can be sold or further filtered. Metallic phosphates are filtered out and routed to the granulated fertilizer feed.<sup>20</sup>

Liquid fertilizer may be produced by first diluting the superphosphoric acid back to 54 percent then ammoniating the acid. Liquid fertilizer is a low volume specialized product produced only on a limited basis.<sup>21</sup>

##### Silicofluoride Recovery

In order to produce low-fluorine animal feed supplements,  $P_2O_5$  must be defluorinated. IMC in Mulberry, Florida defluorinates 600 tons per day of 54 percent  $P_2O_5$  in a batch tank using silica to remove fluoride. IMC uses

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<sup>18</sup> U.S. Environmental Protection Agency, Supplemental Information on Phosphoric Acid Production: Alternative Management of Process Wastewater at Phosphoric Acid Facilities, Office of Solid Waste, December 1990, pp. A1-5.

<sup>19</sup> Ibid., pp. A2-6.

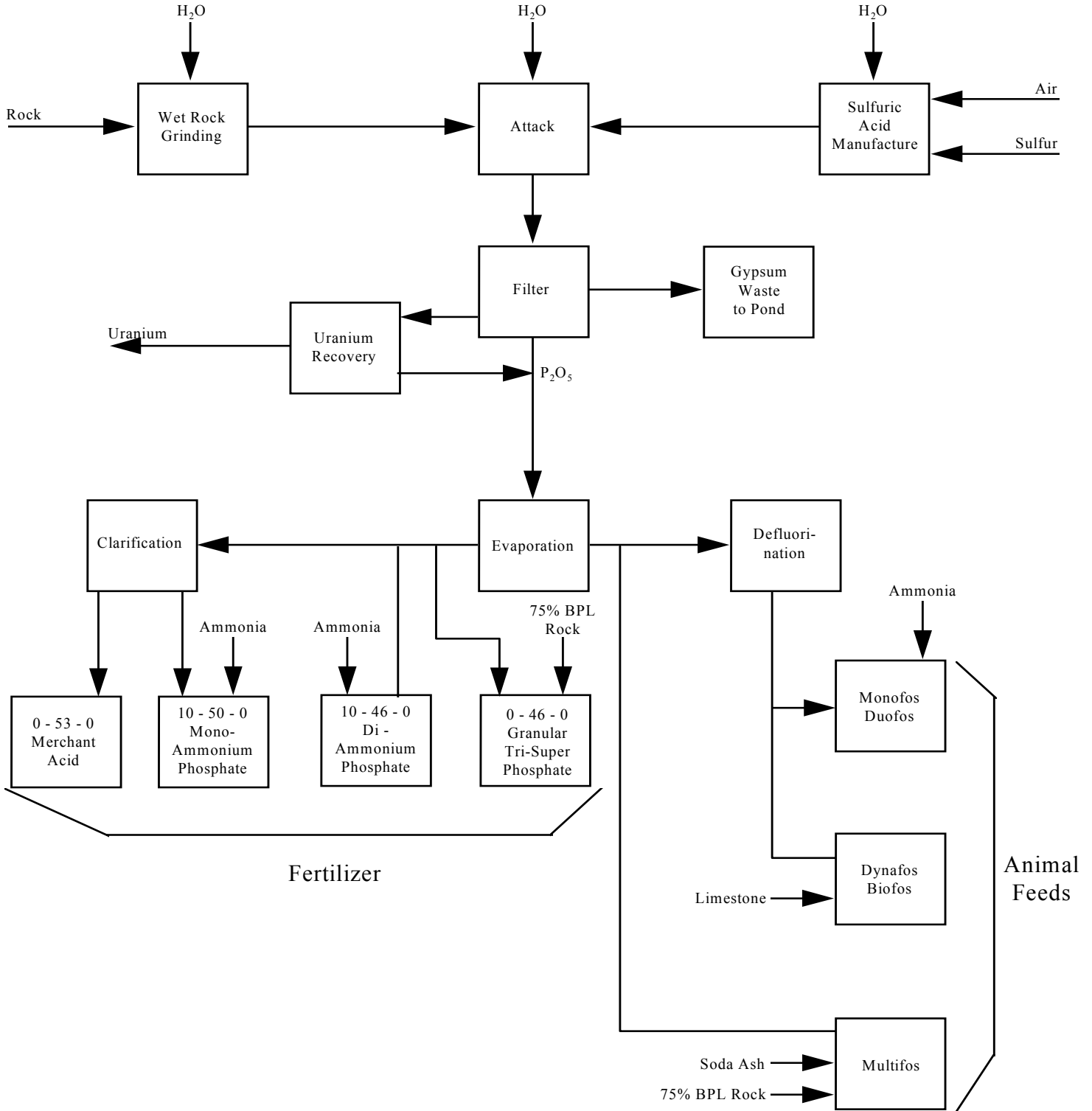
<sup>20</sup> Ibid.

<sup>21</sup> Ibid.

EXHIBIT 5

OVERVIEW OF PHOSPHORIC ACID AND RELATED PRODUCTS PRODUCTION

(Adapted from: Supplemental Information on Phosphoric Acid Production, 1990, pp. A2 - 11.)



16,000 gallons per minute of cooling pond water to condense vapors, which contain  $\text{SiF}_4$  and  $\text{P}_2\text{O}_5$ , from two evaporators using barometric condensers. Upon condensing, the  $\text{SiF}_4$  is converted to  $\text{H}_2\text{SiF}_6$ . IMC sends 6,000 gallons per minute of the flow to the Multifos plant; the remainder is returned to the cooling pond.<sup>22</sup> USAC in Ft. Meade, Florida recovers 25 percent fluosilicic acid (FSA) as a by-product from the phosphoric acid evaporators and from reaction vapors evolved from the reaction stage. Fluorine compounds are recovered from the vapor in fluosilicic absorption towers at a rate of 55 tons per day. Seventy-five percent of the fluoride present in the vapors is removed. USAC sells its recovered fluosilicic acid to a nearby ALCOA plant that manufactures aluminum fluoride.<sup>23</sup> Gardinier in Riverview, Florida also recovers FSA and in 1992 supplied 70 percent of the domestic market for drinking water fluoridation.<sup>24</sup> Agrico in Uncle Sam, Louisiana collects FSA and either sells it or processes it in an on-site plant to produce silicon tetrafluoride.<sup>25</sup> Agrico in Donaldsonville, LA sells the recovered FSA.

### **Multifos Plant**

IMC reacts non-defluorinated 54 percent  $\text{P}_2\text{O}_5$ , soda ash, and phosphate rock in a high temperature calcining kiln to produce 300 tons per day of tricalcium phosphate, also known as Multifos, another low fluorine animal feed supplement. Wastewaters from this process are returned to the cooling ponds at IMC.<sup>26</sup>

### **Sulfuric Acid Production**

Phosphate rock is reacted with sulfuric acid to make phosphoric acid. At many plants, sulfuric acid is produced on-site by burning sulfur. This process is exothermic and the heat generated is often used to run the plant. At Texasgulf in Aurora, North Carolina, fresh water is used to make sulfuric acid after being purified in a lime softening and ion exchange operation. Texasgulf has five sulfuric acid manufacturing process lines using double absorption with vanadium pentoxide catalysts. This produces 3.4 million tons of 95 percent acid annually.<sup>27</sup> IMC in Mulberry, Florida produces 13,000 tons per day of 98.5 percent sulfuric acid.<sup>28</sup> U.S. Agri-Chemicals in Fort Meade, Florida (USAC) produces sulfuric acid in two double absorption contact sulfuric acid manufacturing plants. Each plant has a capacity of 2,000 tons per day of 98 percent sulfuric acid.<sup>29</sup> Gardinier in Riverview, Florida also manufactures sulfuric acid for the wet process.<sup>30</sup>

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

None identified.

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<sup>22</sup> *Ibid.*, pp. A2-6.

<sup>23</sup> *Ibid.*, pp. A3-4.

<sup>24</sup> *Ibid.*, pp. A4-3.

<sup>25</sup> *Ibid.*, pp. A5-4.

<sup>26</sup> *Ibid.*

<sup>27</sup> *Ibid.*, pp. A1-3.

<sup>28</sup> *Ibid.*, pp. A2-3.

<sup>29</sup> *Ibid.*, pp. A3-2.

<sup>30</sup> *Ibid.*, pp. A4-2.

#### 4. Extraction/Beneficiation Boundaries

These processes use a saleable mineral commodity as the primary raw material and as such, are completely outside the scope of the Mining Waste Exclusion.

#### C. Process Waste Streams

##### 1. Extraction/Beneficiation Wastes

None are identified.

##### 2. Mineral Processing Wastes

###### Wet Process

**Process wastewater and phosphogypsum** are the primary waste streams from the wet process. These wastes have been classified as RCRA special wastes, and are exempt from Subtitle C regulation.

The fertilizer industry typically manages its waste streams in the aggregate. Aggregation allows heat that has built up in the system to assist natural evaporation in water management. Aggregate management of waste streams also is essential to maintaining the water balance at phosphate rock processing facilities. Control of the water balance requires close consideration of a number of factors, including the amount of rainfall, the watershed area, and evaporation rates. Generally across the industry, more than 90 percent of the water used is recycled. Because production and cooling are primary uses, water is generally recycled through cooling ponds. The constant reuse and recycling of water results in buildup of acidity to the point that the recirculating water has significant acid values that make it valuable for reuse and causes it to exhibit the corrosivity characteristic.<sup>31</sup>

**Waste scale.** This waste is generated at a rate of 41,700 to 208,300 metric tons per year and is generally sent to a cooling pond.<sup>32</sup> This waste is not expected to be hazardous.

###### Furnace Process

The furnace process uses a refined mineral commodity (elemental phosphorus) and therefore is completely outside the scope of the Mining Waste Exclusion.

**Arsenic sulfide sludge.** Approximately 0.28 kg per kkg of product of arsenic sulfide is formed during product purification.<sup>33</sup>

**Spent filter cake** is a possible waste stream generated from the production of phosphoric acid by the furnace process.

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<sup>31</sup> The Fertilizer Institute. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1995.

<sup>32</sup> U.S. Environmental Protection Agency, Technical Background Document, Data and Analyses in Support of the Regulatory Determination for Special Wastes from Phosphoric Acid Production, Office of Solid Waste, Special Waste Program, 1991.

<sup>33</sup> U.S. Environmental Protection Agency, Supplemental Information on Phosphoric Acid Production: Alternative Management of Process Wastewater at Phosphoric Acid Facilities, Office of Solid Waste, December 1990, pp. A1-5.

### 3. Other Related Wastes

The other related wastes described below are commonly found at phosphoric acid facilities, but are outside of the scope of the Mining Waste Exclusion because they are associated with activities that are downstream of mineral processing and use a saleable commodity as the primary raw material.

#### Ammoniated Fertilizer Production

**Process wastewater** is a likely waste stream from ammoniated fertilizer production. In 1991, the waste generation rate for process wastewater from ammoniated fertilizer production was 132,517,000 metric tons per year.<sup>34</sup> This wastewater may be discharged to a cooling pond and may have a low pH.

**Sludge** is a likely waste stream from ammoniated fertilizer production.

#### Animal Feed Production

**Process wastewater** is a likely waste stream from animal feed production.

**Sludge** is a likely waste stream from animal feed production. The 1991 waste generation rate for this waste stream was 400 metric tons per year.<sup>35</sup>

#### Superphosphoric Acid Production

**Sludge** is a likely waste stream from superphosphoric acid production.

#### Silicofluoride Recovery

**Filter cake** and **process wastewater** are the waste streams likely to result from silicofluoride recovery operations.

#### Sulfuric Acid Production

**Process wastewater** is a likely waste stream from sulfuric acid production. This waste is generated from an ancillary process and as such is outside the scope of this report. At Texasgulf in Aurora, North Carolina, this process wastewater from sulfuric acid production has a pH of about 10 and goes to a neutralization plant. In 1990, the wastewater was discharged via an NPDES outfall at a rate of 80-100,000 gpd.<sup>36</sup> IMC in Mulberry, Florida and USAC in Ft. Meade, Florida create a cooling tower blowdown of pH 7 and a boiler blowdown of pH 11-12. USAC sends these wastewaters to a cooling pond. At IMC, sulfuric acid plant blowdown is kept separate from other process wastewater and is sent to a utility pond.<sup>37</sup>

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<sup>34</sup> Ibid.

<sup>35</sup> U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, Vol. I, August 1992, pp. I-2 - I-8.

<sup>36</sup> U.S. Environmental Protection Agency, Op. Cit., 1990, pp. A1-3.

<sup>37</sup> Ibid., pp. A2-3.

On-site production of sulfuric acid for acidulation of phosphate rock also generates secondary materials such as sulfuric acid production vessel cleanout residues. About once a year, small amounts of secondary materials, such as precipitates are removed from sulfuric acid process vessels and product storage tanks.<sup>38</sup>

#### **D. Non-uniquely Associated Wastes**

Wastes associated with the ancillary processes often found at phosphoric acid plants are not uniquely associated because they are generated from chemical manufacturing activities, not from mineral processing. These wastes include the wastewaters, sludge, and filtercake (described above) resulting from the production of ammoniated fertilizer, animal feed, sulfuric and superphosphoric acid, and silicofluoride recovery.

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), 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**

One commenter provided additional factual information about the phosphoric acid production process (COMM 45). This information, where appropriate, has been included in the sector report.

##### **Sector-specific Issues**

The commenter also addressed the potential negative implications of the Bevill mixture rule at phosphoric acid production facilities. The commenter noted that materials such as precipitates removed from sulfuric acid vessels and sulfuric acid spills may contain significant acid and sulfur values that can be useful in the phosphoric acid production process. The same may be true for wastes generated by recharging spent ion exchange resins (H<sub>2</sub>SO<sub>4</sub> and NaOH). According to the commenter, the Bevill Mixture Rule requires these materials to be neutralized before being reused, resulting in a loss of the sulfur and acid values (COMM 45).

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<sup>38</sup> The Fertilizer Institute. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1995.

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**PLATINUM GROUP METALS (PGM)**

**A. Commodity Summary**

The platinum-group metals refer to six metals: platinum, palladium, rhodium, ruthenium, iridium, and osmium. Commercially, the two most important metals are platinum and palladium. All of the platinum-group metals are valued for their corrosion resistance and their catalytic activity.<sup>1</sup> According to the U.S. Bureau of Mines, ore containing the platinum-group metals is mined, concentrated, and smelted in Montana. The resulting platinum-group matte is sent to Belgium to be refined and separated. Additionally, platinum-group metals are recovered as byproducts of copper refining by two companies in Texas and Utah. Approximately 30 firms refine secondary metal domestically. Platinum-group metals are used by the following industries: automotive, electrical and electronic, chemical, dental, and medical. The metals are primarily used as catalysts in the automotive and petroleum refining industries.<sup>2</sup> Domestic production was reported as 60,000 kilograms in 1994 (sales as reported to industry) and apparent domestic consumption was estimated at 127,000 kilograms during the same period.<sup>3</sup> Exhibit 1 presents the names and locations of all the facilities involved in the production and refining of platinum-group metals.

The six platinum-group metals can be separated into three pairs: platinum and palladium, ruthenium and osmium, and rhodium and iridium. Each pair exhibits similar physical and metallurgical properties. Platinum and palladium are corrosion resistant and the most malleable. Ruthenium and osmium have the strongest abrasion resistance. Osmium alloys are used as pen tips and ruthenium is used as an electrical contact and as a titanium coating alloy. Rhodium and iridium are the least abrasion resistant and often used as alloying elements for platinum. Rhodium, palladium, and platinum are also used as an automotive catalyst for NO<sub>x</sub> reduction<sup>4</sup>, and platinum is used in both automobile oxygen sensors and spark plugs.<sup>5</sup>

**EXHIBIT 1**

**SUMMARY OF PLATINUM-GROUP METALS PROCESSING FACILITIES**

Facility Name	Location	Type of Operations (source)
Stillwater Mine	Nye, MT	Mining and Beneficiation <sup>a</sup>
Allied Signal	Tulsa, OK	Secondary (spent automotive catalysts)
Allied Precious Metals	Tucson, AZ	Secondary (solutions and sludges)
ASARCO	Amarillo, TX	Secondary
AT & T Metals	Staten Island, NY	Secondary (electronic scrap)
Colonial Metals	MD	Secondary (spent industrial catalysts)
Degussa Corp.	South Plainfield, NJ	Secondary (solutions, electronic scrap, catalysts)

<sup>1</sup> J. Roger Loebenstein, "Platinum-Group Metals," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 995.

<sup>2</sup> J. Roger Loebenstein, "Platinum-Group Metals," from Mineral Commodity Summaries, 1995, pp. 126-127.

<sup>3</sup> J. Roger Loebenstein, 1995, Op. Cit., p. 126.

<sup>4</sup> U.S. Environmental Protection Agency, "Platinum-Groups Metals," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, Office of Solid Waste, p. 3-159.

<sup>5</sup> J. Roger Loebenstein, 1992, Op. Cit., p. 997.

**EXHIBIT 1**

**SUMMARY OF PLATINUM-GROUP METALS PROCESSING FACILITIES (CONTINUED)**

Facility Name	Location	Type of Operations (source)
Eastern Smelting and Refining Corp.	Lynn, MA	Secondary (solutions, sludges, catalysts)
Engelhard Corp	Iselin, NJ	Secondary (spent industrial catalysts, electronic scrap)
Gemini Industries	Santa Ana, CA	Secondary (spent industrial catalysts, petroleum catalysts)
Handy and Harman	Fairfield, CT	Secondary
Handy and Harman	South Windsor, CT	Secondary (filter cake, metallic scrap, spent automotive catalysts)
Hauser & Miller	St. Louis, MO	Secondary
JM Ney Co	Bloomfield, CT	Secondary
Johnson Matthey	West Deptford, NJ	Secondary (filter cake, spent automotive catalysts, solutions, unrefined ingot)
Kinsbursky Brothers	Anaheim, CA	Secondary (solutions, electronic scrap, spent automotive catalysts)
Kennecott Copper	Magma, UT	Hydrometallurgical precious metals plant recovers platinum from tankhouse slimes from ore. <sup>6</sup>
Leach and Garner	Attleboro, MA	Secondary
Leytess Metal and Chemical	New York, NY	Secondary
LG Balfour CO	Attleboro, MA	Secondary
Martin Metals	Los Angeles, CA	Secondary (electronic scrap, solid scrap)
McRilley Mark Co.	CA	Secondary
Multimetco, Inc.	Anniston, AL	Secondary (spent automotive catalysts)
Noranda/Micrometallics Corp.	San Jose, CA	Secondary (electronic scrap, filter cakes, sludges, solutions, catalysts, filter media)
Noranda Sampling	Providence, RI	Secondary (electronic scrap, solid scrap)
PGP Industries, Inc.	Santa Fe, CA	Secondary (spent industrial catalysts, sludges, electronic scrap)
Sabin Metals	Rochester, NY	Secondary (electronic scrap, filter cakes, solid scrap)

<sup>6</sup> Kennecott 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.

## EXHIBIT 1

### SUMMARY OF PLATINUM-GROUP METALS PROCESSING FACILITIES (CONTINUED)

Facility Name	Location	Type of Operations (source)
Sipi Metals	Chicago, IL	Secondary (electronic scrap)
Southwest Smelter & Refining	Dallas, TX	Secondary
Stern Metals	Attleboro, MA	Secondary
Techamet, Inc.	Houston, TX	Secondary (spent automotive catalysts, petroleum catalysts)
Technic, Inc.	Providence, RI	Secondary
Texas Instruments	MA	Secondary
Trifari, Krussman	Providence, RI	Secondary
William Gold Refining	Buffalo, NY	Secondary

<sup>6</sup>Stillwater Mines sends ore to its smelter facility in Columbus, MT.<sup>7</sup>

After the ores have been smelted, Stillwater Mines ships the platinum-group metal concentrate to Brussels, Belgium for refining. The concentrates are toll refined and although Stillwater Mines retains ownership of the metals, the products are generally sold overseas.<sup>8</sup>

#### B. Generalized Process Description

##### 1. Discussion of Typical Production Processes

Platinum-group metals can be recovered from a variety of different sources, including electrolytic slimes from copper refineries or metallic ores. Secondary platinum-group metals can also be recovered from used equipment, precious metal scrap, petroleum, and spent catalysts (both industrial and automotive). Each source is associated with a distinct recovery process. In one process the insoluble slimes from copper refining are collected and processed to recover any residual metal content. Alternatively, the production of platinum-group metals from ore involves mining, concentrating, smelting, and refining. In the concentrating step, platinum ore is crushed and treated by froth flotation. The concentrates are dried, roasted (sometimes), and fused in a smelter furnace. This step results in the production of a platinum-containing sulfide matte. Solvent extraction is used to separate and purify the six platinum-group metals in the sulfide matte.<sup>9</sup> Secondary platinum group metals recovered from scrap and spent catalysts are refined and used in the fiber glass industry and various catalytic applications.

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<sup>7</sup> Personal Communication between ICF Incorporated and J. Roger Loebenstein, U.S. Bureau of Mines. October 17, 1994.

<sup>8</sup> *Ibid.*

<sup>9</sup> J. Roger Loebenstein, 1992, *Op. Cit.*, pp. 995-996.

## 2. Generalized Process Flow Diagram

There are several methods for recovering and refining platinum-group metals, depending on the source material used. Exhibit 2 presents the process flow diagrams for the recovery process of the platinum-group metals from electrolytic slimes. Platinum metals can also be recovered from the ores or from scrap materials. After recovery and initial processing, the concentrates are sent for refining. Exhibit 3 presents a typical refining process used to separate each of the six platinum-group metals from a concentrate.

### Recovery From Electrolytic Slimes

Often, platinum-group metals are recovered from the slimes that collect in the electrolytic refining cells used at copper refineries. These slimes are the insoluble material from impure copper anodes that are dissolved as part of the copper refining process. As shown in Exhibit 2, after the slimes are heated,  $H_2SO_4$  is added to the dried slimes which then undergo an acid digestion step. Following acid digestion, the slimes are often, but not always, roasted and then processed by several leaching steps to remove any remaining copper. After the leaching, the resultant decopperized slimes are melted with a soda-silica flux in a reverberatory furnace. This flux helps in the formation of a siliceous slag which is removed from the furnace. Air is then blown through the molten metal followed by the addition of a lime flux. The air oxidizes any remaining lead and the lead oxide forms a slag with the lime which is then removed from the furnace. The siliceous and lead slags are either recycled or sent to a lead smelter. Following slag removal, fused soda ash is added to the furnace to form soda slag which is also removed and sent off-site for tellurium and selenium recovery. The resultant metal is a dore alloy composed of gold, silver, and platinum-group metal and is processed to recover these metal values.<sup>10</sup>

### Recovery From Metal Ores

Although alluvial deposits are the result of natural concentration processes involving weathering and gravity separation phenomena, further treatment is required to yield a product suitable for marketing and refining. At Stillwater, Montana, platinum and palladium are recovered via froth flotation of sulfide minerals. The ore is sent to a concentrator, followed by froth flotation, and then sent to a smelter operation in Columbus, Montana. The resulting precious metals matte (solid form) is then sent to MHO metallurgy in Belgium for refining.<sup>11</sup>

An alternative method of recovering platinum-group metals from ore in South Africa involves initial treatment to reduce the ore to a suitable size via crushing, followed by froth flotation to separate out the platinum-group metal particles. The flotation concentrates are separated into platinum-bearing minerals and free-metallic particles by conventional gravity methods. The remainder is further concentrated by smelting, oxygen blowing, magnetic separation, and pressure leaching.

The froth can be prepared for smelting by thickening, filtering, drying, and pelletizing. The pellets are smelted in an electric smelter with submerged-arc consumable electrodes. Fluxes and additions are made during smelting to obtain a matte that contains principally copper-nickel-iron and platinum-group metals. The matte is then treated by oxygen blowing to produce a high grade matte. The matte is crushed, ground, and magnetically separated. Any non-magnetic portion is treated by pressure leaching to release copper, nickel, and cobalt. The remaining solution is recirculated back into the magnetic stream and this mixture is then pressure leached, yielding a final concentrate. This concentrate along with the mineral material released previously are sent to a refinery for further treatment.<sup>12</sup>

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<sup>10</sup> U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-159.

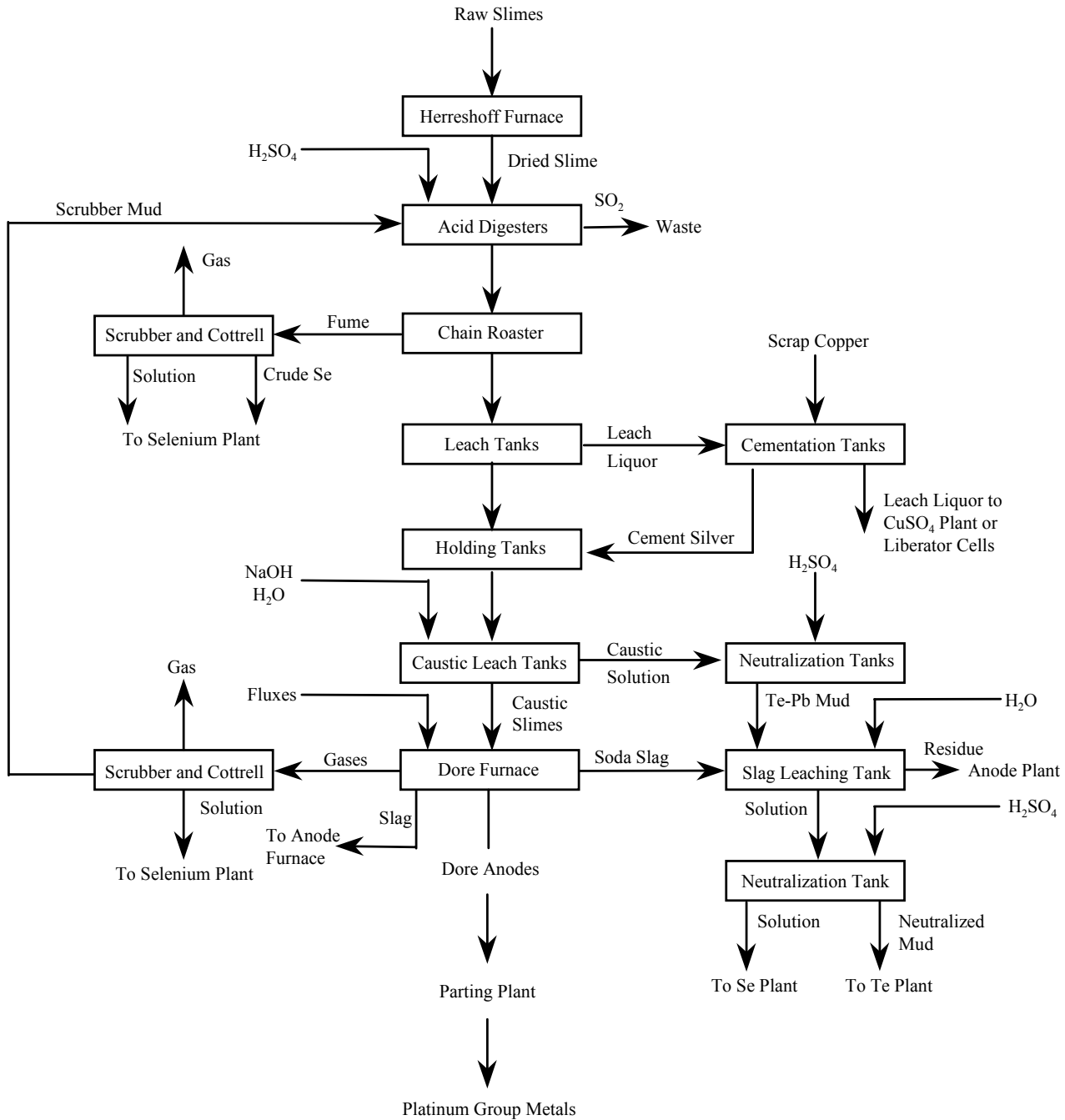
<sup>11</sup> Personal Communication between Jocelyn Spielman, ICF Incorporated and J. Roger Loebenstein U.S. Bureau of Mines, October 17, 1994.

<sup>12</sup> "Platinum-Group Metals," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed. Vol. XVIII, 1982, p. 234.

## EXHIBIT 2

### PLATINUM GROUP METAL RECOVERY FROM COPPER REFINING SLIMES

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-158 - 3-163.)



## Refining

Stillwater Mine sends the platinum-group metal concentrate out of the country for refining after it is processed at their smelting facility in Columbus, Montana.<sup>13</sup> Other platinum-group metals facilities in the United States refine secondary platinum-group metals from used equipment, scrap metals, petroleum, and spent catalysts. The refining process takes advantage of the solubility of platinum and palladium. Each platinum group metal is removed from the platinum-group metal concentrate in order of its solubility. Exhibit 3 presents the typical order of removal. In general, platinum and palladium are removed first, followed by rhodium, ruthenium, osmium, and iridium. Exhibit 3 also presents various compounds that may be produced through further purification of each individual platinum-group metal.

### *Platinum and palladium*

Most refining procedures are based on the ready solubility of gold, platinum, and palladium in aqua regia and the ease with which gold can be reduced to the metallic form from the chloride solution by the addition of ferrous salts or sulfur dioxide. Solvent extraction is used as an alternative method for separating gold at some refineries.<sup>14</sup> In the aqua regia refining process, platinum metal concentrates are treated with aqua regia to dissolve platinum, palladium, and gold. The other platinum-group metals (ruthenium, osmium, iridium, and osmium) and silver are insoluble. After the gold is separated from the solution either by reduction or solvent extraction, the remaining solution is treated with ammonium chloride to precipitate the platinum as ammonium chloroplatinate. The palladium remains in solution.<sup>15</sup>

The filtrate from the platinum-recovery contains palladium chloride and can be treated with ammonia and hydrochloric acid. The solution is heated to yield a solution of palladium (II) tetrammine dichloride. The addition of hydrochloric acid causes the formation of palladium dichloride diammine as a precipitate which can easily be dissolved in cold dilute ammonia. The resultant high-purity salt, when heated, can be converted readily into metal. Some refineries reduce pure palladium salt to palladium black with formic acid. The palladium black can then be ignited to form a palladium sponge. The aqueous byproducts of the formic acid are easier to handle than the corrosive fumes that result from firing the salts.<sup>16</sup>

The undissolved materials remaining after the aqua regia and any platinum-group metals recovered after the removal of platinum and palladium from solution are combined with concentrates high in rhodium, ruthenium, and iridium. Fluxing materials, such as lead carbonate plus carbon, are added, following which the mixture is heated. The molten charge is poured into a conical mold and solidified. After solidification, the slag is removed and the lead which contains rhodium, iridium, ruthenium, and silver is melted, granulated, and treated with nitric acid. The lead and silver are dissolved and removed, leaving an insoluble residue containing the platinum-group metals.<sup>17</sup>

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<sup>13</sup> Personal Communication between ICF Incorporated and J. Roger Loebenstein, U.S. Bureau of Mines, October 17, 1994.

<sup>14</sup> "Platinum-Group Metals," 1982, *Op. Cit.*, p. 238.

<sup>15</sup> *Ibid.*

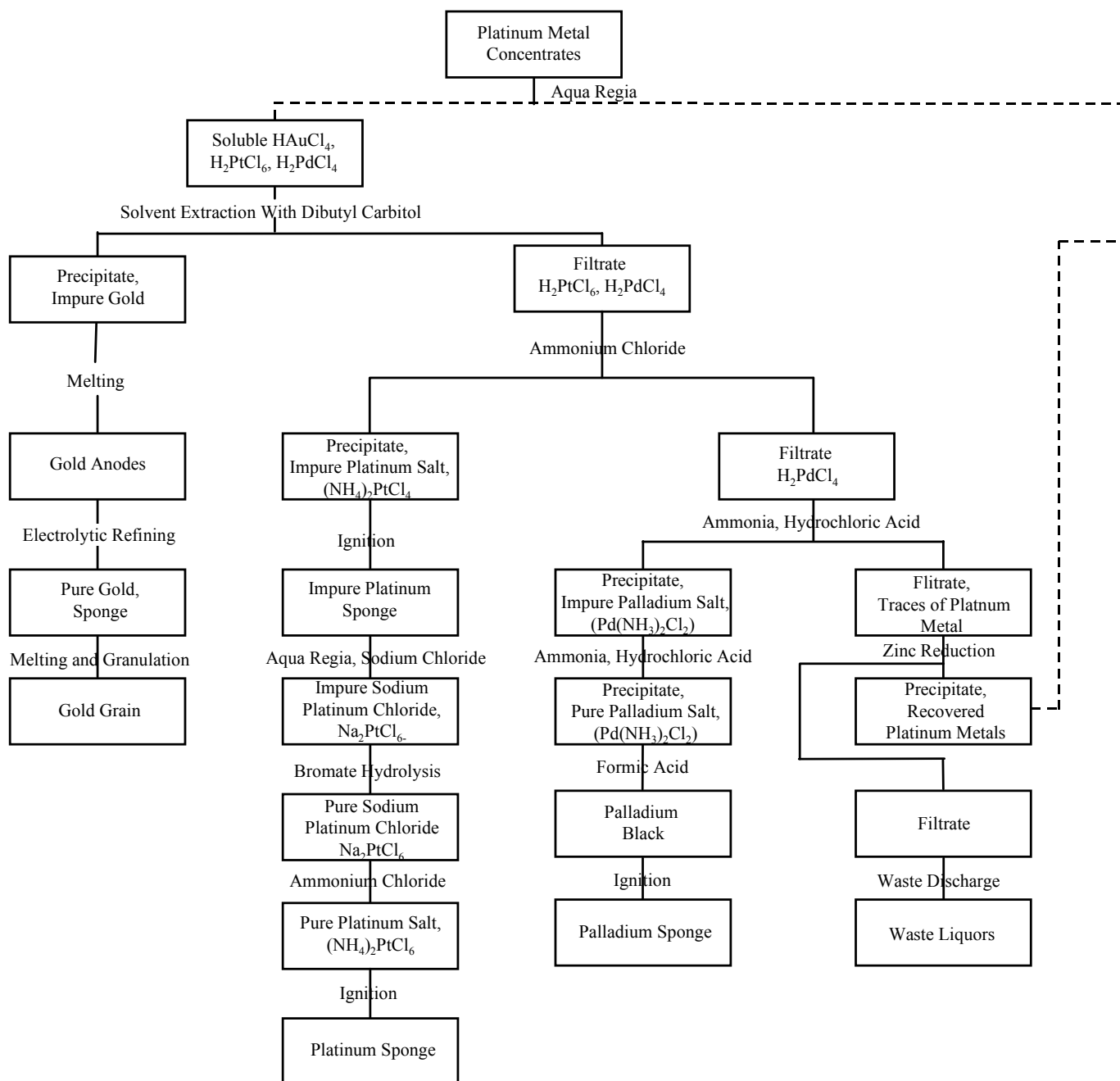
<sup>16</sup> *Ibid.*

<sup>17</sup> *Ibid.*

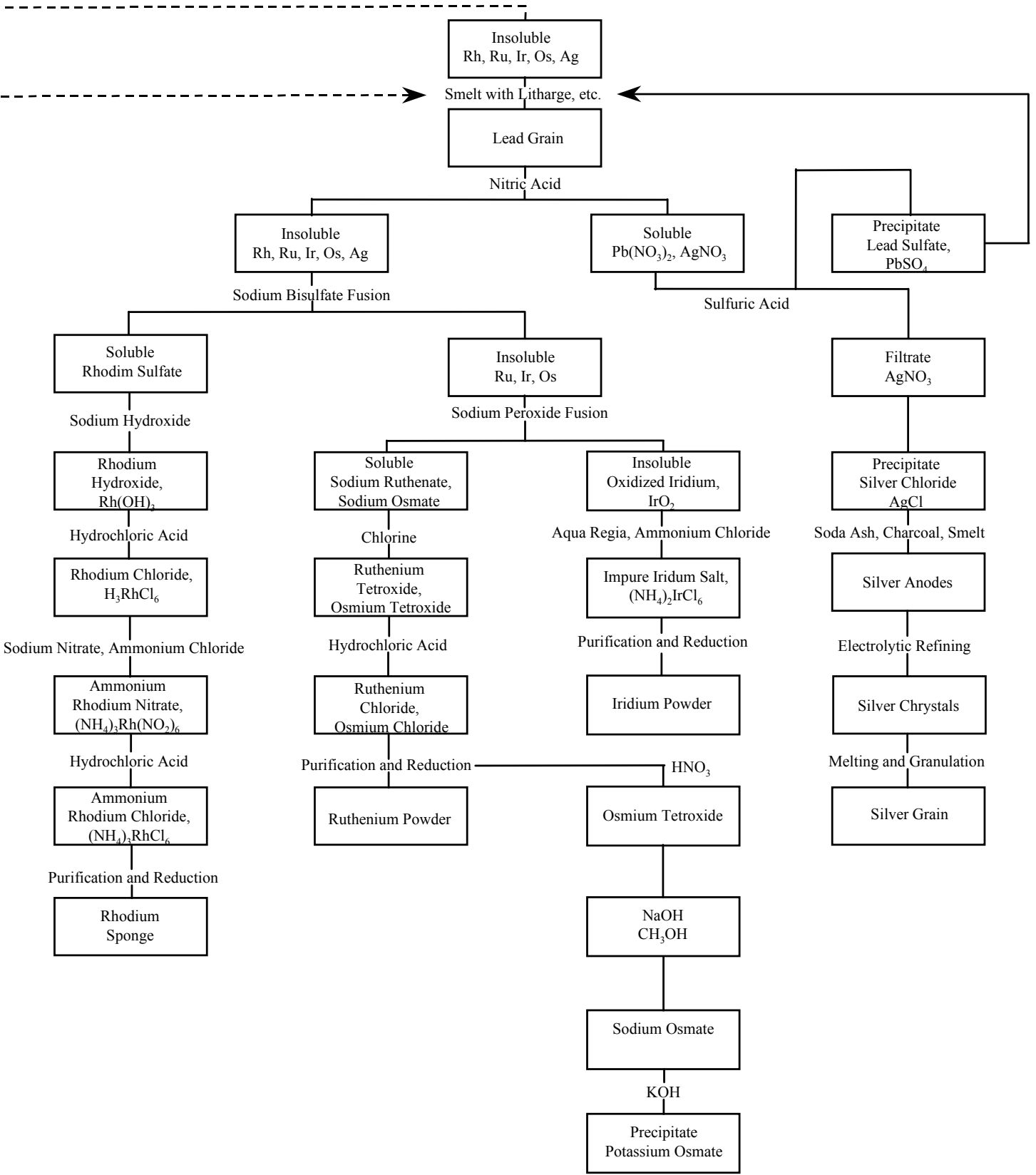
### EXHIBIT 3

## PLATINUM GROUP METAL REFINING

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1982, pp. 228 - 239.)



**EXHIBIT 3 (Continued)**





### *Rhodium*

The residue is then treated with sodium bisulfate and heated to 500° C to convert rhodium into the sulfate. After sodium hydroxide is added, the resultant crude hydroxide is precipitated out, washed, dissolved in hydrochloric acid (HCl), neutralized with sodium carbonate and treated with sodium nitrite. These steps yield the stable complex  $(\text{NH}_4)_3[\text{Rh}(\text{NO}_2)_6]$ . The contaminating base metals can be precipitated out of solution through hydrolysis, while leaving rhodium in solution. Rhodium can be precipitated by the addition of ammonium chloride, following which the ammonium salt is treated with HCl and the solution is passed through an ion exchange column. Ion exchange separates ammonium and any base metals from the high-purity rhodium, leaving it in solution. The rhodium is precipitated as finely divided metal by boiling with formic acid. After washing, the metal is ignited then cooled under hydrogen.<sup>18</sup>

### *Ruthenium*

The ruthenium, osmium, and iridium residue from the bisulfate fusion is mixed with sodium peroxide and heated to 500° C, yielding sodium ruthenate and sodium osmate. These compounds are dissolved in water and treated with chlorine in a distillation apparatus. The resultant ruthenium tetroxide and osmium tetroxide are absorbed in dilute HCl. After boiling, the chloride solution is mixed with nitric acid to remove osmium. The mixture is then treated with ammonium chloride to yield ammonium chlororuthenate crystals. The latter are washed and ignited to yield ruthenium which is treated and cooled in hydrogen to give pure ruthenium powder.<sup>19</sup>

### *Osmium*

Osmium tetroxide is produced in the same process as ruthenium tetroxide. After the osmium is removed from the ruthenium solution, the osmium tetroxide is then converted to sodium osmate. The addition of KOH causes the formation of precipitate potassium osmate. The salt is stored and can be converted to osmium metal.

### *Iridium*

The insoluble iridium dioxide is converted with aqua regia to the chloride which is then precipitated with additional nitric acid and ammonium chloride. This salt is dissolved in a dilute ammonium sulfide solution in which impurities precipitate as sulfides, whereas the iridium remains in solution. Treatment with nitric acid and ammonium chloride yields pure ammonium chloroiridate which, upon ignition and reduction by hydrogen, yields pure iridium powder.

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

None Identified.

### **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.

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<sup>18</sup> Ibid.

<sup>19</sup> 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 this specific mineral commodity sector, the beneficiation/processing line occurs between froth flotation and smelting for the recovery of platinum group metals from metal ores. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the sulfide mineral ore occurs. EPA also determined that all wastes generated during the recovery of platinum group metals from copper electrolytic slimes are mineral processing wastes. 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

Although Exhibits 2 and 3 identify the following wastes as associated with the production of platinum-group metals, no characterization, generation, or management data are available for these wastes.

#### Concentration

**Tailings and Filtrate.** Tailings are generated during the froth filtration and sent to a tailings pond for disposal.

**Wastewater.** Wastewater from the thickening process is likely to contain heavy metals.

### 2. Mineral Processing Wastes

#### Recovery

**Scrubber Off-gases.** As shown in Exhibit 2, off gases are generated from the scrubber following roasting.

**SO<sub>2</sub> Waste.** As shown in Exhibit 2, waste sulfur dioxide is produced from acid digestion.

## Smelting

**Slag.** The slag generated during smelting is likely to contain metallic particles and may be crushed and blended with concentrate for recycling to the electric furnace.<sup>20</sup> 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 5 metric tons/yr, 46 metric tons/yr, and 460 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of toxicity (lead and selenium). This waste is classified as a by-product.

## Refining

**Spent Solvents.** After dissolving the material to be refined in aqua regia, a series of elements (e.g., gold, platinum, and palladium) are precipitated from the solution. 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 300 metric tons/yr, 1,700 metric tons/yr, and 3,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (lead and silver) and ignitability.

**Spent Acids.** Following solvent extraction, the insoluble platinum-group metals (e.g., rhodium, iridium, osmium, and ruthenium) are separated to yield pure metals. The resultant wastes from these processes would most likely be spent acids which might contain residual metals.<sup>21</sup> 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 300 metric tons/yr, 1,700 metric tons/yr, and 3,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (lead and silver), corrosivity, and reactivity.

### **D. Non-uniquely Associated Hazardous Wastes**

Non-uniquely associated 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), and acidic tank cleaning wastes.

### **E. Summary of Comments Received by EPA**

#### **New Factual Information**

One comment was received to correct information about one facility in Utah. EPA has incorporated this new information into the document. (COMM 40)

#### **Sector-specific Issues**

None.

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<sup>20</sup> Gregg J. Hodges, et. al., "Stillwater Mining Co.'s precious metals smelter: From pilot to production, Mining Engineering, July 1991.

<sup>21</sup> U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-162.

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## PYROBITUMENS, MINERAL WAXES, AND NATURAL ASPHALTS

### A. Commodity Summary

Bituminous materials comprise a group of hydrocarbons including pyrobitumens, mineral waxes, and asphalts. Pyrobitumens are mined predominately in Utah and are used in rubber, paints, varnishes, and insulating and waterproofing compounds.

Mineral waxes are not present in the United States as a natural substance, and therefore, must be extracted from lignite or cannel coal. Although coal exists in many parts of the United States, the only known production of mineral waxes from coal occurs in California. The use of this extraction product, known as "Montan Wax," is limited to paints, wood fillers, floor polish, rubber mixtures, and candles.

In the United States, naturally occurring asphalt (gilsonite) is found in commercial quantities only in eastern Utah and western Colorado. There are three types of naturally occurring asphalt: native asphalt (bitumen), lake asphalt, and rock asphalt.<sup>1</sup> Asphalts have a variety of uses including paving, flooring, roofing, and waterproofing. American Gilsonite in Bonanza, Utah is the world's largest producer and exporter of gilsonite (natural asphalt). The only other producer of natural asphalt is Ziegler Chemical and Mineral Corporation, also in Utah.

### B. Generalized Process Description

#### 1. Discussion of Typical Production Processes

The production processes associated with the production of pyrobitumens, mineral waxes, and natural asphalts are limited to a few simple operations, including extraction, grinding, blending, and packaging. Exhibits 1 through 3 present simplified process flow diagrams for the production of pyrobitumens, mineral waxes, and natural asphalts. The production processes and wastes associated with each mineral commodity are discussed below.

#### 2. Generalized Process Flow Diagram

##### Pyrobitumens

As shown in Exhibit 1, the production process for pyrobitumens consists of cracking in a still, recondensing, and grading. Due to the low cost and availability of petroleum refining substitutes, the production of pyrobitumens appears to be low.

##### Mineral Waxes

As shown in Exhibit 2, mineral wax processing consists of solvent extraction from lignite or cannel coal. Cannel coals yield a material that contains 60 to 90 percent light yellow or brown waxy substances. The crude wax is refined by extracting, typically with a mixture of benzene and methanols. Distilling the solvent leaves a wax too darkly colored to be used without added refining. Acid mixtures are used to oxidize and remove the dark materials, leaving a series of bleached waxes.<sup>2</sup> The extraction product is known as "Montan Wax." Extraction solvents used in the production of mineral waxes may be listed in 40 CFR 261 Subpart D.<sup>3</sup>

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<sup>1</sup> "Asphalt," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. III, 1992, pp. 689-724.

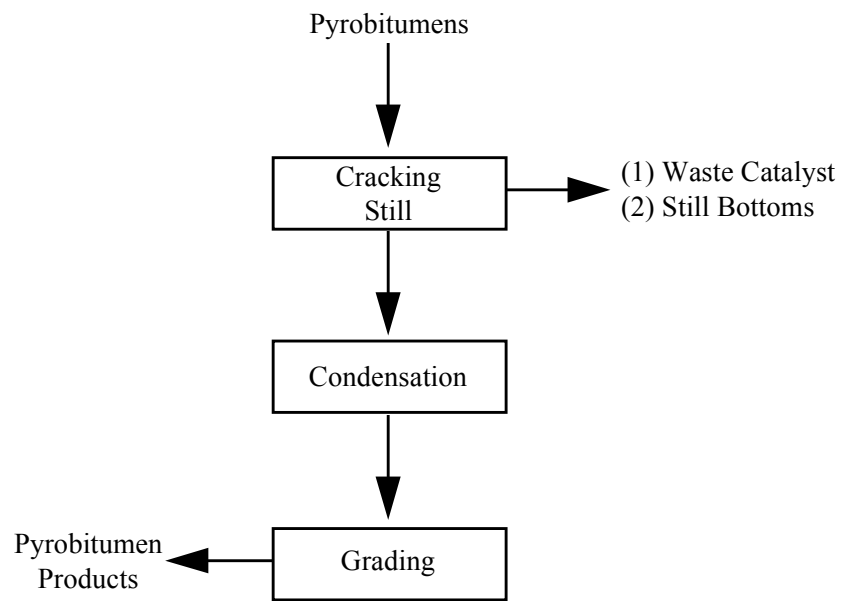
<sup>2</sup> "Lignite," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. XV, 1995, p. 316.

<sup>3</sup> U.S. Environmental Protection Agency, Technical Background Document, Development of the Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, Office of Solid Waste, 1989, pp. A-9.

**EXHIBIT 1**

**PYROBITUMEN PROCESSING**

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988.)

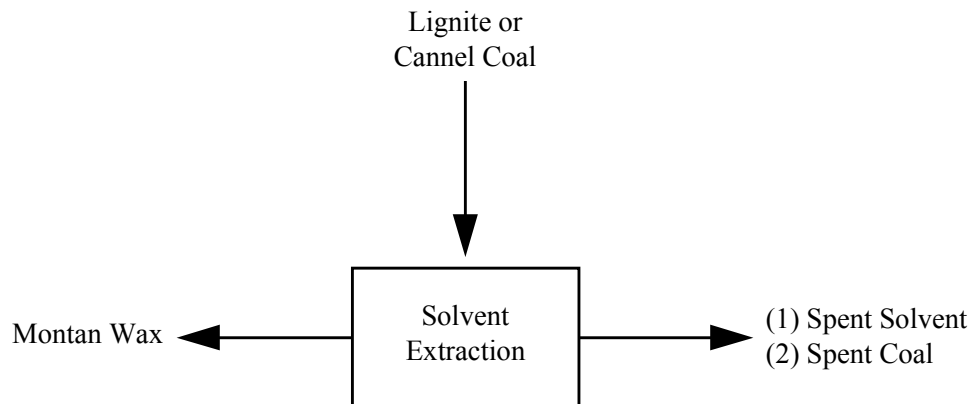


Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988.

**EXHIBIT 2**

**MINERAL WAX PRODUCTION**

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988.)



Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988.

### Natural Asphalts

American Gilsonite operates a 110 ktpy facility in Bonanza, Utah. Mine development begins with the boring of shafts. The shafts are equipped with steel inserts that are comprised of four pipes equally spaced around the perimeter of the shaft. Once a shaft is bored, inserts are lowered into the borehole. As each section is lowered into the shaft the next section is lined up with it, and the two are welded together at the surface. This procedure is repeated until the inserts line the shaft from top to bottom. When a mine is worked out the liner assembly is pulled and reused. Hand-held pneumatic chipping hammers with moilpoint bits are used to break out the ore. Broken ore flows by gravity to the toe of the sloping face at the floor of the drift. From there it is airlifted to the surface through a pipe. When air lifted ore reaches the surface it enters a baghouse. The larger pieces drop first, and the rest is collected in filter bags. All solids are discharged into elevated storage bins and are then transferred by truck to a processing plant.

American Gilsonite's plant consists of concrete storage silos, truck receiving bins, a vibrating bed dryer, pulverizing machinery, and packaging equipment. Pneumatic conveying systems and sophisticated dust control equipment are state-of-the-art and allow for the handling of gilsonite in large quantities. Before entering the processing plant, gilsonite ore is segregated by grade in receiving bins. From these bins the ore is processed through a vibrating bed dryer, where excess moisture is removed. It is then passed over a double-deck screen, where it is classified according to particle size for storage in silos. From the silos, ore is fed to product bins from which it is either loaded directly as bulk product, fed to a bagging machine, or fed to a pulverizer. Pulverized product is segregated into product bins from which it can be loaded directly as bulk product or packaged at a second bagging machine.<sup>4</sup> Exhibit 3 contains the natural asphalt production process diagram.

### **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

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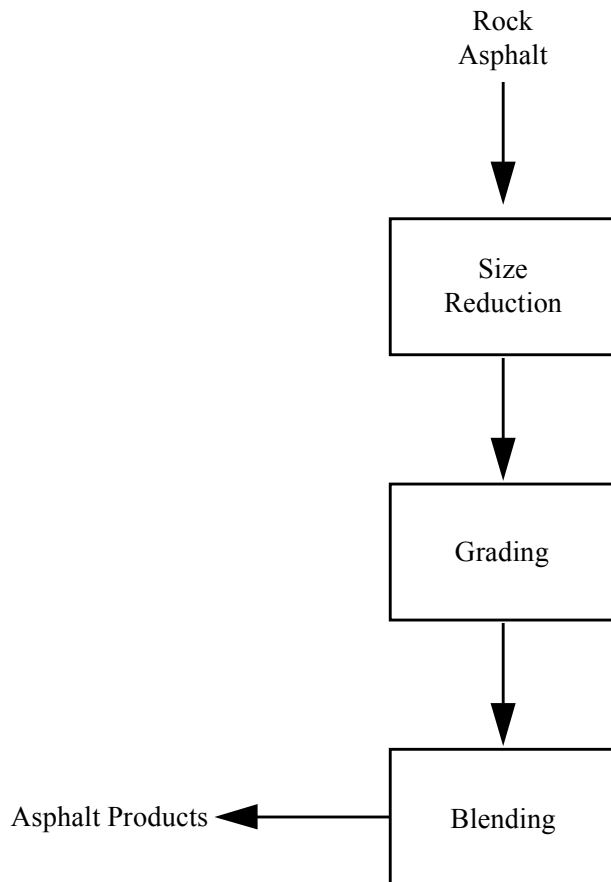
<sup>4</sup> Harry D. Lewis, "Gilsonite," from Industrial Minerals and Rocks, Society of Mining, Metallurgy, and Exploration, 1994, pp. 535-541.



### EXHIBIT 3

#### NATURAL ASPHALT PRODUCTION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988.)



Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988.

information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above.

#### Pyrobitumens

EPA determined that for pyrobitumens, the beneficiation/processing line occurs when the pyrobitumens are thermally cracked in a still to produce a significantly altered material. 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.

#### Mineral Waxes and Natural Asphalts

Based on a review of the processes, there are no mineral processing operations involved in the production of mineral waxes or natural asphalts.

### C. Process Waste Streams

#### 1. Extraction/Beneficiation Wastes

##### Pyrobitumens

None identified.

##### Mineral Waxes

Probable wastes from the production of mineral waxes include **spent solvents** and **spent coal**.

##### Natural Asphalt

None identified.

#### 2. Mineral Processing Wastes

##### Pyrobitumens

**Still bottoms.** 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 2 metric tons/yr, 45,000 metric tons/yr, and 90,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic ignitability.

**Waste catalyst.** 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 2 metric tons/yr, 10,000 metric tons/yr, and 20,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium and selenium. This waste may be recycled and is classified as a spent material.

##### Mineral Waxes

None identified.

##### Natural Asphalt

None identified.

**D. Non-uniquely Associated Wastes**

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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## RARE EARTHS

### A. Commodity Summary

The rare earth elements are comprised of scandium, yttrium, and 15 lanthanide elements, of which cerium, lanthanum, and neodymium are the most abundant. While rare earth elements are found in several minerals, almost all production comes from less than 10 minerals, primarily monazite and bastnasite. Because the scandium industry is, for the most part, separate and distinct from the yttrium and lanthanide industries it is the subject of a separate commodity summary (see the chapter on scandium).

The United States is a major producer and consumer of rare earth ores and compounds that are used in petroleum fluid cracking catalysts, chemical and pollution-control catalysts, metallurgical applications, glass and ceramics, permanent magnets, phosphors, and electronics.<sup>1</sup>

In 1993 two domestic mines, Molycorp, Incorporated and RGC (USA) Minerals Incorporated, produced rare earths. Molycorp, Inc.'s facility in Mountain Pass, CA is the sole producer of rare earth minerals from bastnasite ore.<sup>2</sup> In 1995, Molycorp supplied over 60 percent of U.S.-produced cerium products, with competition from China, the former states of the U.S.S.R., and India.<sup>3</sup> The use of bastnasite ore is preferred in the market over monazite ore because of due to lower concentrations of natural radionuclides which results in lowers worker exposures to low level radiation.<sup>4</sup> The Mountain Pass facility is an integrated mining and beneficiation/processing facility.<sup>5</sup> Twenty facilities produce rare earth materials. Exhibit 1 presents the names, locations, and products of the facilities involved in the production of rare earth materials, however, not all of these facilities engage in primary mineral processing activities.

### B. Generalized Process Description

#### 1. Discussion of Typical Production Processes

Most production of rare earth elements is from the minerals monazite and bastnasite. Processing of these ores is by sulfuric and hydrochloric acid digestion. The compounds recovered from these processes must be processed further to produce and recover rare earth metal compounds. Processes include solvent extraction and reduction.<sup>6</sup> Exhibits 2 through 6 present typical process flow diagrams for the production of rare earths.

Bastnasite is produced only by Molycorp at Mountain Pass, California. It is produced as a mineral concentrate and consumed captively at this facility. Monazite is produced by Associated Minerals at Green Cove Springs, Florida as a byproduct of beach sand mining for titanium and zircon minerals.<sup>7</sup>

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<sup>1</sup> James Hedrick, "Rare Earths," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 134-135.

<sup>2</sup> Molycorp, Inc., Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes, January 25, 1996.

<sup>3</sup> Ibid.

<sup>4</sup> Ibid.

<sup>5</sup> Ibid.

<sup>6</sup> Ibid.

<sup>7</sup> U.S. Environmental Protection Agency, Technical Background Document, Development of the Cost, Economic and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, Office of Solid Waste, 1989, pp. A-21 - A-22.

## 2. Generalized Process Flow

### Mining

At Mountain Pass, Molycorp mines rare earth ore in an open pit approximately 100 meters deep. Blast holes drilled at 3 to 4 meter spacing are routinely assayed for total rare earth oxides and other elements by fluorescence methods. Approximately 300 kilotons per year are mined with a stripping ratio of 5:1. The ore is crushed and blended in stockpiles that contain about 40 kilotons and fed to a mill located less than 100 meters from the pit.<sup>8</sup>

### EXHIBIT 1

#### SUMMARY OF RARE EARTHS PROCESSING FACILITIES

Facility Name	Location	Products
Crucible Materials	Elizabethtown, KY	Rare earth magnets
Delco Remy Division of General Motors	Anderson, IN	Rare earth magnets, neodymium-iron-boron magnet alloys
Hitachi Magnetics	Edmore, MI	Rare earth magnets
IG Technologies	Valparaiso, IN	Rare earth magnets
Molycorp <sup>9</sup>	Mountain Pass, CA	Bastnasite mine
Mountain Pass Mine & Mill	Mountain Pass, CA	Uncertain
Neomet	West Pittsburgh, PA	Neodymium-iron-boron magnet alloys
Nord Resources	Jackson, NJ	Uncertain
Reactive Metals & Alloys Corp.	West Pittsburgh, PA	Mischmetal
Research	Phoenix, AZ	Uncertain
RGC (USA) Mineral Inc.	Green Cove Springs, FL	Byproduct monazite
Rhone-Poulenc Chemicals Co.	Phoenix, AZ Mineville, NY Freeport, TX	Neodymium-iron-boron magnet alloys Uncertain Uncertain
W.R. Grace	Chattanooga, TN	Uncertain

<sup>8</sup> James Hedrick, "Rare Earths, the Lanthanides, Yttrium, and Scandium," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 1035-1047.

<sup>9</sup> Molycorp, Inc., 1996, Op. Cit

Molycorp's mine was the leading producer of rare earths in both the United States and the rest of the world in 1992. In 1993, mine production decreased from the 1992 level of 22,713 tons to 16,465 tons of rare earth oxides.<sup>10</sup>

Almost all mining of heavy mineral sands from surface placer deposits is done by floating cutterhead or bucket wheel dredges that concentrate the heavy minerals onboard and discharge the unwanted tailings back into previously mined areas. An onboard wet mill separates the heavy minerals from the lighter weight fraction through wet gravity equipment that includes a series of screens, hydroclones, spirals, and cones. Wet mill mixed heavy mineral concentrate is sent to a dry mill to separate the individual heavy minerals and produce a concentrate. Dry mill processing includes a combination of scrubbing, drying, screening, electrostatic, electromagnetic, magnetic, and gravity processes. Gravity methods include the use of jigs, spiral and cone concentrators, and shaking tables. Sizing and preconcentration commonly is performed at the mine site by trommels, shaking screens, and gravity separation. Many dredges have such facilities on board or utilize floating preconcentration plants.<sup>11</sup> Monazite can be separated from zircon by electrostatic methods such as electromagnetic or gravity methods. Xenotime is usually separated from monazite by precise gravity methods. Some deposits may require acid leach treatment and calcining to eliminate iron oxide or other grain coatings.

Some sand deposits, too difficult to mine by dredging, are mined using dry methods. Ore is stripped with scrapers, bulldozers, and loaders. Sands recovered by these techniques are crushed, screened, and processed by the wet mill equipment described above.

### **Recovery**

#### Monazite Ore Processing

Rare earth metals are recovered as oxides from monazite ore by sulfuric acid digestion (Exhibit 2). The ore undergoes grinding, spiraling, or other similar operations for the initial coarse purification of the ore. Magnetic separation removes the magnetic ore constituents which can be processed separately or discarded as waste. The refined ore is then digested with sulfuric acid at 200-220°C. Rare earth sulfates and thorium sulfates are then dissolved and removed from the waste monazite solids by filtration. Rare earth elements are then precipitated as oxalates or sulfates. These precipitates undergo caustic digestion or roasting to form rare earth oxides which are finally recovered by filtration. The resulting filtrate is discarded as waste.<sup>12</sup>

#### Bastnasite Ore Processing

To recover rare earths from bastnasite ore, the ore is crushed, ground, classified, and concentrated to increase rare earth concentrations.<sup>13</sup> These processes, as well as the subsequent beneficiation and mineral processing steps, are described in the following paragraphs. The final filtration step yields lead and iron filter cake while the final drying step yields the rare earth concentrates.<sup>14</sup>

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<sup>10</sup> U.S. Bureau of Mines, Rare Earths Annual Report, 1993.

<sup>11</sup> Stephen B. Castor, "Rare Earth Minerals," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 827-837.

<sup>12</sup> U.S. Environmental Protection Agency, "Rare Earths," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174.

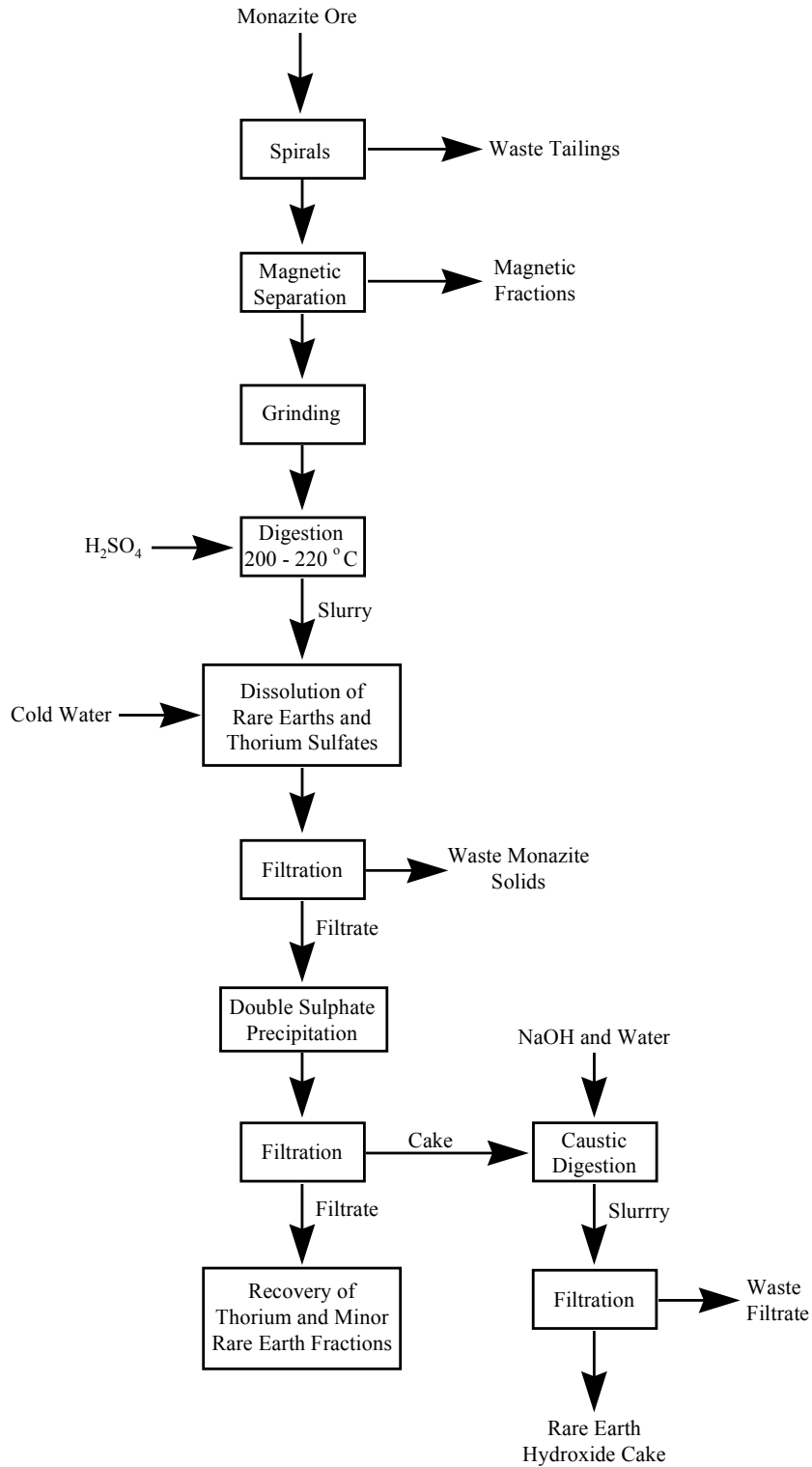
<sup>13</sup> Molycorp, Inc., Comment submitted in response to the Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes, May 12, 1997.

<sup>14</sup> Ibid.

## EXHIBIT 2

### RECOVERY OF RARE EARTHS FROM MONAZITE BY THE SULFURIC ACID PROCESS

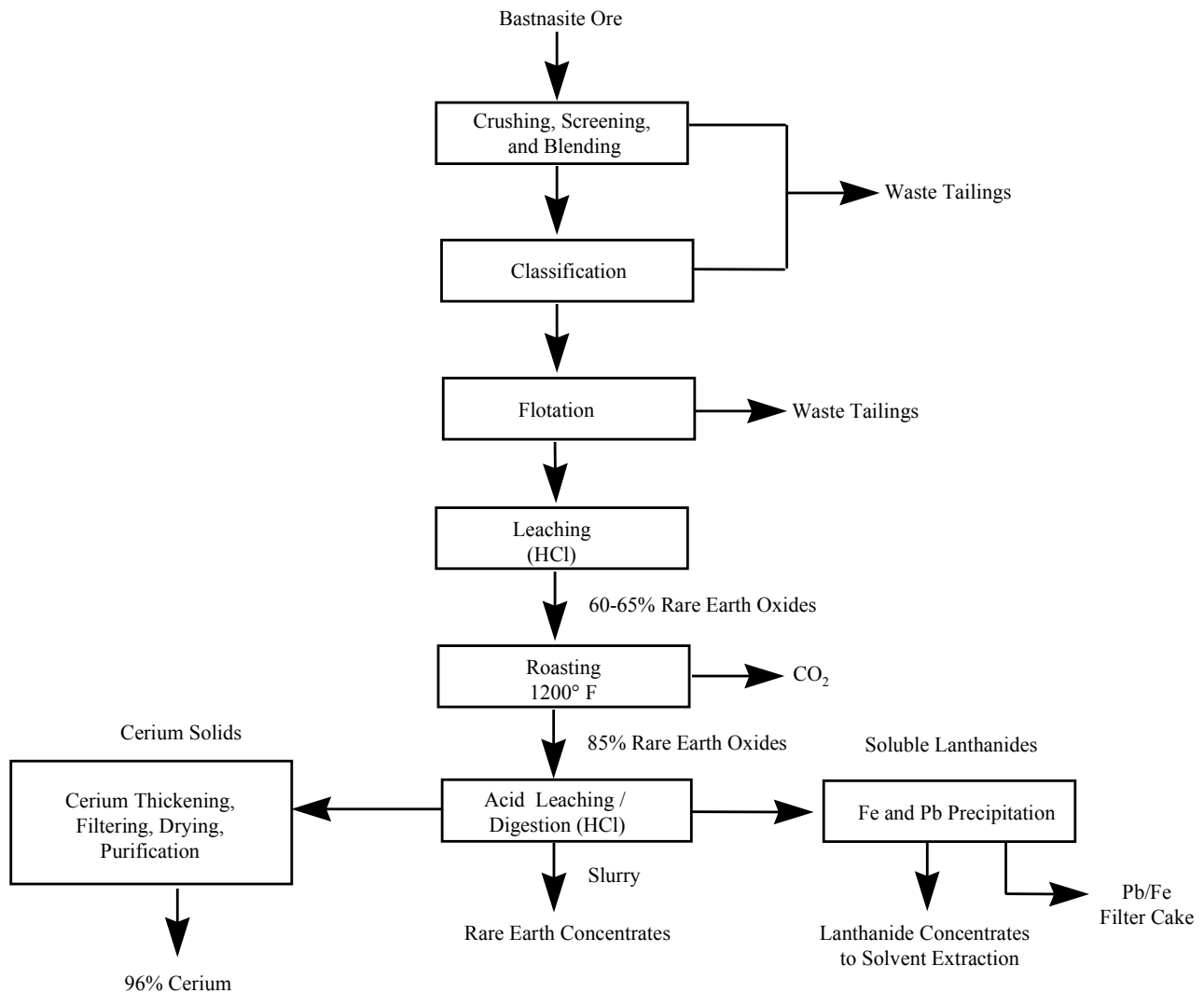
(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174.)





**EXHIBIT 3  
RECOVERY OF RARE EARTH CHLORIDES FROM BASTNASITE ORE**

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174., and Molycorp, Inc., Comment on Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes, May 12th, 1997.)



## Purification/Concentration

### Flotation

Flotation is used at Mountain Pass to make a bastnasite concentrate containing about 60-65 percent rare earth oxides.<sup>15</sup> This concentrate is either used on-site as feed for chemical separation of rare earth elements, leached to produce a 70 percent rare earth oxide concentrate, or shipped off-site to customers.

### Recovery of Concentrate

Recovery of rare earth concentrates from monazite and xenotime is accomplished by digestion in a hot concentrated base or acid solution. At Rhone-Poulenc Inc. plants, which process most of the world's monazite, rare earth elements are extracted in a concentrated solution of sodium hydroxide at 140 to 150°C. After cooling, hydroxides of rare earth elements and thorium are recovered by filtration, and thorium is separated by selective precipitation or dissolution. At Mountain Pass, bastnasite is roasted at 1200°F to drive off CO<sub>2</sub> and leached/digested with dilute, chilled HCl to dissolve most of the trivalent rare earth elements.<sup>16,17</sup> Specifically, in this "leach" step the solid lanthanide ore is reacted with HCl to produce lanthanide chloride. This leaching also produces lead and iron chloride wastes, which are subsequently reacted with ammonia and sodium hydrogen sulfide, respectively, to form small volumes of solid iron hydroxide and lead sulfide wastes. In this step, cerium oxide is also leached to produce a higher concentrate cerium oxide product. In this roasting/leaching sequence, the roasting step converts cerium (III) fluorocarbonate to cerium (IV) oxide, which then undergoes leaching with HCl to produce a cerium oxide concentrate. This second leach step produces a final or intermediate product (low grade cerium concentrate) that does not undergo further beneficiation or processing.<sup>18</sup> The residue, cerium concentrate, is sold as a polishing abrasive.<sup>19,20</sup>

The rare earth hydroxide and chloride concentrates recovered from sulfuric acid and hydrochloric acid leaching/digestion operations must undergo further processing to produce and recover individual rare earth metal compounds such as fluorides, nitrates, carbonates, oxides, and pure metals, for a variety of applications. Processes include solvent extraction and reduction.

### Rare Earth Separation by Solvent Extraction

To separate individual rare earths in a mixture from each other, an aqueous solution containing rare earth salts is sent countercurrent to an immiscible organic stream which selectively extracts one rare earth from the others. Several stages of extractions are needed to separate each rare earth metal. Each organic stream is then scrubbed with an aqueous stream to transfer the rare earth element into an aqueous phase. Because all of the products are aqueous solutions, the spent solvents leave the process as wastes.<sup>21</sup> Exhibit 4 presents a process flow diagram for solvent extraction.

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<sup>15</sup> Ibid.

<sup>16</sup> Molycorp, Inc., 1997, Op. Cit.

<sup>17</sup> Molycorp, Inc., 1996, Op. Cit.

<sup>18</sup> U.S. Environmental Protection Agency, Lowrance, Sylvia K. to Mark A. Smith, Attorney, Unocal Corporation, April 7, 1992.

<sup>19</sup> Stephen Castor, 1994, Op. Cit., pp. 827-837.

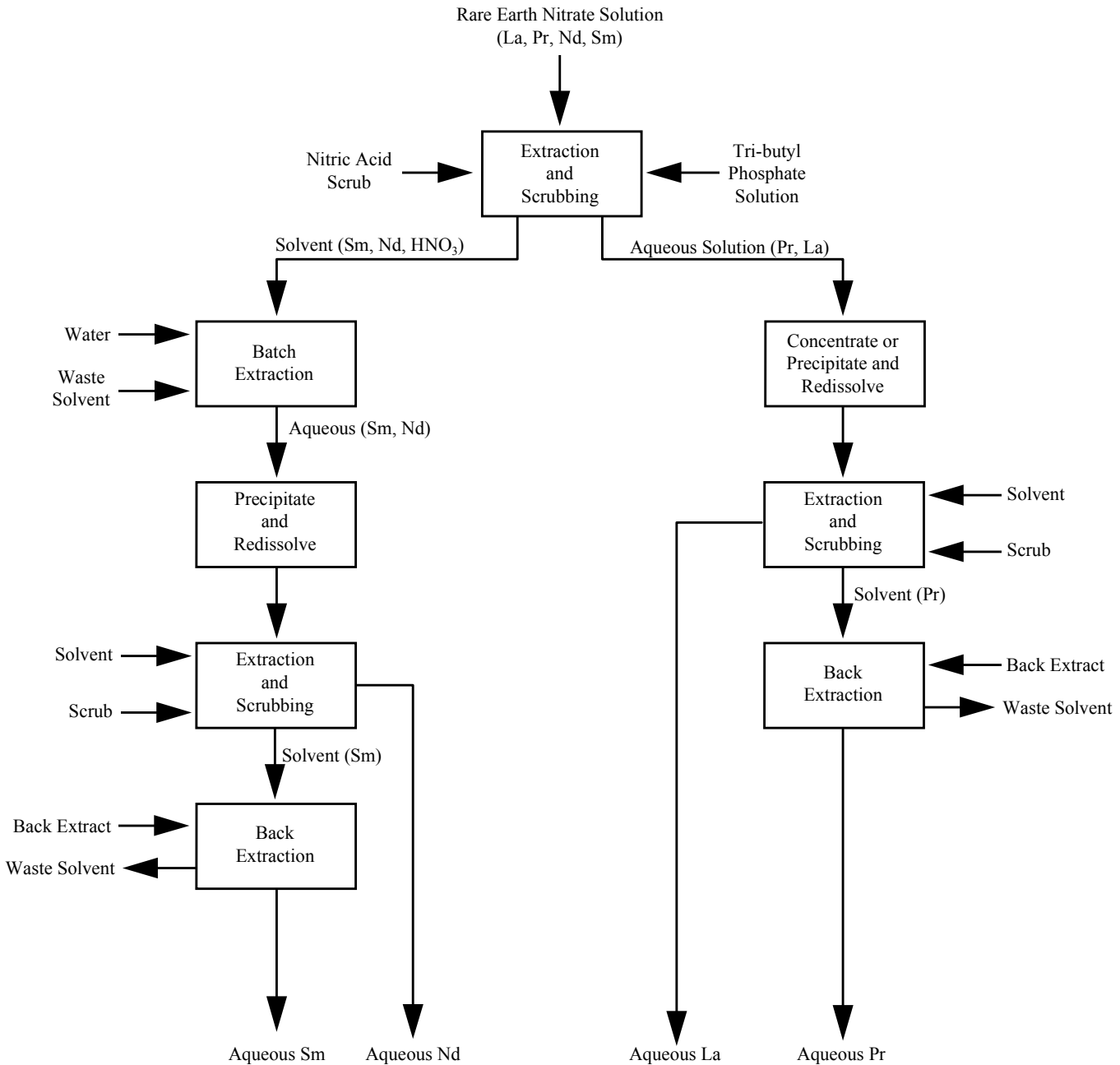
<sup>20</sup> Molycorp, Inc., 1996, Op. Cit.

<sup>21</sup> Molycorp, Inc., 1997, Op. Cit.

# EXHIBIT 4

## RARE EARTH SEPARATION BY SOLVENT EXTRACTION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174.)



### Calcium Reduction

High purity rare earth metals can be produced by the metallothermic reduction of rare earth halides. This process is used when 99.99 percent purity is required. After converting the rare earths into fluorides, they are reduced to the metallic state through contact with calcium or barium at high temperatures.<sup>22</sup> Exhibit 5 presents a flow diagram for calcium reduction.

Ten of the rare earths (lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium dysprosium, holmium, erbium, and lutetium as well as scandium, and yttrium) are produced by calcium reduction. The raw material form of these metals is the metal fluoride. The individual metal fluoride is placed with calcium metal into a reduction vessel where a heat-driven reaction produces pure rare earth metal and calcium fluoride. The metals are further purified by melting in a vacuum to remove impurities. Casting is dependent upon the form in which a buyer wants the metal. Non-contact cooling water is used to cool both the reduction vessels and the melting and casting equipment.

### **Mischmetal**

#### Mischmetal Production

Wet rare earth chlorides or hydrated rare earth compounds must be stripped of their water before electrolytic reduction can take place in order to prevent decay of the graphite anode during electrolysis. The anode could be decayed by the reaction of the liberated oxygen in the electrolyte with the carbon anode to form carbon dioxide. Batch or continuous mode dryers may be used. Both gas heat and electric heat have been used to run the dehydration furnaces.<sup>23</sup>

Dry rare earth chlorides are reduced to mischmetal in electrolytic cells. Batch process electrolysis reduces the rare earth salts to metal in 8 to 12 hours. Excess slag is removed and may be sold for its rare earth chloride content. Following reduction, the mischmetal is cast into bars or ingots for future uses.<sup>24</sup> Exhibits 6 and 7 present process flow diagrams for mischmetal production.

#### Mischmetal Reduction

Mischmetal is an alloy typically composed of cerium, lanthanum, neodymium, praseodymium, other rare earth metals, and iron. Mischmetal processing reduces the oxide form of the rare earth metals (samarium, europium, and ytterbium) to an elemental form. In this reaction, the mischmetal acts as a reducing agent and is oxidized to a mixture of rare earth metal oxides. The process is performed at a low pressure and a temperature below the melting point so that the metals vaporize or sublime. The pure metal is condensed and collected in a crystalline mass of high purity. These solids may be crushed into powder or melted and cast if a solid product form is desired.

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

None identified.

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<sup>22</sup> Ibid.

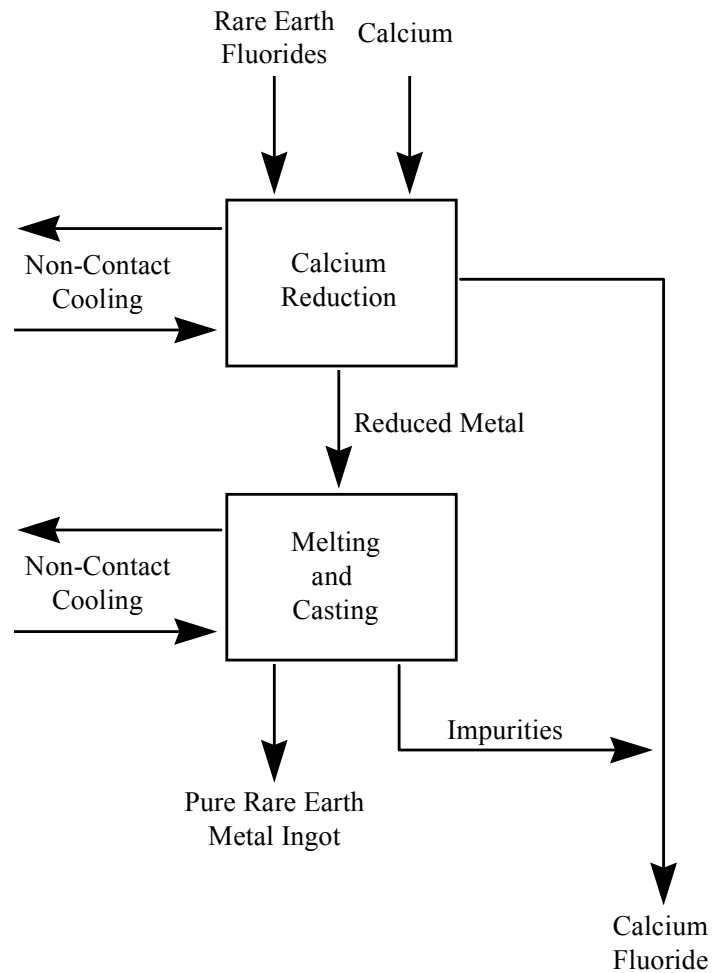
<sup>23</sup> U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Volume X, Office of Water Regulations and Standards, May 1989, pp. 5376-5384.

<sup>24</sup> Ibid.

## EXHIBIT 5

### CALCIUM REDUCTION PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174.)



#### 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 rare earths and mischmetal, the beneficiation/processing line occurs between ore preparation and acid digestion when the ore is vigorously attacked with concentrated acids, resulting in the physical destruction of the ore structure.

After careful analysis of Molycorp's process information, EPA determined in 1991 and 1992, that two distinct operations occur during what Molycorp classifies as its "second leach step." The Agency believes that those determinations are still appropriate. Molycorp submitted extensive comments on EPA's conclusions, which are addressed in the response to comments document in the record.

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

Rare earth element ores and commodities, as well as byproducts and waste materials from rare earth processing, are naturally radioactive, due to contained thorium.

### 1. Extraction/Beneficiation Wastes

**Tailings and magnetic fractions** are possible rare earths extraction/beneficiation wastes.

### 2. Mineral Processing Wastes

**Off-gases from dehydration** from the furnaces are treated by water or alkaline scrubbers to remove particulates and acid. The treated gases are vented.<sup>25</sup> Existing data and engineering judgment indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent iron hydroxide cake.** Existing data and engineering judgment indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent lead and sand filter cinders.** This waste contains waste components (e.g., lead) that originate from the orebody as a result of direct contact with the mineral values (i.e., lanthanides) being processed.

**Spent monazite solids.** Existing data and engineering judgment indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent offgases from electrolytic reduction.** Off-gases from electrolytic reduction include chlorine gas, carbon monoxide and carbon dioxide gases from the carbon in the graphite anodes, and hydrochloric acid fumes. These gases are contacted with water to both cool the gases and to absorb particulates and hydrochloric acid vapors. The partially cleansed gases are then contacted with sodium hydroxide solution, resulting in the formation of sodium hypochlorite. This solution may be sold as a byproduct<sup>26</sup>, and it may not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

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

**Waste solvent.** 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 2,000 metric tons/yr, 1,000,000 metric tons/yr, and 2,000,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of ignitability. EPA does not consider this material to be a waste, because it is fully recycled.

**Spent lead filter cake.** This waste may be stabilized with a polysilicate material and then reinserted into the process for extraction of additional cerium. Tailings containing carbonates are used to precipitate iron. The resulting lead filter cake may exhibit the characteristic of toxicity for lead. 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 3,300 metric tons/yr, 4,200 metric tons/yr, and 5,000 metric tons/yr, respectively. EPA believes this material is fully recycled to recover metal values, and not land stored.

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<sup>25</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 5376-5446.

<sup>26</sup> Ibid.

**Lead backwash sludge.** Existing data and engineering judgment indicate that this waste does not exhibit characteristics of a hazardous waste. Therefore, the Agency did not evaluate the material further. Further, Molycorp, Inc. asserted that its Mountain Pass facility no longer produces this waste.

**Waste zinc contaminated with mercury.** 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 200 metric tons/yr, 45,000 metric tons/yr, and 90,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for mercury. One firm, Molycorp, Inc., asserted that its Mountain Pass facility no longer produces this waste.

**Solvent extraction crud.** 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 200 metric tons/yr, 45,000 metric tons/yr, and 90,000 metric tons/yr, respectively. However, this waste is only generated at one facility and one firm, Molycorp, Inc., indicated that its Mountain Pass facility no longer produces this waste. We used best engineering judgment to determine that this waste may exhibit the characteristic ignitability. This waste may be recycled and formerly was classified as a spent material.

**Spent surface impoundment liquids** are a likely waste stream from rare earth production. Surface impoundment liquids were generated at a rate of 477,000 metric tons per year in 1991.<sup>27</sup> Waste characterization data are presented in Attachment 1. This waste is not expected to be hazardous.

**Spent surface impoundment solids.** This waste stream was generated at a rate of 100 metric tons per year in 1991 and may be toxic for lead.<sup>28</sup> This waste is not expected to be hazardous. Waste characterization data are presented in Attachment 1.

#### Lanthanide Production

**Spent ammonium nitrate processing solution** is a possible waste stream from lanthanide separation. The 1991 waste generation rate for the sector was 14,000 metric tons per year. This waste may exhibit the characteristic of corrosivity.<sup>29</sup> Attachment 1 presents waste characterization data.

#### Cerium Production

**Process wastewater.** This waste stream may be toxic for lead as well as contain detectable levels of ammonium. This wastewater may also be corrosive. The 1991 waste generation rate for the sector was 7,000 metric tons per year.<sup>30</sup> Waste characterization data are presented in Attachment 1. This waste may be recycled and formerly was classified as a spent material.

#### Mischmetal Production

**Spent scrubber liquor** from wet air pollution control is generated from mischmetal production. 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, 500,000 metric tons/yr, and 1,000,000 metric tons/yr, respectively. We used best engineering

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<sup>27</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., Vol. I, pp. I-2 - I-8.

<sup>28</sup> Ibid.

<sup>29</sup> Ibid.

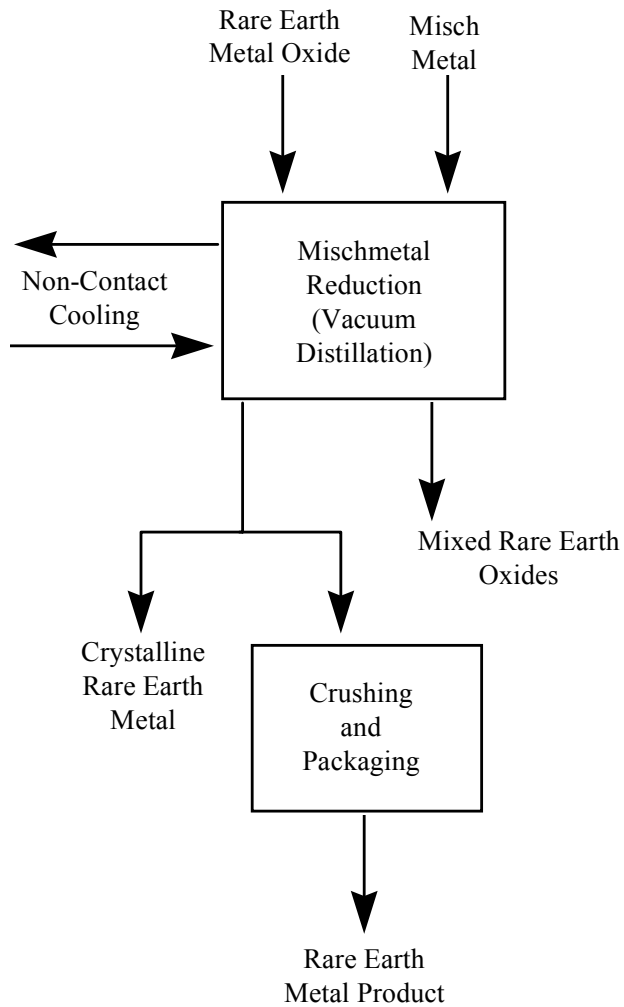
<sup>30</sup> Ibid.



## EXHIBIT 6

### MISCHMETAL REDUCTION PROCESS

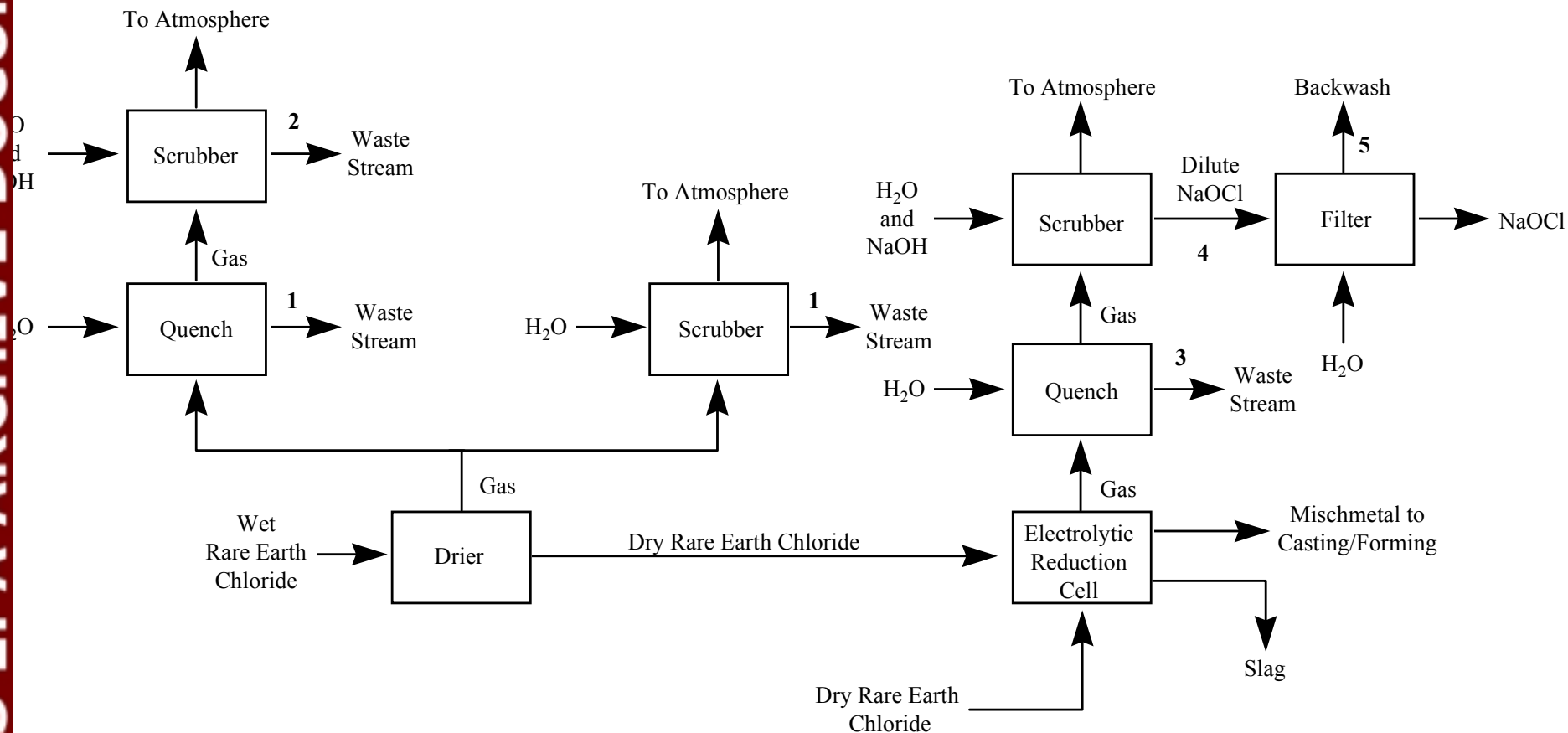
(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-164 - 3-174.)



judgment to determine that this waste may exhibit the characteristic of corrosivity. This water may be recycled or discharged to wastewater treatment. This waste formerly was classified as a spent material.

**EXHIBIT 7**  
**MISCHMETAL PRODUCTION PROCESS**

(Adapted from: Development Document for Effluent Limitations Guidelines, 1989, pp. 5376 - 5446.)



**Wastewater from caustic wet air pollution control.** 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, 500,000 metric tons/yr, and 1,000,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for chromium and lead and corrosivity. Scrubber liquor is recycled and the bleed stream is discharged to treatment. This waste formerly was classified as a spent material.

**Spent electrolytic cell quench water and scrubber water.** Waste characterization data are presented in Attachment 1. This waste is not expected to be hazardous.

**Electrolytic cell caustic wet APC sludge.** 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 70 metric tons/yr, 700 metric tons/yr, and 7,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity. This waste is recycled and is classified as a sludge.

**Spent sodium hypochlorite filter backwash.** The caustic wet air pollution control system following the water quench or water scrubber is designed to recover chlorine present in the gas stream. Sodium hydroxide is circulated through the scrubber and the reaction with chlorine forms sodium hypochlorite. When a 12 to 15 percent sodium hypochlorite concentration is attained, the solution is drawn off and sold for industrial use. This waste is not expected to be hazardous.

#### **D. Non-uniquely Associated Hazardous Wastes**

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), 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. At Molycorp, Inc's facility in Mountain Pass, CA several wastes are considered to be non-uniquely associated. These include pinion grease (contains 50 percent aromatic oils, 35 percent petroleum asphalts, and 0-10 percent 1,1,1 trichloroethane) and spilled solvent cleaned from the chemical plant's floor.

#### **E. Summary of Comments Received by EPA**

##### **New Factual Information**

Two commenters provided new information on facility specific operations and processes (COMM58, COMM68). This new information was incorporated into the Agency's sector report.

##### **Sector-specific Issues**

Two commenters objected to EPA's determination that mineral processing occurs in the rare earth sector, in that they believed this was a reversal of a prior determination by the Agency (COMM40, COMM58, COMM68). One commenter, Molycorp, Inc., responded to both the [Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes](#) and the [Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes](#) (COMM68, COMM40). The concerns of Molycorp, Inc. stem from the Agency determining that mineral processing occurs in the rare earth sector, rather than it being strictly a beneficiation process, which the commenter believed contradicted the 1989 Mining Waste Exclusion Rule.

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**ATTACHMENT 1**

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT SURFACE IMPOUNDMENT LIQUIDS - CERIUM/LANTHANIDES/RARE EARTHS

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
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	0.008	0.008	0.008	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.03	0.03	0.03	1/1	-	-	-	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	-	-	-	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 - SPENT SURFACE IMPOUNDMENT SOLIDS - CERIUM/LANTHANIDES/RARE EARTHS

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	20000	20000	20000	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	-	-	-	0/0	-	-	-	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	20000	20000	20000	1/1	-	-	-	0/0	-	-
Lead	7500	7500	7500	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	2000	2000	2000	1/1	-	-	-	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	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	110000	110000	110000	1/1	-	-	-	0/0	-	-
pH *	-	-	-	0/0	-	-	-	-	2<pH>12	0
Organics (TOC)	33	33	33	1/1	-	-	-	-	-	-

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 - SPENT AMMONIUM NITRATE PROCESSING SOLUTION - CERIUM/LANTHANIDES/RARE EARTHS

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	0.046	0.38	0.97	3/3	-	-	-	0/0	-	-
Antimony	0.229	10.11	20	2/2	-	-	-	0/0	-	-
Arsenic	0.0025	0.01	0.025	4/5	0.002	0.049	0.132	3/3	5.0	0
Barium	0.038	0.07	0.11	5/5	0.006	6.99	20	3/3	100.0	0
Beryllium	0.009	0.01	0.009	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.0025	0.03	0.095	4/5	0.003	0.013	0.03	3/3	1.0	0
Chromium	0.009	0.06	0.24	3/5	0.027	0.048	0.079	3/3	5.0	0
Cobalt	0.054	4.93	9.8	2/2	0.0005	0.065	0.15	2/3	-	-
Copper	0.005	0.04	0.085	2/3	-	-	-	0/0	-	-
Iron	0.053	0.05	0.053	1/1	-	-	-	0/0	-	-
Lead	0.001	0.02	0.03	4/4	0.005	0.014	0.02	2/3	5.0	0
Magnesium	0.005	56.08	221	6/6	-	-	-	0/0	-	-
Manganese	0.005	0.02	0.045	3/4	-	-	-	0/0	-	-
Mercury	0.0001	0.00	0.0005	2/3	0.0065	0.06	0.094	2/3	0.2	0
Molybdenum	-	-	-	0/0	0.009	0.07	0.124	3/3	-	-
Nickel	-	-	-	0/0	0.004	3.28	9.8	3/3	-	-
Selenium	0.0025	0.01	0.016	1/3	0.023	0.05	0.095	3/3	1.0	0
Silver	0.005	0.04	0.097	3/5	0.009	0.02	0.038	3/3	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.001	0.02	0.046	3/4	-	-	-	0/0	-	-
Cyanide	0.005	0.09	0.25	0/3	-	-	-	0/0	-	-
Sulfide	0.025	0.34	0.5	0/3	-	-	-	0/0	-	-
Sulfate	69	595	1,494	3/3	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	1,126	11,108	21,300	3/3	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	0.1	7.07	9.59	9/9	-	-	-	-	2<pH>12	1
Organics (TOC)	107.13	109.17	111.2	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 - PROCESS WASTEWATER - CERIUM\LANTHANIDES\RARE EARTHS

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	27.9	35.7	43.5	2/2	23.2	25.6	28	2/2	-	-
Antimony	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	-	-
Arsenic	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	5.0	0
Barium	0.50	0.50	0.50	0/2	0.50	0.85	1.20	1/2	100.0	0
Beryllium	0.05	0.05	0.05	0/2	0.05	0.05	0.05	0/2	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.00050	0.039	0.054	1/4	0.05	0.05	0.05	0/2	1.0	0
Chromium	0.00050	0.26	0.50	1/4	0.50	0.50	0.50	0/2	5.0	0
Cobalt	0.5	0.50	0.50	0/2	0.50	0.50	0.50	0/2	-	-
Copper	0.5	1.08	1.65	1/2	0.50	1.56	2.62	1/2	-	-
Iron	8.57	10.19	11.80	2/2	7.55	7.76	7.97	2/2	-	-
Lead	0.0005	2.50	8.45	3/4	0.63	5.31	10.0	2/2	5.0	1
Magnesium	154	2,117	4,080	2/2	1,020	4,955	8,890	2/2	-	-
Manganese	3.68	104	204	2/2	2.52	10.4	18.3	2/2	-	-
Mercury	0.00010	0.00010	0.00010	0/2	0.0001	0.0001	0.0001	0/2	0.2	0
Molybdenum	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	-	-
Nickel	0.008	1.25	4.00	2/4	0.50	0.50	0.50	0/2	-	-
Selenium	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	1.0	0
Silver	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	5.0	0
Thallium	2.50	2.50	2.50	0/2	2.50	2.50	2.50	0/2	-	-
Vanadium	0.50	0.50	0.50	0/2	0.50	0.50	0.50	0/2	-	-
Zinc	1.98	8.09	14.20	2/2	1.98	7.24	12.5	2/2	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	152	786	1,420	2/2	-	-	-	0/0	-	-
Fluoride	0.20	15.10	30.0	2/2	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	0.034	1,675	6,490	4/4	-	-	-	0/0	-	-
TSS	0.030	4,740	9,480	2/2	-	-	-	0/0	-	-
pH *	0.4	0.7475	1.1	4/4					2<pH>12	4
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 - SPENT ELECTROLYTIC CELL QUENCH WATER - CERIUM/LANTHANIDES/RARE EARTHS

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.005	0.0067	0.01	3/3	-	-	-	0/0	-	-
Arsenic	0.006	0.0177	0.025	3/3	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.001	0.0010	0.001	3/3	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.001	0.0073	0.02	3/3	-	-	-	0/0	1.0	0
Chromium	0.001	0.0173	0.033	3/3	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.01	0.0230	0.033	3/3	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.14	0.2733	0.4	3/3	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0008	0.002	3/3	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.013	0.0380	0.051	3/3	-	-	-	0/0	-	-
Selenium	0.005	0.0110	0.023	3/3	-	-	-	0/0	1.0	0
Silver	0.001	0.0010	0.001	3/3	-	-	-	0/0	5.0	0
Thallium	0.001	0.0057	0.015	3/3	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.06	0.1167	0.19	3/3	-	-	-	0/0	-	-
Cyanide	0.0003	0.0075	0.022	3/3	-	-	-	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.



**RHENIUM**

**A. Commodity Summary**

The principal source of rhenium is molybdenum concentrates which are derived from porphyry copper deposits. Rhenium-containing products include ammonium perrhenate, perhennic acid, and metal powder. Rhenium is used in high-temperature superalloys (such as those used for manufacturing jet engine components) because it improves the strength properties of nickel alloys at high temperatures (1,000 °C). Rhenium alloys are used in thermocouples, temperature controls, heating elements, ionization gauges, mass spectrographs, electron tubes and targets, electrical contacts, metallic coatings, vacuum tubes, crucibles, electromagnets, and semiconductors. Rhenium is also used in petroleum-reforming catalysts for the production of high octane hydrocarbons for use in lead-free gasoline. Bimetallic platinum-rhenium catalysts have replaced many of the monometallic catalysts.<sup>1</sup> Rhenium is usually traded either as ammonium perrhenate or rhenium metal.<sup>2</sup>

According to the U.S. Bureau of Mines, ores containing rhenium are mined domestically by eight companies. Exhibit 1 presents the names and location of those companies generating molybdenum concentrates that contain rhenium.

**EXHIBIT 1**  
**SUMMARY OF RHENIUM FACILITIES**

Facility Name	Location	Type of Operation
Chino Mines Co.	Hurley NM	Molybdenum concentrates
Cyprus-Climax	Sierrita, AZ	Molybdenum concentrates
Cyprus-Climax	Bagdad, AZ	Molybdenum concentrates
Kennecott Minerals Co.	Bingham Canyon, UT	Molybdenum concentrates
Magna Copper Corp.	San Manuel, AZ	Molybdenum concentrates
Magna Copper Co.	Miami, AZ	Molybdenum concentrates
Phillips Dodge Corporation	Morenci, AZ	Molybdenum concentrates
Sheilds Resources Inc. (Continental Pit)	Butte, MT	Molybdenum concentrates

Although most of these companies typically send their concentrates out of the United States to be toll refined, there is one compnay that recovers and refines rhenium domestically. Cyprus-Climax roasts and recovers rhenium at their Sierrita facility. Additionally, Cyprus-Climax has a rhenium recovery operation at Fort Madison, Iowa.<sup>3</sup> Rhenium consumption was estimated as 6,000 kilograms in 1994.<sup>4</sup>

<sup>1</sup> Blossom, J. W., "Rhenium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 136-137.

<sup>2</sup> Blossom, J.W., "Rhenium," from Mineral Facts and Problems, 1985, p. 667.

<sup>3</sup> Personal communication between Jocelyn Spielman, ICF Incorporated, and J.W. Blossom, U.S. Bureau of Mines, October 17, 1994.

<sup>4</sup> Blossom, J. W., 1995, Op. Cit., p.136.

## B. Generalized Process Description

### 1. Discussion of Typical Production Processes

In general, rhenium is recovered from the off-gases produced when molybdenite, a byproduct of the processing of porphyry copper ores for molybdenum, is roasted. During the roasting process, molybdenite concentrates are converted to molybdic oxide and rhenium is converted to rhenium heptoxide. The rhenium oxides are sublimed and carried off with the roaster flue gas, sulfur oxides, and the entrained dust. Once the technical grade molybdic oxide is separated from the off-gases, it may be further processed to either molybdenum or ferromolybdenum.<sup>5</sup> The off-gases are then processed to recover rhenium as described in detail below. Exhibit 2 provides an overview of the rhenium recovery process and how it is associated with the production of molybdenum.

### 2. Generalized Process Flow Diagram

As shown in Exhibit 3, the rhenium recovery process can be separated into five main steps: (1) scrubbing; (2) solvent extraction or ion exchange; (3) precipitation (addition of H<sub>2</sub>S and HCl) and filtration; (4) oxidation and evaporation; and (5) reduction.

#### Scrubbing

The rhenium heptoxide entrained in flue gas is readily soluble in aqueous ammonia solutions and can be removed by wet scrubbing. Collection efficiencies are on the order of 65% and the unrecovered rhenium remains in the off-gases that escape into the stack.<sup>6</sup>

#### Solvent Extraction or Ion Exchange

The rhenium heptoxide absorbed and dissolved in the scrubber liquor can be recovered at much greater efficiencies than the rhenium from the flue gas. Recoveries of better than 95% have been attained from liquor with rhenium concentrations in excess of 300 ppm. The rhenium is removed from the scrubber liquor via either solvent extraction or selective ion exchange in a solid bed.<sup>7</sup>

#### Precipitation and Filtration

After ion exchange treatment (or solvent extraction) rhenium is stripped from the resin (or solvent) and recovered from the resulting eluviate solution as ammonium perrhenate crystals (NH<sub>4</sub>ReO<sub>4</sub>).<sup>888</sup> As shown in Exhibit 2, the perrhenate solution is precipitated to ReS<sub>2</sub> through the addition of H<sub>2</sub>S, HCl, and NH<sub>4</sub>CNS, followed by filtration. The resulting salt solutions are then sent to further treatment.

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<sup>5</sup> U.S. Environmental Protection Agency, Development Document for Effluent Limitation Guidelines and Standards for Nonferrous Metals Manufacturing Point Source Category, Vol. II, Office of Water Regulations Standards, May 1989, pp. 3363.

<sup>6</sup> Ibid., p.3365.

<sup>7</sup> Ibid.

<sup>8</sup> Ibid.

EXHIBIT 2

MOLYBDENUM AND RHENIUM PRODUCTION PROCESSES

(Adapted from: Development Document for Effluent Limitation Guidelines and Standards for Nonferrous Metals Manufacturing Point Source Category, 1989, pp. 3341 - 3483.)

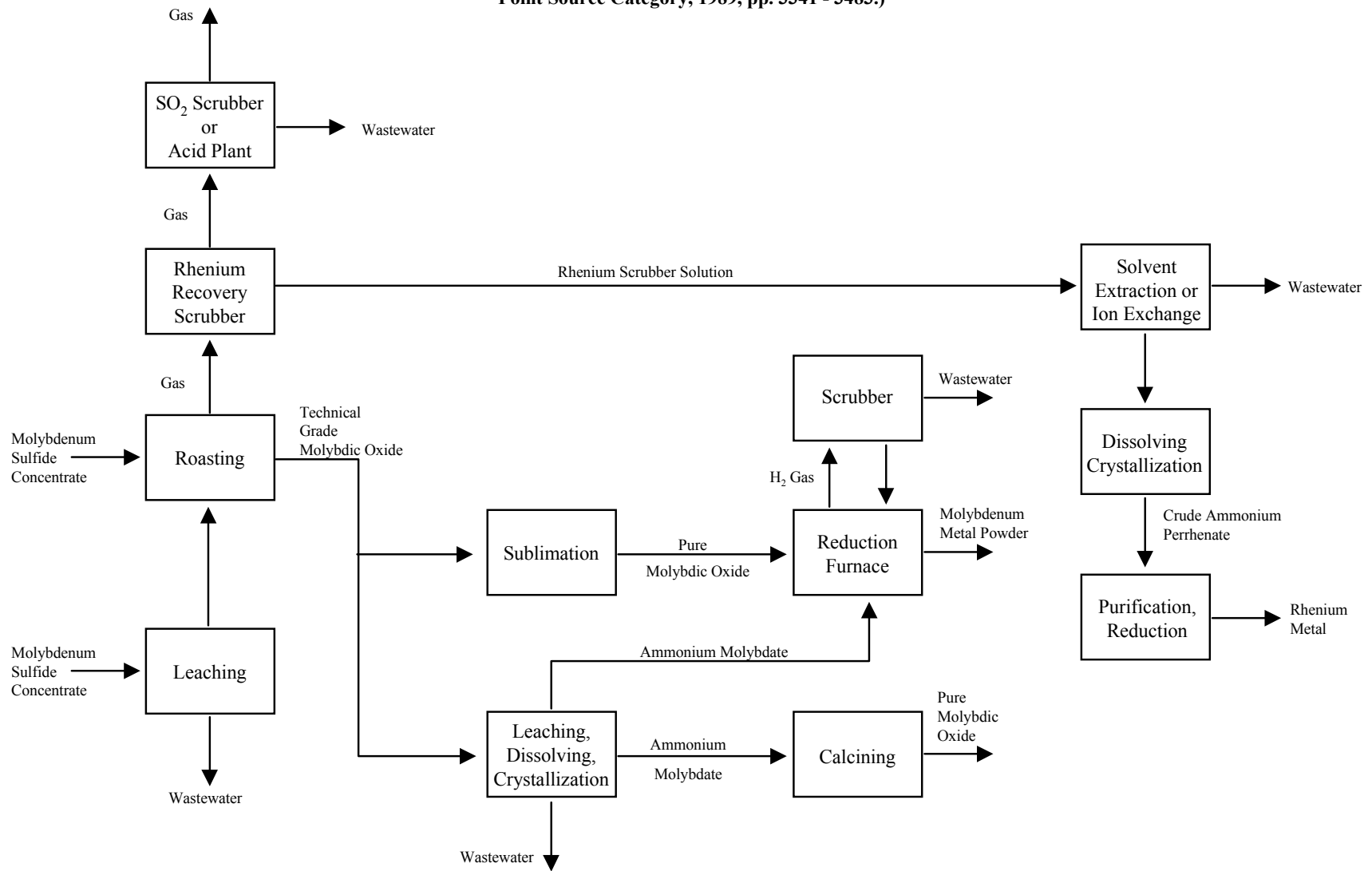
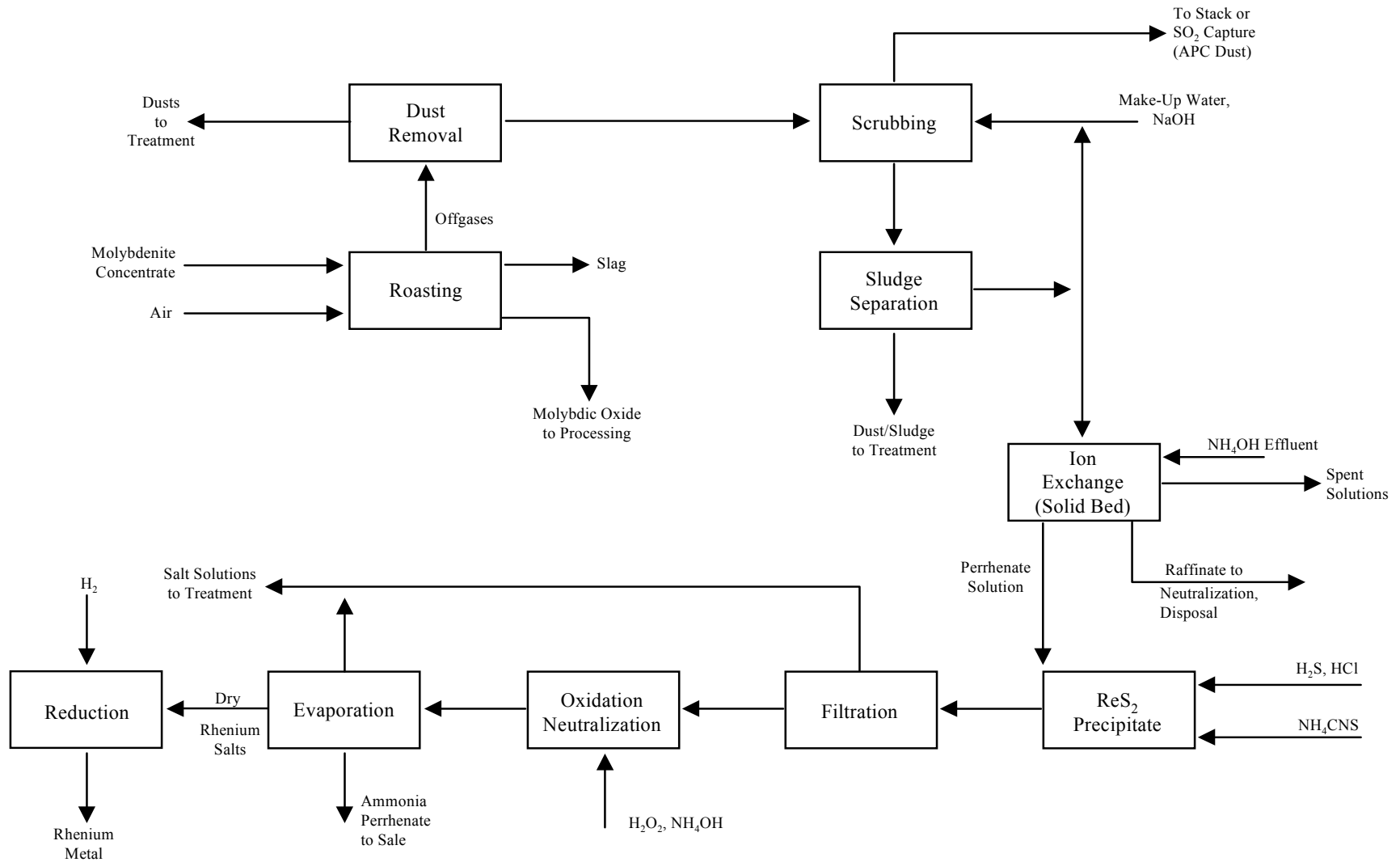


EXHIBIT 3

RECOVERY OF RHENIUM FROM MOLYBDENITE CONCENTRATES

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-175 - 3-178.)



## Reduction

The dry ammonium perrhenate is generally reduced to high purity rhenium metal powder with purified dry hydrogen in an externally heated furnace. The hydrogen reduction is accomplished in two stages, the first at 300° to 350° C and the second at 700° to 800° C. The metal powder is then sintered into bars by compression at 45 to 50 kg per mm<sup>2</sup>, using stearic acid in either stage as a plasticizer. The bars are then rolled to sheet, strip, and foil, or swaged and drawn into rod and wire. These products are annealed at recrystallization temperature after cold working to ensure maximum ductility.<sup>9</sup>

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

None Identified.

### 4. Beneficiation/Processing Boundary

Since rhenium is recovered from off-gases from the production of molybdenum, please see the report for molybdenum presented elsewhere in this background document for a description of where the beneficiation/processing boundary occurs for this mineral commodity sector.

## C. Process Waste Streams

### 1. Extraction/Beneficiation Wastes

None Identified.

### 2. Mineral Processing Wastes

Exhibits 2 and 3 identify the following wastes associated with the recovery of rhenium.

## Roasting and Wet Scrubbing

**Slag.** Slag is produced during roasting. 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.

**Roaster Dust.** Dust removed after the roasting of molybdenum concentrates is sent to further treatment. 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.

**APC Dust/Sludge.** After wet scrubbing, unrecovered rhenium remains in the off-gases that are captured in the stacks. The captured dust and sludge are sent to further treatment. 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.

**Spent Barren Scrubber Liquor.** Barren scrubber liquor generated during wet scrubbing contains treatable concentrations of toxic metals, particularly selenium. Although it is discharged as a wastewater stream, the two plants that report this waste stream achieve zero discharge. Specific practices at these two plants through lime addition and sedimentation, total reuse in other plant processes, evaporation, and contract hauling.<sup>10</sup> 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, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine

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<sup>9</sup> J.W. Blossom, 1985, Op. Cit., p. 667.

<sup>10</sup> U.S. Environmental Protection Agency, 1989. Op. Cit. p. 3430



that this waste may be recycled and may exhibit the characteristic of toxicity for selenium. This waste was formerly classified as a spent material.

#### Ion Exchange and Solvent Extraction

**Spent Rhenium Raffinate.** As shown in Exhibit 3, raffinate results from the solid bed ion exchange and is sent for neutralization and disposal. This waste stream has a reported waste generation rate of 88 metric tons/yr. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

**Spent Ion Exchange Solutions.** Two facilities reporting this waste stream from ion exchange achieve zero discharge through treatment, reuse, evaporation ponds, and contract hauling. Although no analytical data are available for this waste stream, one facility reported that the solution contains treatable concentrations of selenium as well as high concentrations of molybdenum and iron. When rhenium recovery is achieved using solvent extraction, the resultant solution may also contain priority organics.<sup>11</sup> 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.

#### Precipitation and Filtration

**Spent Salt Solutions.** The salt solutions that result from filtration are sent to further treatment. 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**

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 and other lubricants.

#### **E. Summary of Comments Received by EPA**

EPA received no comments that address this specific sector.

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<sup>11</sup> U.S. Environmental Protection Agency, 1989. Op. Cit. p. 3381

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## **RUTILE (Synthetic)**

### **A. Commodity Summary**

Synthetic rutile ( $\text{TiO}_2$ ) is manufactured through the upgrading of ilmenite ore to remove impurities (mostly iron) and yield a feedstock for production of titanium tetrachloride through the chloride process. The chemical composition of synthetic rutile is similar to that of natural rutile, but differs in physical form. Synthetic rutile concentrates are composed of very fine crystals and are porous, whereas natural rutile grains are composed of single crystals.<sup>1</sup>

Since 1977, Kerr-McGee Chemical Corporation has produced synthetic rutile at its Mobile, Alabama plant; it is the only U.S. producer of synthetic rutile today. Because of its purity in comparison with ilmenite, rutile and synthetic rutile are the preferred feedstocks for production of titanium tetrachloride intended for sponge and metal production. The development of processes to produce synthetic rutile was necessitated by the small quantity of economic reserves of natural rutile worldwide.<sup>2</sup> Thus, despite the fact that the U.S. has large reserves of ilmenite, the majority of sponge produced is manufactured from imported rutile and synthetic rutile, primarily from Australia and Malaysia.<sup>3</sup>

Because it is relatively free of impurities, less wastes are generated using rutile and synthetic rutile to produce titanium tetrachloride and titanium dioxide pigment than with ilmenite. The process of converting ilmenite to synthetic rutile generates 0.7 tons of waste per ton of product, and the chloride process generates about 0.2 tons of waste per ton of  $\text{TiO}_2$  product using rutile as a feedstock. In comparison, direct chlorination of ilmenite generates approximately 1.2 tons of waste (primarily ferric chloride) per ton of  $\text{TiO}_2$ .<sup>4</sup>

### **B. Generalized Process Description**

#### **1. Discussion of Typical Production Processes**

Several processes using oxidation, reduction, leaching, and/or chlorination have been developed to remove iron from low-grade, beach sand ilmenite and produce synthetic rutile having 90 to 97%  $\text{TiO}_2$  and very low levels of impurities. These processes can be organized in three categories:

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<sup>1</sup> J. Gambogi, Annual Report: Titanium-1992, U.S. Bureau of Mines, December 1993, p. 1.

<sup>2</sup> U.S. Environmental Protection Agency, Technical Background Document: Development of the Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, Office of Solid Waste, August 1989, p. B-39.

<sup>3</sup> J. Gambogi, 1993, Op. Cit., pp. 5, 18.

<sup>4</sup> J. Gambogi, "Rutile," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 141.

- (1) Processes in which the iron in the ilmenite ore is completely reduced to metal and separated either chemically or physically;
- (2) Processes in which the iron is reduced to the ferrous state and chemically leached from the ore; and
- (3) Processes in which selective chlorination is used to remove the iron.<sup>5</sup>

Kerr-McGee uses the Benelite Cyclic process, in which hydrochloric acid is used to leach iron from reduced ilmenite. The plant has an annual capacity of almost 91,000 metric tons. The plant recycles most of its waste streams and reportedly discharges no liquid wastes.<sup>6</sup>

## 2. Generalized Process Flow Diagram

### Benelite Cyclic Process

In the Benelite Cyclic process (Exhibit 1), developed by the Benelite Corporation of America, raw ilmenite sand containing 54 to 65%  $\text{TiO}_2$  is roasted with heavy fuel oil in a rotary kiln at  $870^\circ\text{C}$ . The fuel oil functions as a reducing agent, converting ferric iron ( $\text{Fe}^{3+}$ ) in the ilmenite to the ferrous ( $\text{Fe}^{2+}$ ) state. The fuel oil is burned at the discharge end of the kiln, and the resulting gases are passed through a cyclone and an incinerator to remove solids and unreacted hydrocarbons.<sup>7</sup>

The reduced ilmenite is then batch-digested in rotary-ball digesters with 18-20%  $\text{HCl}$  at  $140^\circ\text{C}$ . Ferrous oxide in the ilmenite is converted to soluble ferrous chloride, and the  $\text{TiO}_2$  portion of the ilmenite is left as a solid. Spent acid liquor, which contains excess  $\text{HCl}$  and ferrous chloride, is sent to an acid regeneration circuit. The  $\text{TiO}_2$  solids are washed with water and filtered and calcined at  $870^\circ\text{C}$ , yielding synthetic rutile with approximately 94%  $\text{TiO}_2$ . Exhaust gases from the calciner are treated to remove solids and acidic gases before they are released to the atmosphere.<sup>8</sup>

In the acid regeneration circuit, the spent acid liquor is sent to a preconcentrator where one-fourth of the water in the liquor is evaporated. The concentrated liquor is sprayed through atomizers, causing the droplets to dry out, yielding  $\text{HCl}$  gas and ferric oxide powder. The gas is cycloned and then sent to an absorber to remove  $\text{HCl}$  for reuse. The ferric oxide powder is slurried with water to create the waste stream iron oxide slurry.

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<sup>5</sup> J. Gambogi, 1993, Op. Cit., p. 3.

<sup>6</sup> D. Carr, ed., Industrial Minerals and Rocks, Society for Mining, Metallurgy, and Exploration, Inc., 1994, p. 1085.

<sup>7</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40.

<sup>8</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40.

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

High-grade synthetic rutile (98% TiO<sub>2</sub>) has been generated through batch-scale and continuous rotary kiln carbothermic metallization of ilmenite, followed by treatments such as catalytic rusting, acidic chloride leaching, and oxidation-leaching.<sup>9</sup>

### **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.

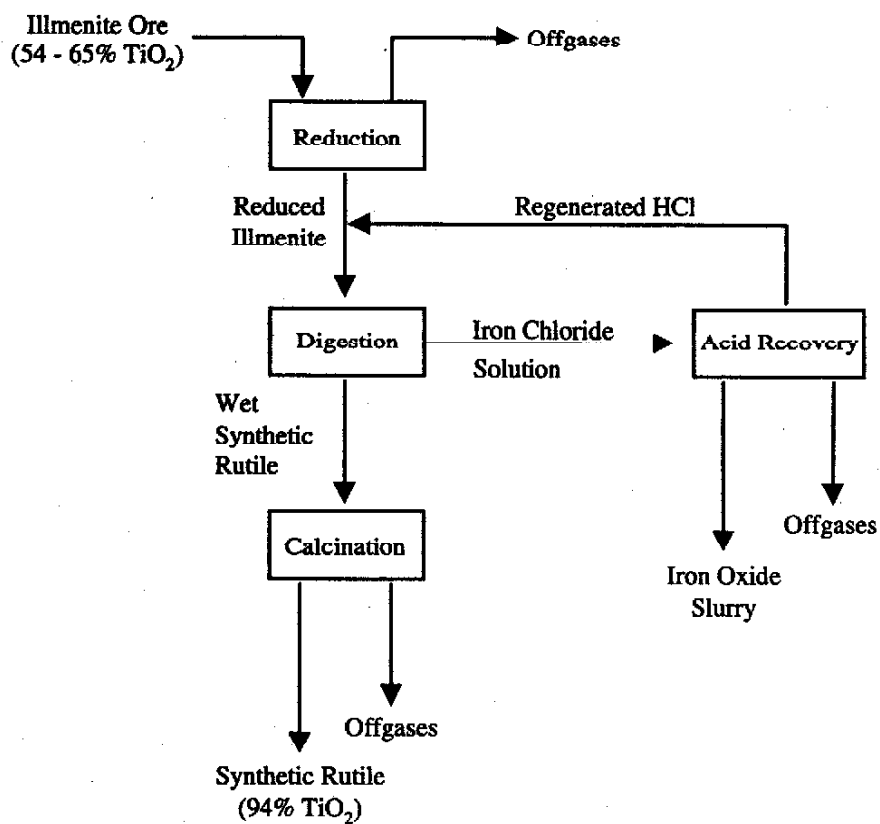
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<sup>9</sup> A. Damodaran, *et al.*, "On Extraction of High Grade Synthetic Rutile from Indian Ilmenite," *The Minerals, Metals & Materials Society*, 1992, p. 1079.

**EXHIBIT 1**

**BENELITE CYCLIC PROCESS FOR SYNTHETIC RUTILE PRODUCTION**

(Adapted from: Kerr-McGee Corp., Comments on Notice of Proposed Rulemaking, 1989.)



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

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between screening/cleaning of sand and reduction in a rotary kiln. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the ilmenite 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**

Beach/alluvial sands containing ilmenite are excavated by dragline, front-end loader, or suction dredging; the sands are spiral concentrated to remove low density tailings. The sands are then dried and separated electrostatically to remove quartz and other nonconducting minerals, which are processed to produce zircon and monazite product and wastes consisting of quartz and epidote minerals. Conducting materials are magnetically separated to sort ilmenite from rutile,

followed by screening and cleaning. No wastes from beach sand processing are expected to exhibit hazardous characteristics.<sup>10</sup>

## **2. Mineral Processing Wastes**

The **Benelite Cyclic** process for manufacturing synthetic rutile generates three mineral processing wastes, as described below.

### **Air Pollution Control Dust/Sludges**

Air pollution control (APC) dust/sludges are generated by the cycloning of off-gases from the roasting step to remove solids. Solids are also removed from off-gases from the calcining step. Off-gases from the spray roaster used in the acid regeneration circuit are also cycloned to remove entrained solids, and subsequent gases from the absorber are scrubbed. APC dust/sludge is believed to be recycled back into the production process (possibly to the roasting step) and is not regarded as a solid waste.<sup>11</sup> This waste stream has a reported waste generation rate of 30,000 mt/yr. Although no published information regarding characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (cadmium and chromium).<sup>12,13</sup> This waste stream is fully recycled and is classified as a sludge.

### **Spent Iron Oxide Slurry**

Iron oxide slurry is the primary waste stream generated in the production of synthetic rutile; it is generated in the acid regeneration circuit. Approximately one-half metric ton of slurry is generated for every metric ton of synthetic rutile. The disposal method for this waste is unknown.<sup>14</sup> This waste stream has a reported waste generation rate of 45,000 mt/yr. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity (cadmium and chromium). This waste is classified as a by-product.

### **Spent Acid Solution**

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<sup>10</sup> U.S. Environmental Protection Agency, "Titanium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. p. 3-219.

<sup>11</sup> D. Carr, ed., 1994, Op. Cit., p. 1085.

<sup>12</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-39.

<sup>13</sup> U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, August 1992, p. I-6.

<sup>14</sup> U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40 - B-41.



Spent acid solution is generated in the digestion step. Spent acid liquor, which contains excess HCl and ferrous chloride, is sent to an acid regeneration circuit to recover HCl for recycle back to the digester. This waste stream is generally recycled back into the process and is not regarded as a solid waste.<sup>15</sup> This waste stream has a reported waste generation rate of 30,000 mt/yr. Although no published information regarding characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (cadmium and chromium) and corrosivity. This waste stream is classified as a spent material.

#### **D. Non-uniquely Associated Wastes**

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 and other lubricants.

#### **E. Summary of Comments Received by EPA**

EPA received no comments that address this specific sector.

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<sup>15</sup> Ibid.

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