

## CADMIUM

#### A. Commodity Summary

Four companies are responsible for producing all of the domestic primary cadmium. According to the U.S. Bureau of Mines, cadmium is used in batteries, 71%; pigments, 10%; coating and plating, 8%; stabilizers for engineering plastics and similar synthetic products, 5%; and alloys and other miscellaneous uses, 6%.<sup>1</sup>

Cadmium is produced mainly as a byproduct of refining zinc metal from sulfide ore concentrates. It is also produced as a byproduct of beneficiating and refining lead ores or complex copper-zinc ores. Cadmium minerals are not found alone in commercially viable deposits. Greenockite (CdS) is the only cadmium mineral of importance. It is not found in any isolated deposits, but is nearly always associated with sphalerite (ZnS).<sup>2</sup>

Exhibit 1 shows the names and locations of the four primary cadmium producers. Three of the four companies (Big River Zinc Corporation, ZCA, and Jersey Miniere Zinc Company) recover cadmium as a byproduct of smelting domestic and imported zinc concentrates. The fourth company (ASARCO) recovered cadmium from other sources such as lead smelter baghouse dust.<sup>3</sup>

## **EXHIBIT 1**

#### SUMMARY OF CADMIUM PRODUCING FACILITIES

Facility Name	Location
ASARCO	Denver, CO
Big River Zinc Corporation	Sauget, IL
Jersey Miniere Zinc Company	Clarksville, TN
ZCA	Bartlesville, OK

# B. Generalized Process Description

# 1. Discussion of Typical Production Processes

Cadmium is mainly a byproduct of the production of zinc metal from sulfide ore concentrates. The mined zinc ores are crushed and ground to liberate the zinc sulfide particles from the waste host rock. The ground ore is usually treated by a differential flotation process to separate the zinc-bearing particles from the waste rock, yielding a high-grade zinc concentrate and waste tailings. About 90% to 98% of the cadmium present in zinc ores is recovered in the mining and beneficiating stages of the extraction process. Zinc concentrate is converted from zinc sulfide to zinc oxide by roasting, and at the same time most of the sulfur is removed as sulfur dioxide. The sulfur dioxide offgas is stripped of all entrapped dust and other impurities and then converted to sulfuric acid in an acid

<sup>&</sup>lt;sup>1</sup> Peter Kuck, "Cadmium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 36-37.

<sup>&</sup>lt;sup>2</sup> Thomas O. Llewellyn, "Cadmium," from <u>Minerals Yearbook Volume 1. Metals and Minerals</u>, U.S. Bureau of Mines, 1992, pp. 271-276.

plant.<sup>4</sup> Cadmium is recovered from zinc and zinc lead concentrates as precipitates from solution (hydrometallurgical process) or as cadmium-lead fume (pyrometallurgical process), respectively, as shown in Exhibit 2. Cadmium may also be recovered as a byproduct of beneficiating and refining lead ores or complex copper-zinc ores.

#### 2. Generalized Process Flow

#### **Cadmium from Zinc**

#### Hydrometallurgical Process

The hydrometallurgical process is used to recover cadmium as a precipitate. In this process, cadmium, copper, and zinc are dissolved in the sulfuric acid leach of the roasted zinc ore. Copper and cadmium are among the most common interfering impurities that are removed before the purified solution is subjected to electrolysis for zinc recovery. Most of the cadmium is precipitated using a zinc dust addition. The purified zinc sulfate solution is sent to the cellroom, and metallic zinc is recovered from the solution by electrowinning. The cadmium precipitate is sent to the cadmium plant where it is filtered and pressed into a cake containing cadmium, zinc, and minor amounts of copper and lead. Impurities are separated and a sufficiently pure cadmium sponge is dissolved in sulfuric acid. Metallic cadmium is recovered by electrolysis of this solution where cadmium is deposited on cathodes. After deposition, the cathodes are removed from the cells and stripped and the cadmium metal is melted and cast into shapes. Exhibit 3 presents a process flow diagram of the production of cadmium from zinc.<sup>5</sup>

#### Pyrometallurgical Process

During the pyrometallurgical extraction of zinc, calcine from a roaster can be sintered with coke in a sintering machine to give a dense desulfurized product. The sintering operation results in considerable volatilization of cadmium and lead compounds, enhanced by the presence of chloride, leading to a 90-99% recovery of cadmium. The fume and dust from the sintering machine are collected in a baghouse. Cadmium not removed during sintering and subsequent operations follows the zinc metal and often is recovered during zinc metal purification by distillation.<sup>6</sup>

The cadmium content in the feed to lead and copper smelters is lower than that generally encountered in zinc plants, and this necessitates upgrading the initial cadmium level in the fume by one or more refuming steps in a kiln or reverberatory furnace. The final fume may contain as much as 45% cadmium. Fumes usually require more processing and purification steps for cadmium recovery than do purification residues from electrolytic zinc plants. Galvanic precipitation is the most frequently adopted method for the final recovery of cadmium in pyrometallurgical plants, but electrolysis may also be used.<sup>7</sup>

Exhibit 4 presents a process flow diagram of cadmium recovery from cadmium bearing fumes. Depending on composition, the fume may have to be roasted with or without sulfuric acid or oxidized using sodium chlorate or chlorine in order to convert cadmium into a water- or acid-soluble form and to eliminate volatile constituents.

<sup>5</sup> Ibid.

<sup>7</sup> <u>Ibid</u>.

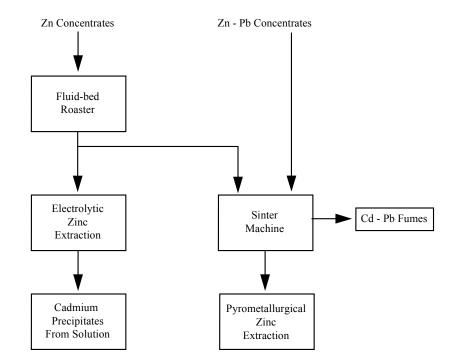
<sup>&</sup>lt;sup>4</sup> U.S. Environmental Protection Agency, "Cadmium," from <u>1988 Final Draft Summary Report of Mineral Industry</u> <u>Processing Wastes</u>, 1988, pp. 3-64 - 3-71.

<sup>&</sup>lt;sup>6</sup> "Cadmium and Cadmium Alloys," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 4th ed., Vol. IV, 1993, pp. 749-754.

EXHIBIT 2

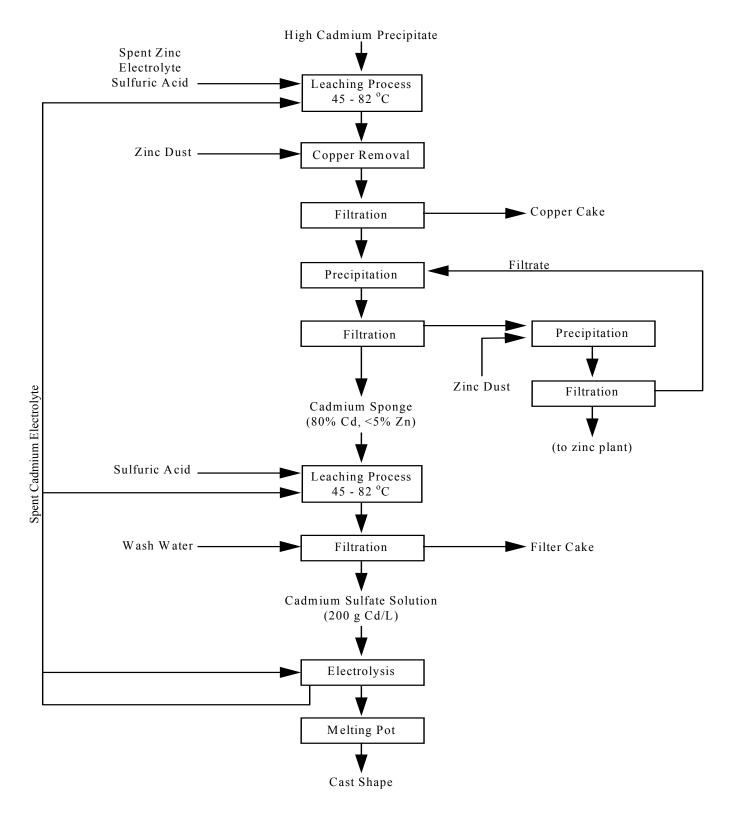
# PRELIMINARY CADMIUM ROASTING PROCESSES

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1992, pp. 749 - 754.)



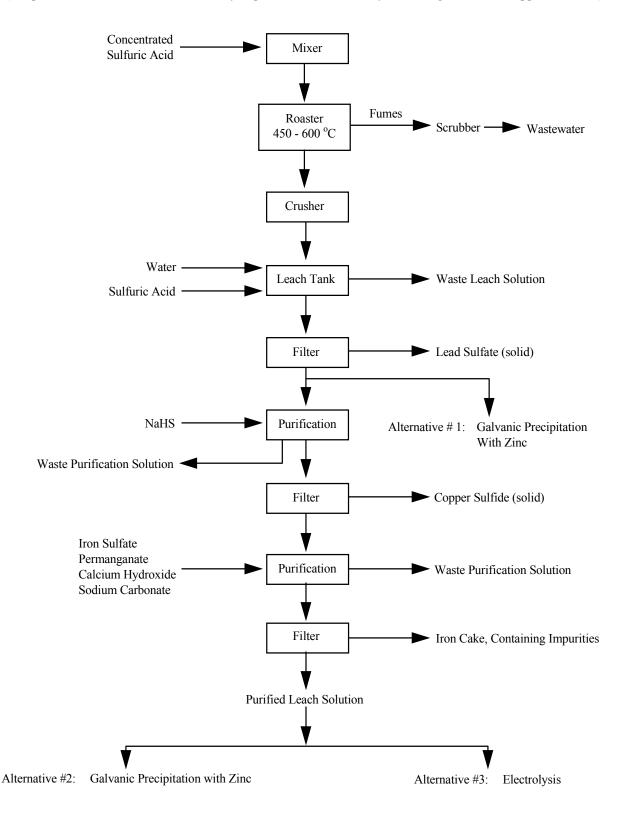
# HYDROMETALLURGICAL PROCESS

# (Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.)



#### **PYROMETALLURGICAL PROCESS**

#### (Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.)



However the leach solution is obtained, it must generally be purified to remove arsenic, iron, copper, thallium, and lead. The cadmium may also be galvanically precipitated from the leach solution and then redissolved (see Exhibit 5).<sup>8</sup>

Alternative 2 in Exhibit 5 indicates the most common method for the recovery of cadmium from purified leach solution by galvanic displacement with zinc in the form of dust, sheets, or even rods or rectangular anodes. The final processing depends on the grade of zinc. In most cases, the pH for galvanic precipitation is below 2, although one plant operates at pH 6.2. In most plants, the final cadmium sponge is washed to remove soluble impurities, and then compacted by briquetting. The briquettes may be melted under a flux of sodium hydroxide or ammonium chloride or be distilled for final purification.<sup>9</sup>

Electrolysis is the third alternative for cadmium recovery. Exhibit 6 presents a process flow diagram of this operation. The electrolysis may be operated on a semi-continuous basis with the cadmium eventually being stripped completely from the electrolyte, which is then discarded after suitable treatment. Instead of the usual silver-lead anodes, high silicon-iron anodes, such as Duriron, are commonly used.<sup>10</sup>

#### **Cadmium from Lead**

Cadmium may also be obtained from flue dust collected at lead or copper smelters. Concentrates of copper, and especially lead, contain considerable amounts of cadmium. In copper smelters, the flue dusts are collected and recycled through the smelter system to upgrade the cadmium content. At the lead smelters the cadmium is fumed off and collected in the blast furnace baghouses. The baghouse dust is recycled to upgrade the cadmium content and is later used as feed material for the cadmium refinery plant.<sup>11</sup>

The cadmium upgraded dusts are charged into a tank and dissolved with sulfuric acid. The resultant solution is filtered to remove impurities and to obtain a purified cadmium sulfate solution. Next, metallic cadmium, called sponge because of its appearance, is precipitated from the solution using zinc dust. The sponge is usually briquetted, remelted, and cast into ingots.

Some plants produce cadmium oxide and/or metallic cadmium powder. Cadmium oxide is produced by melting the ingots and keeping a controlled oxidizing atmosphere in the retort. To produce metal powder, the melted ingots in the retort are kept under an inert atmosphere while cadmium is distilled into a condenser as metallic powder.<sup>12</sup>

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

None identified.

#### 4. Beneficiation/Processing Boundaries

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

<sup>9</sup> <u>Ibid</u>.

<sup>10</sup> <u>Ibid</u>.

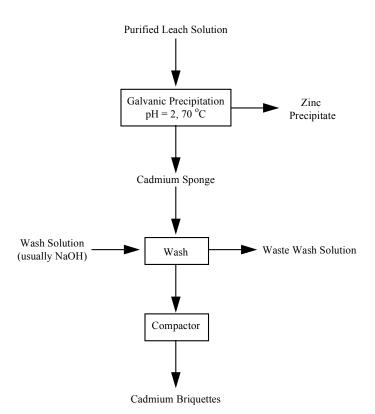
<sup>12</sup> Ibid.

<sup>&</sup>lt;sup>8</sup> Ibid.

<sup>&</sup>lt;sup>11</sup> Thomas Llewellyn, 1992, Op. Cit., pp. 271-276.

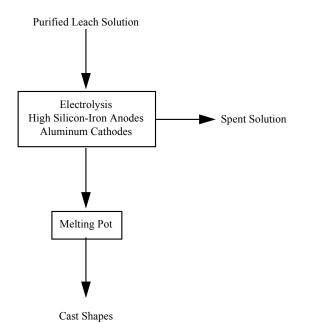
# ALTERNATIVES 1 AND 2 GALVANIC PRECIPITATION WITH ZINC

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.)



# ALTERNATIVE 3 ELECTROLYSIS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-64 - 3-71.)



**US EPA ARCHIVE DOCUMENT** 

# C. Process Waste Streams

#### 1. Extraction/Beneficiation Wastes

Waste tailings.

# 2. Mineral Processing Wastes

Since cadmium is toxic to humans and certain other living organisms, care must be taken during the production, use, and disposal of cadmium and its compounds to avoid the dispersal of cadmium fumes and dusts or the release of cadmium-bearing effluents into the environment so that exposure is minimized.<sup>13</sup> Listed below are possible waste streams from cadmium production. Generally, all wastes are recycled or treated with other refinery wastes.

## Hydrometallurgical Process

**Copper removal filter cake.** 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled and is classified as a byproduct.

**Post-leach filter cake.** 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled to extraction/beneficiation units and is classified as a byproduct.

**Spent electrolyte** may contain thallic sulfate. Information regarding thallium removal from the spent electrolyte remains unclear. However, according to the U.S. Bureau of Mines, there was no domestic production of thallium metal in 1993; suggesting that thallium is not recovered domestically from cadmium production operations. However, sludges from cadmium processing which are used for recovery of metals such as germanium may contain thallium. Since there is no domestic production of germanium, the thallium contained in these sludges may be recovered in other countries.<sup>14</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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity.

#### **Pyrometallurgical Process**

**Copper sulfide and lead sulfate filter cakes.** 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium and lead. This waste may be recycled and is classified as a byproduct.

**Iron containing impurities.** 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,

<sup>&</sup>lt;sup>13</sup> Patricia A. Plunkert, "Cadmium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 111-119.

<sup>&</sup>lt;sup>14</sup> Personal communication between Peter Kuck, U.S. Bureau of Mines and ICF Incorporated, October 12, 1994.

medium, and high annual waste generation rate of 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium.

Lead sulfate waste (solid). 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium and lead. This waste may be recycled and is classified as a byproduct.

**Spent leach 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for arsenic, cadmium, and lead and corrosivity. This waste may be recycled and is classified as a spent material.

**Spent purification 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity.

**Scrubber wastewater.** 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity. This waste may be recycled and is classified as a spent material.

#### **Galvanic Precipitation**

**Caustic washwater 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for cadmium and corrosivity. This waste may be recycled and is classified as a spent material.

**Zinc precipitate.** 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 190 metric tons/yr, 1,900 metric tons/yr, and 19,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium. This waste may be recycled and is classified as a byproduct.

# 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.

# BIBLIOGRAPHY

"Cadmium and Cadmium Compounds." <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>. 4th ed. 1992. Vol. IV. pp. 749-754.

Kuck, Peter. "Cadmium." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 36-37.

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Personal communication between Peter Kuck, U.S. Bureau of Mines and ICF Incorporated, October 12, 1994.

Plunkert, Patricia. "Cadmium." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 111-119.

U.S. Environmental Protection Agency. "Cadmium." From <u>1988 Final Draft Summary Report of Mineral</u> <u>Industry</u> <u>Processing Wastes</u>. 1988. pp. 3-64 - 3-71.

# CALCIUM METAL

#### A. Commodity Summary

Pure calcium is a bright silvery-white metal. Under normal atmospheric conditions, however, freshly exposed surfaces of calcium rapidly become covered with an oxide layer. The metal is extremely soft and ductile, having a hardness between that of sodium and aluminum.<sup>1</sup> Calcium is very reactive and reacts vigorously with water, liberating hydrogen and forming calcium hydroxide,  $Ca(OH)_2$ . Calcium does not readily oxidize in dry air at room temperature, but is quickly oxidized in moist or dry oxygen at about 300° C.<sup>2</sup>

Calcium is an excellent reducing agent, and at elevated temperatures it reacts with oxides or halides of almost all metallic elements to form the corresponding metal. Calcium is used in lead refining (for removal of bismuth), steel refining (as a desulfurizer and deoxidizer), and as an alloying agent for aluminum, silicon, and lead. Calcium is also used in the recovery of refractory metals (e.g., chromium, rare earth metals, and thorium) from their oxides and in the reduction of uranium dioxide.<sup>3</sup>

Pfizer Chem (Quigley Company), located in Canaan, Connecticut is the only domestic producer of calcium metal. Pfizer Chem uses the retort process. Calcium alloys, however, are produced by several companies, including Elkem in Pittsburgh, Pennsylvania.

# B. Generalized Process Description

#### 1. Discussion of Typical Production Processes

Calcium metal is produced by the aluminothermic method involving the high temperature vacuum reduction of calcium oxide. The raw materials for this process are limestone and aluminum. In this process, aluminum metal acts as the reducing agent. Exhibits 1 and 2 present flow diagrams for the typical process for producing calcium metal.

#### 2. Generalized Process Flow Diagram

#### Aluminothermic Process

As shown in Exhibit 1, high calcium limestone,  $CaCO_3$ , is quarried and calcined to form calcium oxide. As shown in Exhibit 2, the calcium oxide is then ground to a small particle size and dry blended with the desired amount of finely divided aluminum. This mixture is then compacted into briquettes to ensure good contacts for reactants. The briquettes are then placed in horizontal tubes, i.e., retorts, made of heat resistant steel and heated to 1100-1200°C. The open ends of the retort protrude from the furnace and are cooled by water jackets to condense the calcium vapor. The retorts are then sealed and evacuated to a pressure less than 13 Pa. After the reaction has been allowed to proceed for approximately 24 hours, the vacuum is broken with argon and the condensed blocks of about 99% pure calcium metal, known as crowns, and calcium aluminate residue are removed.<sup>4</sup>

<sup>&</sup>lt;sup>1</sup> "Calcium," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 777.

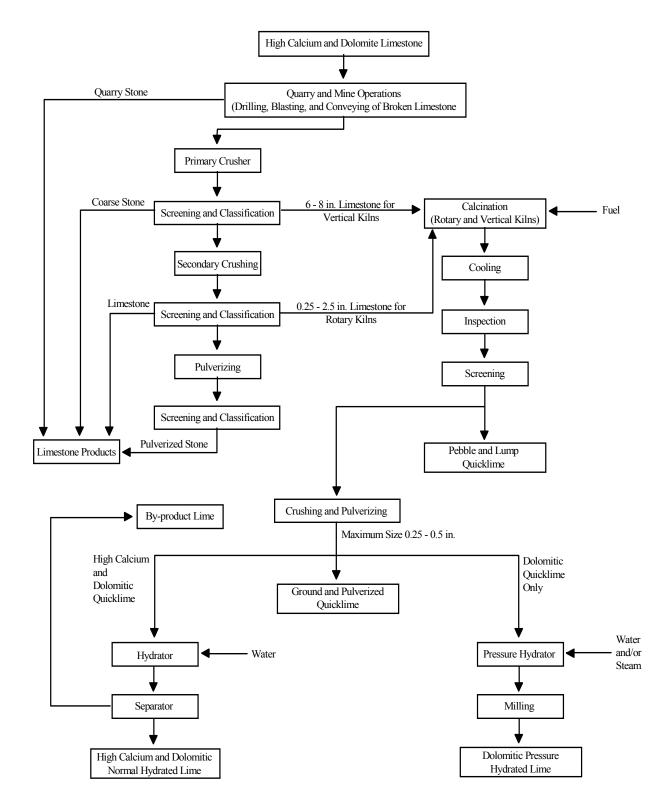
<sup>&</sup>lt;sup>2</sup> <u>Ibid</u>., p. 778.

<sup>&</sup>lt;sup>3</sup> <u>Ibid</u>., p. 777.

<sup>&</sup>lt;sup>4</sup> <u>Ibid</u>., pp. 779-780.

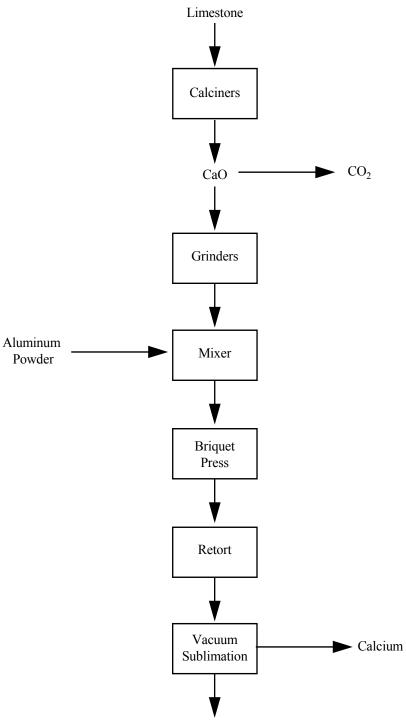
# LIME AND LIMESTONE PRODUCTION

# (Adapted from: Industrial Minerals and Rocks, 1994, p. 592.)



# **ALUMINUM REDUCTION PROPCESS**

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, pp. 777 - 782)



Residue

#### Redistillation

In applications involving the reduction of other metal compounds, a purity greater than 99% calcium is required. The necessary higher purities can be achieved through redistillation. For one method of redistillation, crude calcium is placed at the bottom of a large vertical retort made of heat-resistant steel equipped with a water cooler condenser at the top. The retort is sealed and evacuated to a pressure of less than 6.6 Pa while the bottom is heated to 900-925°C. Under these conditions calcium quickly distills to the condensing section leaving behind the bulk of the less volatile impurities. Any processing that takes place after this point must be in the absence of moisture to avoid oxidation.<sup>5</sup> Redistillation does not reduce those impurities that result from volatile materials, such as magnesium. Volatile alkali metals can be separated from calcium by passing the vapors over refractory oxides such as  $TiO_{22}$   $ZrO_{23}$   $CrO_{3}$  to form nonvolatile Na<sub>2</sub>O and K<sub>2</sub>O.<sup>6</sup>

## 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.

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 briquet pressing of calcium oxide and retorting. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where calcium oxide undergoes a chemical change to produce calcium metal. 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,

<sup>6</sup> Ibid.

<sup>&</sup>lt;sup>5</sup> <u>Ibid</u>., pp. 780-781.

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

**Overburden.** No waste characterization data or generation rates are available for overburden resulting from the mining operations. However, the overburden is likely left at the mining site.

**Off-gases**. The gases that result from the calciner operation are generally vented to the atmosphere, and consist primarily of  $CO_2$  and water vapor.

#### 2. Mineral Processing Wastes

The aluminothermic process employed at the Pfizer plant in Connecticut generates two main sources of mineral processing wastes. It is not clear whether the land surface is on or off site. The description of the wastes does not specify whether the terms reactive and non-combustible refer to RCRA definitions.

**Calcium Aluminate Wastes.** The calcium aluminate is a non-reactive waste and is generally disposed of in a land surface storage area. 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.

**Dust with Quicklime**. While dust collected from the system is recycled, some fugitive dust is accumulated due to contamination concerns. The dust is reactive, non-combustible, and disposed of on the land surface. This waste stream has a reported waste generation rate of 40 mt/yr. We used best engineering judgment to determine that this waste stream may exhibit the characteristic of corrosivity. This waste stream is fully recycled and is classified as a sludge.

#### 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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"Calcium." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. pp. 777-782.

# **CESIUM/RUBIDIUM**

#### A. Commodity Summary

The properties of cesium and its compounds are similar to those of rubidium and its compounds. As a result, cesium and rubidium compounds are often used interchangeably. Although neither cesium nor rubidium is recovered domestically from mined ores, according to the U.S. Bureau of Mines each is manufactured by primarily one company domestically (Cabot Corp. - Revere, PA). Cesium products are manufactured from imported pollucite ore and used commercially in electronics, photoelectric, and medical applications. Rubidium products are manufactured from imported lepidolite ore and also used commercially in the electronic and medical industries. Both cesium and rubidium were used in the form of chemical compounds in research and development endeavors.<sup>1</sup> Exhibit 1 presents the names and locations of the facilities once involved in the production of cesium/rubidium.

#### **EXHIBIT 1**

Facility Name	Location	Type of Operations
Cabot Corp	Revere, PA	Recovery of both cesium and rubidium
Callery Chem	Pittsburgh. PA	Uncertain
Carus Corp	La Salle, IL	Acid Digestion
Corning Glass	Corning, NY	Uncertain

#### SUMMARY OF CESIUM/RUBIDIUM FACILITIES

#### B. Generalized Process Description

# 1. Discussion of Typical Production Processes

*Cesium.* The production of cesium metal from pollucite can be achieved through three basic methods: direct reduction with metals, decomposition with bases, and acid digestion. Acid digestion is the primary commercial process for cesium production and is described in further detail below.<sup>2</sup> Exhibit 2 presents the generalized process flow diagram for the production of cesium.

*Rubidium.* Rubidium is found widely dispersed in potassium minerals and salt brines. Lepidolite, a lithium mica, is the principal source of rubidium. Because pollucite ore also contains some rubidium dioxide (RbO<sub>2</sub>), some rubidium is processed as a by-product of cesium manufacture from this ore. The traditional methods for recovering rubidium involve extraction of mixed alkali alums from the ore and are described in further detail below.<sup>3</sup> Exhibits 3 through 6 present generalized process flow diagrams for the production of rubidium.

<sup>&</sup>lt;sup>1</sup> Robert G. Reese, Jr., "Cesium" and "Rubidium," from <u>Mineral Commodity Summaries</u>, 1995, pp. 40-41 and pp. 138-139.

<sup>&</sup>lt;sup>2</sup> "Cesium," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 4th ed., Vol V, 1993, p. 753.

<sup>&</sup>lt;sup>3</sup> "Rubidium," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 3rd ed., Vol XX, 1982, p. 493.

#### 2. Generalized Process Flow Diagram

#### Cesium

As shown in Exhibit 2, the recovery of cesium from pollucite requires that the raw ore be crushed and ground, and mixed with water to form a slurry.<sup>4</sup> Some sources indicate that no further concentration is necessary at this point and the pollucite can be digested with an acid.<sup>5</sup> Other sources indicate that following the production of the pollucite slurry, froth flotation can be used to yield a pollucite concentrate that is acidified through the addition of sulfuric acid. Waste gangue is discarded and the acidified concentrate is treated with hydrofluoric acid, aluminum sulfate, and a cationic reagent (e.g., cocoamine acetate) for conditioning. This conditioned pulp is then sent through froth flotation for a second time and the resultant product is a relatively pure pollucite which is prepared for acid digestion. Any non-pollucite minerals are separated through the froth filtration and discarded.<sup>6</sup>

Either hydrochloric, hydrobromic, hydrofluoric, or sulfuric acid can be used for the acid digestion step to produce the cesium salt that can be evaporated to yield a dried cesium salt.<sup>7</sup> Other sources suggest that hydrobionic acid could be used as well.<sup>8</sup>

#### Rubidium

As shown in Exhibit 3, the recovery of rubidium from either pollucite or lepidolite ore requires that the ore be leached for a prolonged period of time in sulfuric acid to form alkali alums. The alum solution is filtered from the residue, which is washed with water. Calcination of the ore prior to leaching increases the yield. The other alkali metals are separated from the rubidium solution by fractional recrystallization. The purified rubidium alum is converted to rubidium hydroxide, by neutralization to precipitate the aluminum. The addition of barium hydroxide precipitates the sulfate.

As shown in Exhibit 4, the chlorostannate method requires a partial separation of rubidium from the potassium-bearing ore. The dissolved carbonates are converted to chlorides, and the solution is treated with enough stannic chloride to precipitate cesium chlorostannate, which is less soluble than its rubidium counterpart. The cesium-free chloride solution is treated with an excess of stannic chloride to precipitate rubidium chlorostannate which may be decomposed to separate the rubidium and tin chlorides by pyrolytic, electrolytic, or chemical methods. As shown in Exhibit 5, solvent extraction and ion exchange can also be used to separate rubidium from other alkalimetal compounds.<sup>9</sup>

<sup>&</sup>lt;sup>4</sup> U.S. Environmental Protection Agency, "Cesium," from <u>1988 Final Draft Summary Report on Mineral Industry</u> <u>Processing Wastes</u>, Office of Solid Waste, 1988, p. 3-72.

<sup>&</sup>lt;sup>5</sup> "Cesium," 1993, <u>Op. Cit.</u>, p. 753.

<sup>&</sup>lt;sup>6</sup> U.S. Environmental Protection Agency, 1988, <u>Op. Cit.</u>, p. 3-72.

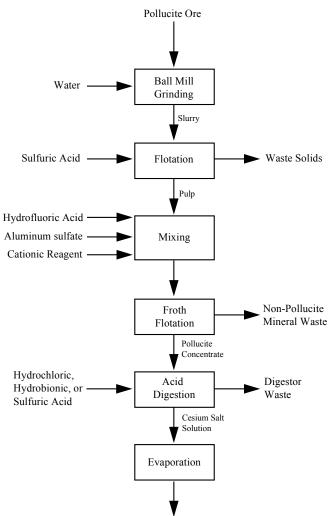
<sup>&</sup>lt;sup>7</sup> "Cesium," 1993, <u>Op. Cit.</u>, p. 753.

<sup>&</sup>lt;sup>8</sup> U.S. Environmental Protection Agency, 1988, <u>Op. Cit.</u>, p. 3-73.

<sup>&</sup>lt;sup>9</sup> "Rubidium," 1982, <u>Op. Cit.</u>, p. 493.

#### **CESIUM RECOVERY FROM POLLUCITE ORE**

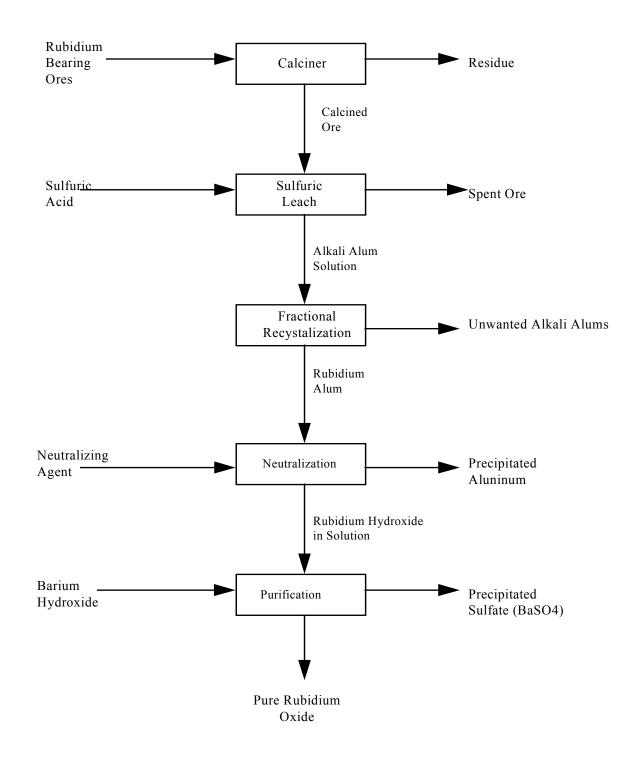
(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-179 - 3-186.)



Dried Cesium Salt

# EXHIBIT 3 Rubidium Alums, Extraction

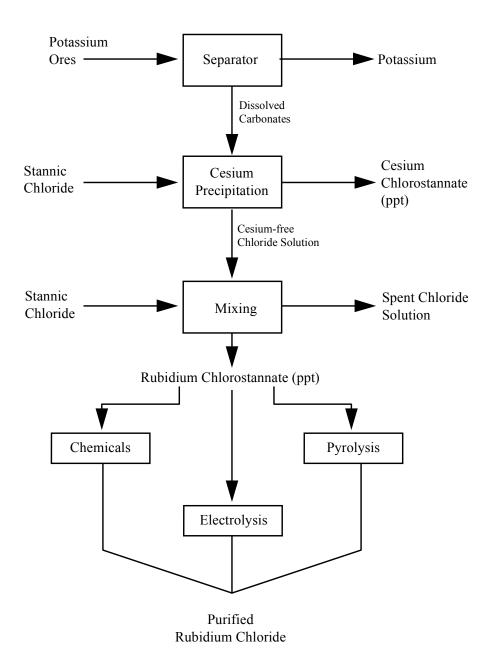
(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes 1988, pp.3-179 - 3-186)



# Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-179-3-186.

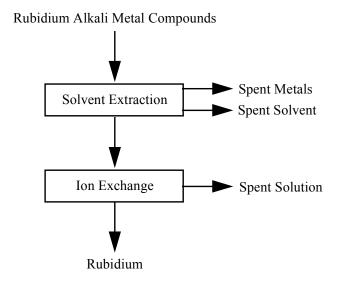
# **RUBIDIUM STANNIC CHLORIDE PRECIPITATION**

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-179 - 3-186.)



# **RUBIDIUM FROM ALKALI METALS**

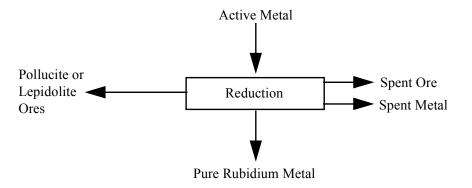
(Adapted from: 1988 Final Draft Summary of Mineral Industry Processing Wastes, 1988, pp. 3-179 - 3-186.)



# **EXHIBIT 6**

# **RUBIDIUM REDUCTION**

(Adapted from: 1988 Final Draft Summary of Mineral Industry Processing Wastes, 1988, pp. 3-179 - 3-186.)



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

#### Cesium

In the process used by Carus Corp, the pollucite is digested with sulfuric acid to produce cesium alum that is dissolved in an aqueous hydroxide solution to form cesium alum hydroxide and potassium sulfate. Cesium permanganate can then be directly precipitated by the addition of potassium permanganate.<sup>10</sup>

Alternatively, if hydrochloric acid is used in the acid digestion, permangante can be added to the resulting cesium chloride after the removal of excess iron and alumina as hydroxides. The resultant cesium permanganate can be converted to the carbonate or chloride by reduction with methanol.<sup>11</sup>

#### Rubidium

As shown in Exhibit 6, pure rubidium metal can be obtained by reducing either pollucite or lepidolite ores with an active metal. Alternatively, pure rubidium compounds can be reduced thermochemically to yield pure rubidium metal.<sup>12</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.

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 the cesium recovery process within this specific mineral commodity sector, the beneficiation/processing line occurs between froth flotation and acid digestion. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where the pollucite ore undergoes a significant chemical change. For the stannic chloride precipitation process, EPA determined that the beneficiation/processing line occurs between the production of rubidium chlorostannate and pyrolysis, electrolysis,

<sup>&</sup>lt;sup>10</sup> "Cesium," 1993, <u>Op. Cit.</u>, p. 753.

<sup>&</sup>lt;sup>11</sup> <u>Ibid</u>., p. 754.

<sup>&</sup>lt;sup>12</sup> "Rubidium," 1982, <u>Op. Cit.</u>, p. 493.

or chemical addition. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where rubidium chlorostannate undergoes a significant chemical change to produce rubidium chloride. EPA also determined that rubidium alum extraction and rubidium recovery from alkali metals do not generate any mineral processing wastes. Also, all wastes generated during the rubidium reduction process 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

The wastes generated during the recovery of cesium and rubidium are listed below. Waste characterization data, including information on generation rates and waste management are not available.

Cesium

Waste Gangue. Waste gangue is generated from froth flotation. Non-Pollucite Mineral Waste

Rubidium

Alum Extraction

Calciner Residues Spent Ore Alkali Alums Precipitated Aluminum Precipitated Barium Sulfate

Stannic Chloride Precipitation

**Cesium Chlorosonnate Spent Chlorine Solution** 

Solvent Extraction

Spent Metal Spent Solvent Spent Ion-exchange solution

#### 2. Mineral Processing Wastes

Existing data and engineering judgment suggest that the following materials do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

# Acid Digestion

#### **Digester waste**

# Stannic Chloride Precipitation

# Pyrolytic Residue Electrolytic Slimes Chemical Residues

Reduction

Slag

# 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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# **US EPA ARCHIVE DOCUMENT**

ATTACHMENT 1

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

	Total Co	onstituent Ar	nalysis - PPI	Л	EP Tox	EP Toxicity Analysis - PPM					# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Dete	cts	Level	In Excess
Aluminum	-	-	· -	0/0		-	-	-	0/0	-	-
Antimony	-	-	· -	0/0		-	-	-	0/0	-	-
Arsenic	-	-	· -	0/0		-	-	-	0/0	5.0	0
Barium	-	-	· -	0/0		-	-	-	0/0	100.0	0
Beryllium	-	-	· -	0/0		-	-	-	0/0	-	-
Boron	-	· -	· -	0/0		-	-	-	0/0	-	-
Cadmium	-	· -	· -	0/0		-	-	-	0/0	1.0	0
Chromium	0.008	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</ph>	0
Organics (TOC)	-	· -		0.10						-	-

	Total Co	nstituent Ar	nalysis - PPI	Л	EP Toxicity Analysis - PPM					# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
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</ph>	0
Organics (TOC)	33	33	33	1/1					-	-

	Total C	onstituent Ar	nalysis - PPI	N	EP Toxic	TC	# Values			
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
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</ph>	1
Organics (TOC)	107.13	109.17	111.2	2/2					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT AMMONIUM NITRATE PROCESSING SOLUTION - CERIUM/LANTHANIDES/RARE EARTHS

	Total Co	onstituent Ar	alysis - PPN	N	EP Toxic	TC	# Values			
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
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	-	· <u> </u>	-	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	-	-
рН *	0.4	0.7475	1.1	4/4					2 <ph>12</ph>	4
Organics (TOC)	-	-	-	0/0					-	-

	Total Cor	nstituent Anal	ysis - PPM		EP Toxicity Analysis - PPM					# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
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</ph>	0
Organics (TOC)				0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT ELECTROLYTIC CELL QUENCH WATER - CERIUM/LANTHANIDES/RARE EARTHS

# CHROMIUM, FERROCHROMIUM, AND FERROCHROMIUM-SILICON

#### A. Commodity Summary

Chromite ore, the starting material for chromium metal, alloys, and other chromium products, is not mined in the United States.<sup>1</sup> The metallurgical and chemical industry consumed 93 percent of the imported chromite ore used domestically in 1994; the refractory industry consumed the remainder. The major end uses of chromium metal and ferroalloys were stainless and heat-resisting steel (78 percent), full-alloy steel (8 percent), superalloys (2 percent) and other miscellaneous uses (12 percent).<sup>2</sup> Exhibit 1 summarizes the producers of chromium products in 1992. Only a small amount of the chromite is processed to produce ductile chromium; the rest is used in an intermediate form.<sup>3</sup>

# **EXHIBIT 1**

#### SUMMARY OF PRODUCERS OF CHROMIUM PRODUCTS (IN 1992)<sup>a</sup>

Facility Name	Location	Industry	
American Chrome & Chemicals Inc.	Corpus Christi, TX	Chemical	
Elkem AS, Elkem Metals Co.	Marietta, OH	Metallurgical	
Elkem AS, Elkem Metals Co.	Alloy, WV	Metallurgical	
General Refractories Co.	Lehi, UT	Refractory	
Harbison-Walker Refractories <sup>b</sup>	Hammond, IN	Refractory	
Macalloy Corp.	Charleston, SC	Metallurgical	
National Refractories and Mining Corp.	Moss Landing, CA	Refractory	
National Refractories and Mining Corp.	Columbiana, OH	Refractory	
North American Refractories Co. Ltd.	Womelsdorf, PA	Refractory	
Occidental Chemicals Corp.	Castle Hayne, NC	Chemical	
Satra Concentrates Inc.	Steubenville, OH	Metallurgical	

<sup>a</sup> - Papp, John. "Chromium," <u>Minerals Yearbook Volume 1. Metals and Minerals 1992.</u> United States Bureau of Mines. 1992. p. 355. <sup>b</sup> - a division of Dresser Industries Inc.

Ferrochromium, an alloy of iron and chromium, is used as an additive in steel making. There are three major grades of ferrochromium: low carbon, high carbon, and charge grade. In the past, low carbon ferrochromium was required by steel makers to keep the carbon content of steel low. However, improved ladle refining techniques

<sup>&</sup>lt;sup>1</sup> John Papp, "Chromium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, p. 43.

<sup>&</sup>lt;sup>2</sup> <u>Ibid</u>, p. 42.

<sup>&</sup>lt;sup>3</sup> "Chromium and Chromium Alloys," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 4th ed., Vol. VI, 1993, p. 230.

such as argon oxygen decarburization, have allowed the steel industry to use high carbon ferrochromium, which is less expensive.<sup>4</sup>

Ferrochromium-silicon is used in the metallurgical industry to produce stainless, alloy, and tool steels and cast irons.<sup>5</sup> Ferrochromium-silicon is a smelted product of chromite ore; silicon is added during the smelting process. Although a high silicon ferrochromium is sometimes produced as an intermediate in the production of low carbon ferrochromium, no ferrochromium-silicon is being produced in the United States, and it is unlikely to be produced domestically again.<sup>6,7</sup> Ferrochromium-silicon typically contains 34 to 42 percent chromium, 38 to 45 percent silicon and 0.05 to 0.06 percent carbon.<sup>8</sup>

# B. Generalized Process Description

#### 1. Discussion of Typical Production Processes

Chromite ore is prepared for processing using several methods, depending on the ore source and the end use requirements. Course clean ore is hand sorted, while fine clean ore is gravity separated. Lumpy ore mixed with host rock may require heavy-media separation. If the chromite mineral occurs in fine grains intermixed with host rock, crushing, gravity separation and magnetic separation may be used.<sup>9</sup> Chromite ore is typically beneficiated before it is sold, hence many of these operations may not be conducted in the United States.<sup>10</sup> Exhibit 2 is a conceptual diagram of chromite ore processing. Either ferrochromium or sodium chromate is produced, and may be sold or further processed to manufacture other chromium compounds, as well as chromium metal.

# 2. Generalized Process Flow Diagram

# Ferrochromium

Ferrochromium is made by smelting chromite ore in an electric arc furnace with flux materials (quartz, dolomite, limestone, and aluminosilicates) and a carbonaceous reductant (wood chips, coke, or charcoal.) Lumpy ore may be fed directly to the furnace, while finer ore must be agglomerated before it is added to the furnace. In efficiently operated smelters, furnace dust is collected and resmelted, and slag is crushed and processed to recover chromium. The chromium content of the ferrochromium is determined by the chromite ore's chromium to iron ratio.<sup>11</sup> The production of low carbon ferrochromium requires top blowing with oxygen. Aluminum, or more frequently, silicon is used as the reducing agent. Extremely low carbon ferrochromium is made by the simplex process, in which high carbon ferrochromium and oxidized ferrochromium are heated under high vacuum. The

<sup>8</sup> <u>Ibid</u>, p. 234.

<sup>9</sup> John Papp, 1992, <u>Op. Cit.</u>, p. 327.

<sup>10</sup> John Papp, "Chromite," <u>Industrial Minerals and Rocks</u>, 6th Ed., Society for Mining, Metallurgy, and Exploration, 1994, p. 210.

<sup>11</sup> John Papp, 1992, <u>Op. Cit.</u>, p. 328.

<sup>&</sup>lt;sup>4</sup> John Papp, "Chromium," <u>Minerals Yearbook Volume 1. Metals and Minerals 1992</u>, U.S. Bureau of Mines, 1992, p. 325.

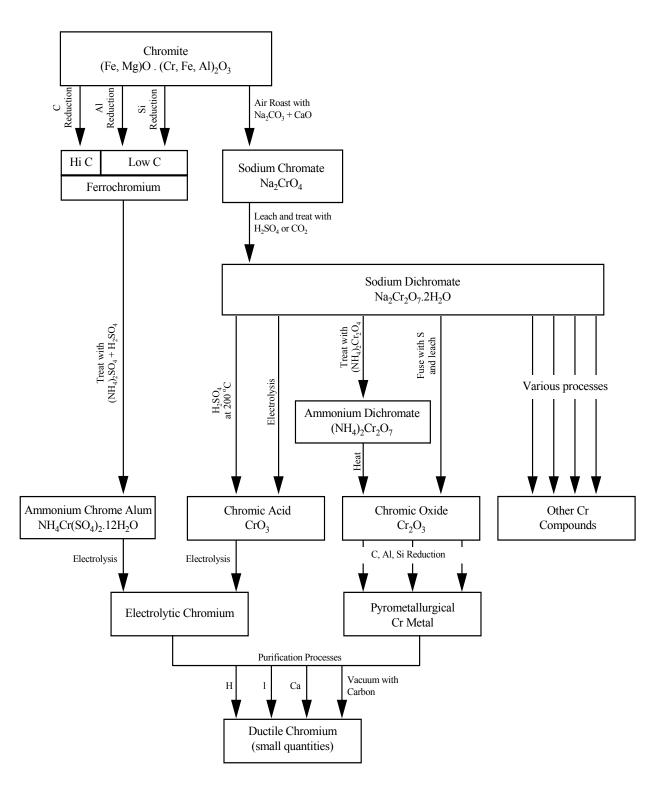
<sup>&</sup>lt;sup>5</sup> John Papp, "Chromium," <u>Mineral Facts and Problems</u>, U.S. Bureau of Mines, 1985, p. 141.

<sup>&</sup>lt;sup>6</sup> Personal Communication between ICF Incorporated and John Papp, U.S. Bureau of Mines, March 1994.

<sup>&</sup>lt;sup>7</sup> "Chromium and Chromium Alloys," 1993, <u>Op. Cit.</u>, p. 232.

# CONCEPTUAL DIAGRAM OF CHROMITE ORE PROCESSING

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1993, p. 275.)



carbon and oxygen form carbon monoxide, leaving a pure ferrochromium with a carbon content of about 0.01 weight percent.<sup>12</sup>

#### Sodium Chromate and Dichromate

Sodium chromate and dichromate are produced at two facilities by a hydrometallurgical process during which ground chrome ore and soda ash are mixed (lime and/or leached calcine are sometimes added as well), roasted in an oxidizing atmosphere, and leached with weak chromate liquor or water, as shown in Exhibit 3.<sup>13</sup> The resulting leach liquor is separated from the remaining leach residue. At the American Chrome and Chemicals facility, the roasting/leaching sequence is repeated, that is, two complete chromium extraction cycles are performed prior to removal of the residue. The leach residue is then treated, as discussed below. The treatment residue from this operation is classified as a RCRA special waste; it is disposed on-site at both facilities.<sup>14</sup> The leach solution contains unrefined sodium chromate; this liquor is neutralized and then filtered (not shown) to remove metal precipitates (primarily alumina hydrate).<sup>15</sup> The alumina-free sodium chromate may be marketed, but the predominant practice is to convert the chromate to the dichromate form. Occidental Chemicals Corp. uses a continuous process that involves treatment with sulfuric acid, evaporation of sodium dichromate, and precipitation of sodium sulfate (see left output stream from leaching and precipitation operation in Exhibit 3.) Sodium sulfate may be sold as a byproduct or disposed. American Chrome and Chemicals uses carbon dioxide (CO<sub>2</sub>) to convert the chromate to dichromate (see right output stream from leaching and precipitation operation in Exhibit 3.) This process confers the advantage of not generating a sludge. The dichromate liquor may be sold as 69 percent sodium dichromate solution or returned to the evaporators, crystallized, and sold as a solid.<sup>16</sup>

#### **Chromium Oxide**

Sodium dichromate can be converted into both anhydrous chromic oxide and hydrated chromic oxide.<sup>17</sup> To produce anhydrous chromic oxide (not shown), sodium dichromate, sulfur and wheat flour are blended with water, and the resultant slurry is heated in a kiln. The material recovered from the kiln is slurried with water, filtered, washed, dried, ground to size, screened and packaged. To produce hydrated chromic oxide (not shown), sodium dichromate solution and boric acid are blended and heated in a kiln. The reacted material is slurried with water and washed. Most of the washwater from the process is treated with sulfuric acid to recover boric acid. A waste stream containing boric acid and sodium sulfate leave the boric acid recovery unit. The product with some of the final washwater is filtered, ground, screened and packaged.<sup>18</sup>

<sup>12</sup> "Chromium and Chromium Alloys," 1993, Op. Cit., p. 232.

<sup>13</sup> <u>Ibid</u>., p. 275.

<sup>14</sup> American Chrome and Chemicals and Occidental Chemical, 1989. Company Responses to the "National Survey of Solid Wastes from Mineral Processing Facilities", U.S. EPA, 1989.

<sup>15</sup> Marks, et al., editors, <u>Encyclopedia of Chemical Technology</u>, Wiley Interscience, New York, NY, 1978, pp. 93-94.

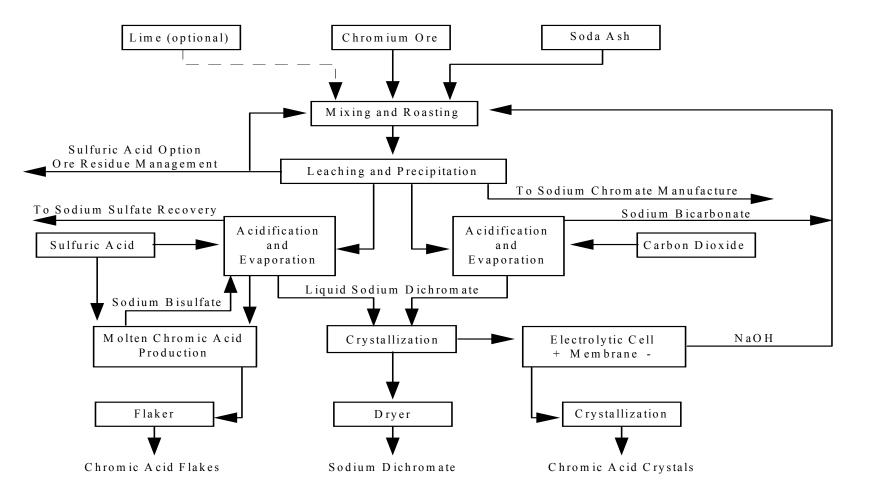
<sup>16</sup> U.S. Environmental Protection Agency, <u>Report to Congress on Special Wastes from Mineral Processing</u>, Volume II, Office of Solid Waste, July 1990, p. 4-2.

<sup>17</sup> Processing of either form of chromic oxide, as well as chromium metal are not primary mineral processing, and are therefore outside the scope of this report. Brief descriptions of these processes have been included for completeness.

<sup>18</sup> Versar, Inc., <u>Multi-Media Assessment of the Inorganic Chemicals Industry</u>, Vol. II, Prepared for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, August 1980, pp. 3-13 - 3-16.

# SODIUM CHROMATE AND SODIUM DICHROMATE PRODUCTION

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1993, p. 275.)



#### **Chromium Metal**

Chromium metal can be made either pyrometallurgically or electrolytically. In the pyrometallurgical method (not shown), chromium oxide ( $Cr_2O_3$ ) reacts with aluminum powder in a refractory lined vessel after being ignited with barium peroxide and magnesium powder. Chromium metal may also be made from the oxide by reduction with silicon in an electric arc furnace. The chromium from this process is similar to that obtained by the aluminothermic process, except the aluminum content is lower and the silicon content may approach 0.8 percent. Chromium may also be made by reducing chromium oxide briquets with carbon at low pressure and temperatures of 1,275 to 1,400°C.<sup>19</sup>

Exhibit 4 shows the production of electrolytic chromium by the chrome alum process conducted at the Elkem Metals Company's Marietta Plant. High carbon ferrochromium is ground and leached with a hot solution of reduced anolyte, chrome alum mother liquor, and makeup sulfuric acid. Cold mother liquor is added, and the slurry is filtered to remove the undissolved solids, which are mostly silica. The filtrate is conditioned at elevated temperature for several hours to convert the chromium to the non-alum form. The filtrate is then cooled to 5°C, allowing a crude ammonium sulfate to crystallize. This iron salt is further treated to form technical ferrous ammonium sulfate, which can be sold as fertilizer and other purposes. The filtrate is clarified and aged, allowing ammonium chrome alum to precipitate. The slurry is filtered, and the chrome alum is dissolved in hot water. The chrome alum solution is clarified and fed to the electrolysis cell. After the electrolysis is complete, the cathodes are removed, washed, and the metal is removed by air hammers. The metal is crushed, washed, and dehydrogenated.<sup>20</sup>

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

Research is being conducted to investigate the feasibility of using plasma smelting both worldwide, as a more efficient way of processing ferrochromium, and in the United States, to utilize low quality chromium bearing ores.<sup>21</sup>

# 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 typically does not 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.

<sup>&</sup>lt;sup>19</sup> "Chromium and Chromium Alloys," 1993, Op. Cit., pp. 232-234.

<sup>&</sup>lt;sup>20</sup> <u>Ibid.</u>, pp. 234-236.

<sup>&</sup>lt;sup>21</sup> J.E. Goodwill, "Developing Plasma Applications for Metal Production in the USA," <u>Iron and Steelmaking</u>, 17, No. 5, 1990, p. 352.

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

# Ferrochromium and Ferrochromium-Silicon

EPA determined that for ferrochromium and ferrochromium-silicon, mineral processing first occurs when the chromite ore undergoes smelting in an electric arc furnace and the physical/chemical structure of the chromite ore is significantly altered. 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.

# Sodium Chromate/Dichromate

EPA determined that for sodium chromate/dichromate, mineral processing occurs at the "leaching" sequence of the process because the ore is vigorously attacked (digested) with a concentrated acid to significantly change the physical structure of the ore. 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.

# Chromium Oxide

Since chromium oxide is produced from sodium dichromate, all of the wastes generated during chromium oxide production are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the sodium chromate/dichromate section above.

# Chromium Metal

Since chromium metal is produced from either ferrochromium or chromium oxide, all of the wastes generated during chromium oxide production are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the ferrochromium and chromium oxide sections above.

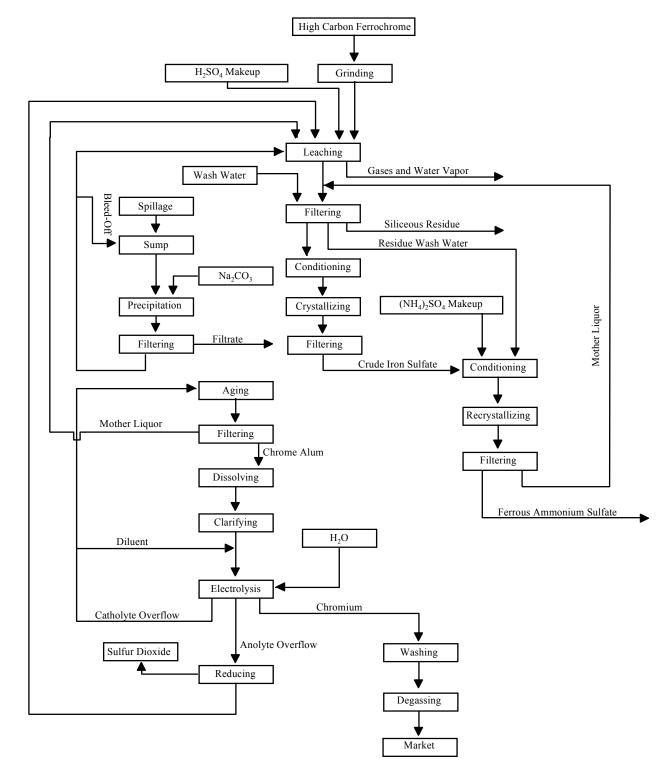
# C. Process Waste Streams

# 1. Extraction and Beneficiation Wastes

Wastes from the extraction and beneficiation of chromite may include gangue, and tailings. No information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

# **ELECTROLYTIC CHROMIUM METAL PRODUCTION**

# (Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1993, p. 235.)



# 2. Mineral Processing Wastes

The following waste streams have been associated with the production of sodium dichromate, ferrochromium, and ferrochromium-silicon.

#### Ferrochromium

**Dust or Sludge** was a listed hazardous waste (K091) that has been remanded. EPA has decided not to "relist" this waste. Data from the Newly Identified Mineral Processing Waste Characterization Data Set indicate the presence of chromium and selenium above toxicity characteristic levels for the remanded electrostatic precipitator (ESP) dust. This waste is thus considered to be a characteristic hazardous waste under RCRA Subtitle C. At the present time, there is only one generator of this characteristic D007 waste.<sup>22</sup> The generator treats the material by adding ferrous sulfate to reduce the leachable level of chromium to below regulatory levels. The non-hazardous ESP dust is either disposed of in an off-site sanitary landfill or is used as a binding agent in Macalloy's briquetting process. This facility reported producing approximately 3,000 metric tons of ESP dust annually.<sup>23</sup>

This facility also produces gas conditioning tower sludge (or GCT sludge) that it recycles back to the electric arc furnace. The commenter stated that this sludge usually does not exhibit the toxicity characteristic for chromium. Although no information was available on the generation rate of this waste, EPA estimated a low, medium, and high annual waste generation rate of 30, 300, and 3,000 metric tons/yr, respectively. The GCT sludge is fully recycled. This material formerly was classified as a sludge.

**Slag and Residues**. According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 47,000 metric tons of slag and residue are produced annually in the United States, and the available data do not indicate that the waste is hazardous.<sup>24</sup>

# Sodium Dichromate Production

**Treated roast/leach residue** is classified as a RCRA special waste. We note, however, that prior to treatment, the roast/leach residue is not a RCRA special waste. Treatment of the leach residue consists of treating the residue slurry with either a ferrous or sulfide ion to reduce hexavalent chromium followed by treatment with sulfuric acid to lower the pH level. American Chrome and Chemicals pumps the leach residue directly to a dedicated treatment unit, in which sulfuric acid and sodium sulfide are used to induce the desired chemical changes in the residue, while at Occidental Chemicals Corp., the untreated residue is pumped to a wastewater treatment plant which receives, and apparently combines, several other influent streams prior to treatment with several different chemical agents. At both plants, the treated residue is pumped in slurry form to disposal surface impoundments.<sup>25</sup>

The treated residue from roasting/leaching of chrome ore, is a solid material, though it typically is generated as a slurry containing particles between 2 mm and about 0.08 meters (3 inches) in diameter. The treated roast/leach residue is composed primarily of metallic oxides, such as those of iron, aluminum, silicon, magnesium, and

<sup>24</sup> U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Vol. I, Office of Solid Waste, August 1992, p. I-3.

<sup>25</sup> U.S. Environmental Protection Agency, 1990, Op. Cit., p. 4-2.

<sup>&</sup>lt;sup>22</sup> The Ferroalloys Association. Comment submitted in response to the <u>Supplemental Proposed Rule Applying</u> Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

<sup>&</sup>lt;sup>23</sup> Nexsen, Pruet, Jacobs & Pollard, LLP (Counsel to Macalloy Corporation). Comment submitted in response to the <u>Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. May 12, 1997.

chromium, as well as sulfates.<sup>26</sup> Using the available data on the composition of treated roast/leach residue, EPA evaluated whether the residue exhibited any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. The limited available data indicated that the waste did not exhibit any of the four hazardous waste characteristics.

According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 102,000 metric tons of treated leach residue are produced annually in the United States.<sup>27</sup>

# Ferrochromium-silicon

**Dust or Sludge** was a listed hazardous waste that has been remanded.<sup>28</sup> EPA has decided not to re-list this waste. According to the Newly Identified Mineral Processing Waste Characterization Data Set, there is presently no domestic production of ferrochromium-silicon. Additional data is provided in Attachment 1.

# D. Non-uniquely Associated Wastes

There are no non-uniquely associated wastes in this specific sector. However, standard 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

# **New Factual Information**

Two commenters provided new factual information that has been included in the sector report (COMM 3, COMM 48). Macalloy Corporation also provided comments on the May 1997 Second Supplemental Proposed Rule. These comments also have been captured in the sector report.

# Sector-specific Issues

One commenter indicated that it was encouraged to learn that the effort to obtain a chromium listing as K091 would be eliminated. However, the commented believes that EPA's Proposed Rule circumvents the remanding by Federal Court by calling the waste a so-called "newly identified" mineral processing waste, subject to the even more stringent UTS criteria. The commenter believes that EPA has ignored the wishes of the courts and has yielded to groups that desire only tougher regulations, apparently just for the sake of more regulation.<sup>29</sup> EPA does not agree that it is yielding to any influences and reaffirms that any solid waste that possesses one or more of the TCLP characteristics is indeed a hazardous waste that must be regulated under Subtitle C of RCRA.

<sup>28</sup> <u>Ibid</u>.

<sup>&</sup>lt;sup>26</sup> Occidental Chemical Corp., Company Responses to the "National Survey of Solid Wastes from Mineral Processing Facilities", U.S. EPA, 1989.

<sup>&</sup>lt;sup>27</sup> U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Vol. I, Office of Solid Waste, August 1992, p. I-3.

<sup>&</sup>lt;sup>29</sup> Macalloy Corporation. Comment submitted in response to the <u>Second Supplemental Proposed Rule Applying</u> <u>Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. May 12, 1997.

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# **US EPA ARCHIVE DOCUMENT**

ATTACHMENT 1

	Total Co	Total Constituent Analysis - PPM		EP Toxicity Analysis - PPM			тс	# Values		
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	12,100	12,100	12,100	1/1	1.39	1.39	1.39	1/1	-	-
Antimony	0.60	0.60	0.60	0/1	0.023	0.023	0.023	1/1	-	-
Arsenic	50.00	50.00	50.00	0/1	0.40	0.40	0.40	0/1	5.0	0
Barium	138	138	138	1/1	0.60	0.60	0.60	1/1	100.0	0
Beryllium	0.52	0.52	0.52	1/1	0.00050	0.00050	0.00050	0/1	-	-
Boron	-	-		. 0/0	-			- 0/0	-	-
Cadmium	0.15	0.15	0.15	0/1	0.0015	0.0015	0.0015	0/1	1.0	0
Chromium	41.00	801	1,560	2/2	2.07	12.69	27.00	3/3	5.0	2
Cobalt	1.00	1.00	1.00	1/1	0.0015	0.0015	0.0015	0/1	-	-
Copper	3.50	3.50	3.50	1/1	0.0015	0.0015	0.0015	0/1	-	-
Iron	1,270	1,270	1,270	1/1	0.0020	0.0020	0.0020	0/1	-	-
Lead	273	273	273	1/1	0.0010	0.02	0.03	2/2	5.0	0
Magnesium	121,000	121,000	121,000	1/1	954	954	954	1/1	-	-
Manganese	1,510	1,510	1,510	1/1	5.08	5.08	5.08	1/1	-	-
Mercury	0.049	0.049	0.049	0/1	0.00010	0.00010	0.00010	0/1	0.2	0
Molybdenum	0.145	0.145	0.145	0/1	0.0082	0.0082	0.0082	1/1	-	-
Nickel	16.20	16.20	16.20	1/1	0.033	0.033	0.033	1/1	-	-
Selenium	5.50	5.50	5.50	1/1	0.069	0.069	0.069	1/1	1.0	0
Silver	0.15	0.15	0.15	0/1	0.0015	0.0015	0.0015	0/1	5.0	0
Thallium	23.90	23.90	23.90	1/1	0.029	0.029	0.029	0/1	-	-
Vanadium	1.50	1.50	1.50	1/1	0.011	0.011	0.011	1/1	-	-
Zinc	3,270	3,270	3,270	1/1	1.63	1.63	1.63	1/1	-	-
Cyanide	-	-		. 0/0	-			- 0/0	-	-
Sulfide	-	-		. 0/0	-			- 0/0	-	-
Sulfate	-	-		. 0/0	-			- 0/0	-	-
Fluoride	-	-		. 0/0	-			- 0/0	-	-
Phosphate	-	-		0/0	-			- 0/0	-	-
Silica	-	-		0/0	-			- 0/0	-	-
Chloride	-	-		0/0	-			- 0/0	-	-
TSS	-	-		0/0	-			- 0/0	-	-
рН *	-	-		a (a					2 <ph>12</ph>	0
Organics (TOC)	-	-		0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - DUST OR SLUDGE - FERROCHROME - SILICON

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

	Total Co	Total Constituent Analysis - PPM EP Toxicity Analysis		ity Analysis -	nalysis - PPM		TC	# Values		
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	28,100	29,200	30,300	2/2	0.017	0.068	0.12	2/2	-	-
Antimony	3.85	11.43	19.00	1/2	0.039	0.047	0.055	2/2	-	-
Arsenic	2.65	2.85	3.05	0/2	0.006	0.014	0.040	1/4	5.0	0
Barium	75.60	76.00	76.40	2/2	0.083	0.575	1.60	4/4	100.0	0
Beryllium	0.66	1.33	2.00	2/2	0.00050	0.00050	0.00050	0/2	-	-
Boron	-			- 0/0	-			- 0/0	-	-
Cadmium	0.70	0.78	0.85	0/2	0.0015	0.0027	0.0050	0/3	1.0	0
Chromium	3,390	5,360	6,470	3/3	0.010	17.99	63.20	18/21	5.0	12
Cobalt	9.20	9.20	9.20	1/1	0.00150	0.00150	0.00150	0/2	-	-
Copper	9.20	24.35	39.50	2/2	0.0020	0.0020	0.0020	0/2	-	-
Iron	6,240	15,170	24,100	2/2	0.0020	0.0020	0.0020	0/2	-	-
Lead	300	1,290	1,860	3/3	0.0050	0.57	4.73	10/17	5.0	0
Magnesium	188,000	188,500	189,000	2/2	409	880	1,350	2/2	-	-
Manganese	5,750	5,770	5,790	2/2	0.013	0.72	1.43	2/2	-	-
Mercury	0.26	0.32	0.38	1/2	0.00010	0.00053	0.00100	0/3	0.2	0
Molybdenum	3.20	3.75	4.30	2/2	0.022	0.037	0.052	2/2	-	-
Nickel	128	130	131	2/2	0.003	0.006	0.009	1/2	-	-
Selenium	37.00	42.90	48.80	2/2	0.02	22.79	68.20	2/3	1.0	1
Silver	5.60	5.95	6.30	2/2	0.0020	0.0050	0.010	2/4	5.0	0
Thallium	27.10	130	232	2/2	0.066	0.077	0.088	2/2	-	-
Vanadium	17.70	19.35	21.00	2/2	0.0015	0.0025	0.0035	1/2	-	-
Zinc	13,600	14,300	15,000	2/2	0.0010	0.0015	0.0020	1/2	-	-
Cyanide	0.59	0.59	0.59	1/1	-			- 0/0	-	-
Sulfide	5.05	5.05	5.05	0/1	-			. 0/0	-	-
Sulfate	-			- 0/0	-			- 0/0	-	-
Fluoride	485	485	485	1/1	-			- 0/0	-	-
Phosphate	-			- 0/0	-			- 0/0	-	-
Silica	-	-		- 0/0	-			- 0/0	-	-
Chloride	-	-		- 0/0	-			- 0/0	-	-
TSS	-			- 0/0	-			- 0/0	-	-
рН *	-	-		- 0/0					2 <ph>12</ph>	0
Organics (TOC)				- 0/0						-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - DUST OR SLUDGE - FERROCHROME

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

# COAL GAS

#### A. Commodity Summary

In 1992, more than 997,545,000 short tons of coal were produced by 2,746 mines located in the United States.<sup>1</sup> Coal is classified into four general categories: bituminous, subbituminous, lignite, and anthracite coal. Nearly all coal is used in combustion or coking. At least 80 percent is burned directly in boilers for generation of electricity or steam. Small amounts are used for transportation, space heating, and firing of ceramic products. The rest is essentially pyrolyzed to produce coke, coal gas, ammonia, coal tar, and light oil products from which many chemicals are produced. Combustible gases and chemical intermediates are also produced by the gasification of coal, and different carbon products are produced by various heat treatments. A small amount of coal is used in miscellaneous applications such as fillers, pigments, foundry material, and water filtration.<sup>2</sup>

Coal gasification produces a synthetic gas that is either further processed and sold as synthetic natural gas or used to fire a gas turbine, generating electricity in an integrated gasification combined cycle (IGCC) system. As shown in Exhibit 1, there is only one commercial scale synthetic gas producer, and two commercial scale IGCC plants.<sup>3</sup> The Tennessee Eastman facility is used in the production of acetic anhydride. There are also several demonstration scale projects funded, at least in part, by the U.S. Department of Energy's Clean Coal Technology (CCT) program, including two coal preparation technologies, one mild gasification project, and one indirect liquefaction project, as well as six IGCC systems.<sup>4</sup> Exhibit 2 lists the Clean Coal Projects, their sponsors, locations, types of technology, and status. In addition to the CCT demonstration projects, there may be other planned or operating private demonstration scale projects. The profitability of existing facilities and the potential for the opening of new plants will be affected by the prices of traditional fuel sources such as oil and gas.

# **EXHIBIT 1**

# SUMMARY OF COMMERCIAL COAL GASIFICATION FACILITIES

Facility Name	Location	Type of Process	
Great Plains Coal Gasification Plant, Dakota Gasification Co. <sup>a</sup>	Beulah, ND	Synthetic Gas	
Louisiana Gasification Technology, Inc. <sup>a</sup>	Placamine, LA	IGCC	
Tennessee Eastman <sup>b</sup>	NA	IGCC	

<sup>a</sup> - U.S. EPA, <u>Report to Congress on Special Wastes from Mineral Processing</u>, July 1990, p. 5-1.

<sup>b</sup> - "Coal Conversion Processes (Gasification)," <u>Kirk-Othmer Encyclopedia of Chemical Technology.</u> Vol 6. 4th. ed. 1993. pp. 543.

<sup>&</sup>lt;sup>1</sup> U.S. Department of Energy, <u>Coal Production 1992</u>, Energy Information Administration, October 1993, p. 18.

<sup>&</sup>lt;sup>2</sup> "Coal," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 4th ed., Vol VI, 1993, p. 424.

<sup>&</sup>lt;sup>3</sup> A fourth subsidized commercial scale facility (Cool Water) operated from 1982 to 1988 in Daggett, California. This facility shut down after the Department of Energy funding ended.

<sup>&</sup>lt;sup>4</sup> U.S. Department of Energy, <u>Clean Coal Technology Demonstration Program: Program Update 1993</u>," December 31, 1993, pp. 7-2 - 7-3.

#### Project Name Sponsor Location Technology Project Stage Custom Coals Central City, Coal Self-Scrubbing Coal: An Design/ Integrated Approach to Clean Preparation International PA Permitting Air Advanced Coal Conversion Rosebud SynCoal Colstrip, MT Coal Operating Process Demonstration Partnership Preparation ENCOAL Mild Coal ENCOAL Near Gillette, Mild Operating **Gasification Project** Corporation WY gasification Commercial Scale Air Products and Kingsport, TN Indirect **Project Definition** Demonstration of the Liquid-Chemicals, Inc. Liquefaction Phase Methanol (LPMEOH) Process Springfield, IL IGCC Combustion Engineering ABB Combustion Assessing Project Engineering, Inc. IGCC Repowering Project Options Camden Clean Energy Negotiating Duke Energy Corp. Camden, NJ IGCC Demonstration Project Cooperative Agreement Sierra Pacific Reno, NV IGCC Pinon Pine IGCC Power Design Project Power Company TAMCO Power Toms Creek IGCC Coeburn, VA IGCC **Project Definition Demonstration Project** Partners Tampa Electric Integrated Tampa Electric Lakeland, FL IGCC Design/ Gasification Combined Cycle Company Permitting Project Wabash River Coal Wabash River Coal West Terre IGCC Construction Gasification Repowering Gasification Haute, IN **Repowering Project** Project Joint Venture

#### SUMMARY OF CLEAN COAL TECHNOLOGY DEMONSTRATION PROJECTS<sup>a</sup>

<sup>a</sup> - U.S. Department of Energy, "Clean Coal Technology Demonstration Program: Program Update 1993," December 31, 1993, pp. 6-22, 6-23, & 6-27.

# B. Generalized Process Description

# 1. Discussion of Typical Production Processes

Coal gasification is essentially incomplete combustion of coal, producing a product gas and heat instead of carbon dioxide and heat. In combustion, oxygen in stoichiometric excess reacts with the combustible matter in coal, mostly carbon and hydrogen, to produce heat, the primary product of interest, as well as carbon dioxide and water. Gasification involves the incomplete combustion of coal in the presence of steam. Only 20-30 percent of the oxygen theoretically required for complete combustion to carbon dioxide and water is used; therefore, only a fraction of the carbon in the coal is oxidized completely to carbon dioxide, the rest forms a mixture of gases including carbon

monoxide, methane, hydrogen and hydrogen sulfide. The heat released by the partial combustion provides the bulk of the energy necessary to drive the gasification reactions.<sup>5,6</sup> When synthetic gas is produced as a product, lignite coal is sized, and gasified with steam and oxygen producing raw gas, ash, and gasifier liquor. The gas is cooled, purified in several steps, and sold. This process is described in greater detail below.

#### 2. Generalized Process Flow Diagram

There is currently one facility, the Great Plains Coal Gasification Plant, which produces synthetic natural gas on a commercial scale. Exhibit 3 illustrates the production of synthetic natural gas at this facility. The facility employs 12 Lurgi Mark IV high pressure coal gasifiers, with two gasifiers on standby for spare capacity. Exhibit 4 is a schematic diagram of a Lurgi Mark IV Gasifier. Lignite coal, which is taken from four mines that are co-located with the facility, is crushed and fed to the top of individual gasifiers through a lock-hopper system; steam and compressed oxygen are introduced at the bottom of each gasifier.<sup>7</sup> The steam and oxygen travel up through the coal/ash bed. As steam and oxygen contact the coal in the gasifier, the resulting combustion reactions produce two major gases, carbon dioxide and carbon monoxide. The further reaction of these gases with carbon and steam results in "gasification," the formation of carbon oxides, methane, and hydrogen.<sup>8</sup>

After gasification occurs, excess carbon remains in the form of "char." The char is combusted in a hightemperature exothermic (heat releasing) reaction to provide energy for a series of reactions, including drying, devolatization, and gasification, most, but not all, of which are endothermic (heat using) reactions. The char is then converted to energy in the "combustion zone," roughly the middle of the gasifier. The residue of this combustion is the gasifier ash. The gases formed in these reactions rise to the top of the unit, where their heat dries and drives off volatiles liberated from the coal that has just entered the gasifier.<sup>9</sup> Because not all of the flue gas constituents are converted in the gasification process, the exiting gas stream contains both flue gas and product gas. These two gaseous streams are separated downstream of the gasifiers and the product gas is converted to salable methane.<sup>10</sup>

The ash remaining in the bed after the reaction is removed by a rotating grate at the bottom of the gasifier and is discharged through a gas lock. The ash is discharged into an enclosed ash sluiceway, where recirculating ash sluice water is introduced to cool the ash and transport it to the ash handling and disposal area. The hot crude product gas leaving the gasifiers goes through several operations, including quenching (to cool and clean), shift conversion (to alter the ratio of hydrogen to carbon monoxide), further cooling of the gas, and processing through the Rectisol unit (to remove sulfur compounds and carbon dioxide). The desulfurized crude gas is sent to the methanation unit; the product gas is then compressed and dried for delivery to a pipeline for distribution.<sup>11</sup>

<sup>7</sup> CDM Federal Programs Corporation, <u>Draft Report American Natural Gas Special Study</u>, Prepared for U.S. Environmental Protection Agency, Office of Waste Programs Enforcement, March 19, 1987, pp. 14-27.

<sup>8</sup> Dakota Gasification Company, "Letter to Mr. Robert Tonetti and Mr. Bob Hall, Office of Solid Waste, U.S. EPA", August 12, 1991, p. 5.

<sup>9</sup> Ibid.

<sup>10</sup> Dakota Gasification Company, "Lurgi Gasification and Flue Gas Scrubbing Simplified," Memorandum to D. W. Peightal from T. G. Towers, July 29, 1991.

<sup>11</sup> CDM Federal Programs Corporation, 1987, <u>Op. Cit.</u>, pp. 14-27.

<sup>&</sup>lt;sup>5</sup> "Coal Conversion Processes (Gasification)," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 4th ed., Vol. VI, 1993, p. 551.

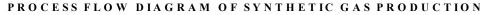
<sup>&</sup>lt;sup>6</sup> "Steam," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 3rd ed., Vol. XXI, 1983, pp. 543-544.

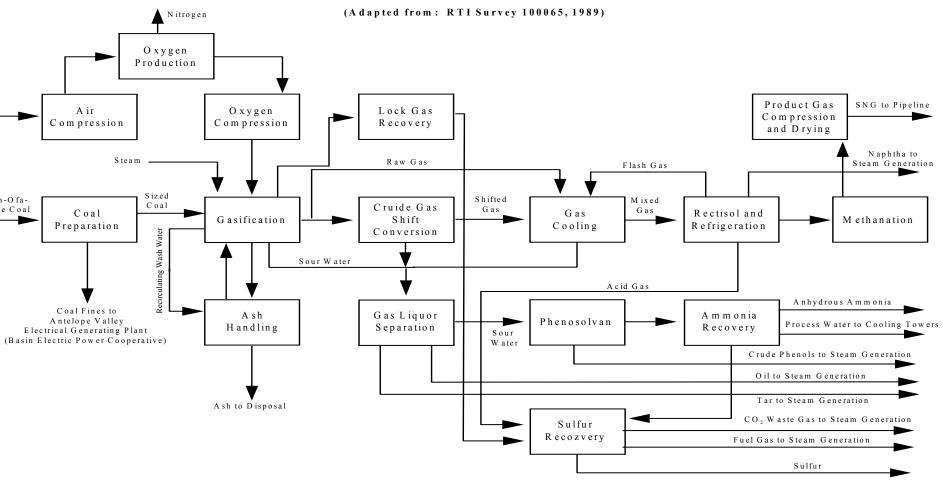
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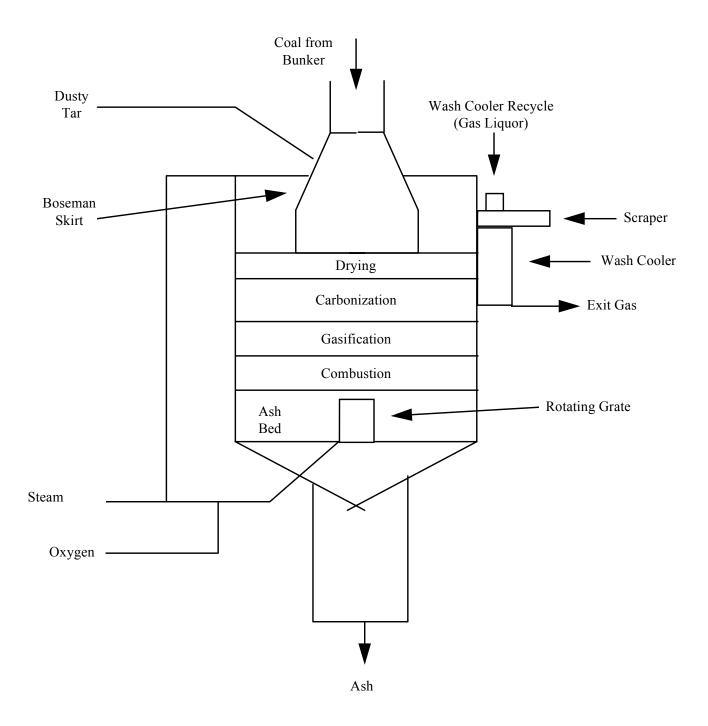
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# SCHEMATIC DIAGRAM OF LURGI MARK IV GASIFIER

(Adapted from: Dakota Gasification Company, July 29, 1991.)



The quenching operation described above, in addition to cooling the raw gas, serves to remove entrained particles from the gas and to condense and remove unreacted steam, organic compounds, and soluble gases. This cooling operation generates an aqueous stream known as quench liquor (labelled "sourwater" in Exhibit 3). This quench liquor, along with similar streams from the shift conversion, gas cooling, and rectisol units, are sent to the gas liquor separation unit (for removal of tar and oil), to a phenosolvan unit (for phenol recovery), and to a phosam-W ammonia recovery unit (for ammonia recovery). The process water leaving the phosam-W unit, known as stripped gas liquor, is classified as a RCRA special waste.

This process wastewater is used as makeup water for a water cooling system that is needed to cool the gasifiers during operation. The hot water is routed to a cooling tower used to remove heat from the system. Evaporation from the cooling tower exceeds the quantity of stripped gas liquor generated on an annual basis; hence, all stripped gas liquor is used as makeup water. The stripped gas liquor passes through the cooling tower (not shown) where it is concentrated, reducing the volume by a factor of ten, and through the Multiple Effects Evaporator (not shown) where it is concentrated again, further reducing the volume by a factor of ten. This concentrate then goes to the Liquid Waste Incinerator (LWI) for incineration. The blowdown water from the LWI is used as makeup water to the ash sluice system.<sup>12,13</sup>

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

In an IGCC unit, oxygen, pulverized coal, and sometimes steam are gasified, and the syngas is cooled, cleaned and combusted to power a gas turbine, to generate electricity. Excess heat is also recovered to generate electricity using a steam turbine. IGCC, coking, and pyrolysis are considered to be energy producing operations rather than mineral processing, and are therefore outside the scope of this report.

# 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.

<sup>&</sup>lt;sup>12</sup> North Dakota State Department of Health, Letter to Robert L. Duprey, Director, Waste Management Division, EPA, June 10, 1986. p. 1.

<sup>&</sup>lt;sup>13</sup> CDM Federal Programs Corporation, 1987, <u>Op. Cit.</u>, pp. 41-42.

EPA determined that for the production of coal gas, the beneficiation/processing line occurs between coal preparation and coal gasification due to the chemical reaction that occurs between oxygen, steam, and coal within the gasification unit that significantly changes the physical/chemical structure of coal. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

# C. Process Waste Streams

# 1. Extraction and Beneficiation Wastes

Wastes from the extraction and beneficiation of coal may include gangue, fines, baghouse coal dust, and coal pile runoff. Run-of-mine lignite from neighboring mines is crushed to less than 2 inches. Fines are removed by screening and are sent to an adjacent power plant. Baghouses collect the dust from crushing, conveying, sizing, and storage operations. Coal dust collected in the baghouses is returned to the process. Coal pile runoff is handled by the plant's storm drainage system, which includes a coal pile runoff retention pond. This pond provides sufficient retention time to permit coal particles, soil sediments, and dust suspended in the stormwater to settle out. The clarified water from the pond is discharged to the stormwater pond through an overflow weir.<sup>14</sup>

# 2. Mineral Processing Wastes

**Gasifier Ash** is classified as a RCRA special waste. This ash is removed from the bottom of the gasifier, quenched, passed through crushers to reduce the maximum size to eight centimeters, and sluiced into ash sumps for settling and dewatering. The dewatered ash is trucked to an on-site clay-lined landfill, where it is disposed of along with ash from boilers, superheaters, and incinerators, and settled solids from process water management units (e.g., impoundments, API separators.)<sup>15</sup> The North Dakota Department of Health reported that the Beulah facility had considerable problems with their dewatering system which resulted in the disposal of large quantities of very wet ash.<sup>16</sup> According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 301,000 metric tons of gasifier ash are produced annually in the United States.<sup>17</sup>

**Process Wastewater** is classified as a RCRA special waste.<sup>18</sup> According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 5,143,000 metric tons of process wastewater are produced annually in the United States.<sup>19</sup> The management of the process wastewater (i.e., stripped gas liquor) is reuse; the water is used as make-up water for the water-cooling system that cools the gasifiers. Specifically, the process wastewater is routed from the cooling tower to the multiple effect evaporators, to the liquid waste incinerator, and finally to the gasifier ash handling system.

<sup>16</sup> North Dakota State Department of Health, 1986, <u>Op. Cit.</u>, pp. 1-2.

<sup>17</sup> U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Vol. I, Office of Solid Waste, August 1992, p. I-3.

<sup>18</sup> U.S. Environmental Protection Agency, 1990, <u>Op.Cit.</u>, p. 5-3.

<sup>&</sup>lt;sup>14</sup> <u>Ibid.</u>, pp. 63-64.

<sup>&</sup>lt;sup>15</sup> U.S. Environmental Protection Agency, <u>Report to Congress on Special Wastes from Mineral Processing</u>, Volume II, Office of Solid Waste, July 1990, p. 5-3.

<sup>&</sup>lt;sup>19</sup> U.S. Environmental Protection Agency, 1992, <u>Op.Cit.</u>, p. I-3.

According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 646,000 metric tons of cooling tower blowdown are produced annually in the United States.<sup>23</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further. Multiple Effects Evaporator Concentrate. Cooling tower blowdown is treated in a multiple effects evaporator (MEE) unit. Distillate from this treatment is returned to the cooling system or used as other facility utility water. The remaining residual, MEE concentrate, is returned as feed to the gasifier or is sent to an on-site liquid waste incinerator (LWI). Separate surge ponds are used for storage of MEE distillate and concentrate.<sup>24</sup> MEE concentrate has been found to exhibit the characteristic of EP toxicity for arsenic and selenium. The arsenic levels range from 3-29 ppm and the selenium levels from 15-44 ppm.<sup>25</sup> This waste stream is partially recycled and classified as a by-product. Although no published information regarding the 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

> Multiple Effects Evaporator Pond Sludge. Approximately 100 cubic yards of MEE pond sludge are generated annually in the United States.<sup>26</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

generation rate of 0 metric tons/yr, 0 metric tons/yr, and 65,000 metric tons/yr, respectively.

Liquid Waste Incinerator Blowdown. Spent cooling water from the LWI unit, referred to as LWI blowdown, is sent to the coal ash sluice area to be included as make-up water for ash handling. Any incinerator

- <sup>22</sup> U.S. Environmental Protection Agency, 1990, Op.Cit., p. 5-4.
- <sup>23</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-3.
- <sup>24</sup> U.S. Environmental Protection Agency, 1990. Op. Cit., p. 5-4.

<sup>25</sup> North Dakota State Department of Health, 1986, Op. Cit., p. 1.

<sup>26</sup> Versar, Inc. Draft Site Visit Report on Dakota Gasification Company, Prepared for U.S. Environmental Protection Agency, Office of Solid Waste, August 4, 1989. p. 3.

Surface Impoundment Solids (Cooling Tower Pond Sludge). When the supply of process wastewater generated on a daily basis exceeds the need for cooling system make-up water, the process wastewater is stored in an impoundment until it is needed. No long-term accumulation of waste occurs in this unit; the water is pumped to the cooling tower and any settled solids are dredged (approximately 13 metric tons in 1988) and sent to the solid waste disposal landfill.<sup>20</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Zeolite Softening PWW. Available data do not indicate that the waste exhibits hazardous characteristics.<sup>21</sup> Therefore, the Agency did not evaluate this material further.

Cooling Tower Blowdown. Evaporation of water inside the cooling water system increases the concentration of any impurities in the make-up water remaining in the cooling system; these impurities can lead to scaling or other operational problems in the system. Therefore, the cooling water in the system is bled off at a rate of 360-500 gpm to prevent concentrations of impurities from reaching unacceptable levels. This concentrated bleed, known as cooling tower blowdown, was generated at a rate of approximately 766,000 metric tons in 1988. The cooling tower blowdown is treated in a multiple effects evaporator (MEE) unit.<sup>22</sup>

<sup>&</sup>lt;sup>20</sup> U.S. Environmental Protection Agency, 1990, <u>Op.Cit.</u>, p. 5-3.

<sup>&</sup>lt;sup>21</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-3.

ash/solids in the blowdown are, therefore, combined with the gasifier ash and managed as such.<sup>27</sup> LWI blowdown was found to exhibit the characteristic of EP toxicity for arsenic and selenium. The arsenic levels range from 6-16 ppm and the selenium levels from 7-54 ppm.<sup>28</sup> Although no published information regarding the 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 0 metric tons/yr, 0 metric tons/yr, and 45,000 metric tons/yr, respectively. LWI blowdown is recycled in process, therefore, it is not included in the analysis.

**Liquid Waste Incinerator Pond Sludge**. Approximately 300 cubic yards of liquid waste incinerator pond sludge are generated annually in the United States.<sup>29</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent Methanol Catalyst**. The methanation unit uses a nickel catalyst to upgrade the synthetic gas to methane. The spent catalyst is recycled.<sup>30</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, 5,000 metric tons/yr, and 45,000 metric tons/yr, respectively. This waste stream is not hazardous, therefore, it is not included in the analysis.

**Stretford Solution Purge Stream**. The Stretford process uses a dilute solution of sodium carbonate, sodium bicarbonate, sodium metavanadate, and anthraquinone disulfonic acid (ADA) to remove hydrogen sulfide from a number of gas streams and convert it to elemental sulfur. After hydrogen sulfide removal, the treated gas stream is incinerated in the boilers for its fuel value. The Stretford solution purge stream contains vanadium salts, thiosulfate, thiocyanate, and ADA. The purge stream is collected in a wastewater tank, concentrated in a crystallizer, and subsequently disposed of as a liquid. This liquid crystallizes into a solid during cooling after it is transported to a secure disposal site. The liquid removed during concentration is used as cooling tower makeup water.<sup>31</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 5,000 metric tons/yr, 17,000 metric tons/yr, and 45,000 metric tons/yr, respectively. This waste stream is not hazardous, therefore, it is not included in the analysis.

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

# Oily Water Treatment System

Oily water from all paved process areas drain to the oily water sewer. In addition, contaminated stormwater and other contaminated waters may be diverted to the oily water sewer, which drains into the oily water treatment system. This treatment system is intended to process contaminated water streams from the plant by reducing the oil content from between 10 and 100 ppm free oils to less then 5 ppm free oils. The system consists of American Petroleum Institute (API) separators, dissolved air flotation units, vacuum filtration of sludges and froths, and pressure media filtration. Effluent from this system is discharged to the cooling tower.

<sup>&</sup>lt;sup>27</sup> As reported by Dakota Gasification Company, approximately 32,000 metric tons of LWI blowdown was generated in 1988 with a solids content of 5 percent; these approximately 1,600 metric tons of solids are assumed to be included in the total volume of gasifier ash reported by the company.

<sup>&</sup>lt;sup>28</sup> North Dakota State Department of Health, 1986, <u>Op. Cit.</u>, p. 1.

<sup>&</sup>lt;sup>29</sup> Versar, Inc., 1989, <u>Op. Cit.</u>, p. 3.

<sup>&</sup>lt;sup>30</sup> CDM Federal Programs Corporation, 1987, <u>Op. Cit.</u>, p. 6.

<sup>&</sup>lt;sup>31</sup> <u>Ibid.</u>, pp. 52-58.

The oily water is pumped to two API separators in parallel. Oils are skimmed off and sent to the slop oil decanting tanks, while sludge is scraped off the bottom and transferred to the froth sump. The slop oil is used as fuel for the boilers. Effluent from the API separators is transferred to the dissolved air flotation units where air, coagulant aid, and caustic or acid are added to assist in removing any remaining oils. Under some plant operating conditions, this API separator effluent is routed to cooling tower surge ponds following treatment.

Oils from the top and sludges from the bottom of the DAF unit are transferred to the froth sump. DAF effluent is passed through sand filters before it is used as cooling tower makeup water. The API/DAF sludge in the froth sump is sent to the vacuum precoat drum filter. This equipment is operated only when sufficient quantities of sludge have accumulated. The filter cake is collected in hoppers for off-site disposal and the filtrate is returned to the oily water sewer.<sup>32</sup>

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

**API Oil/Water Separator Sludge**. Approximately 1,500 cubic yards of API oil/water separator sludge are generated annually in the United States.<sup>33</sup> These sludges are disposed of off-site.<sup>34</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

**Dissolved Air Flotation Sludge**. Approximately 2,688 cubic yards of dissolved air flotation sludge are generated annually in the United States.<sup>35</sup> The DAF sludges are disposed of with the gasifier ash.<sup>36</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

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

**Vacuum Filter Sludge**. The vacuum filter sludge is generated intermittently. This stream is disposed of with the ash in the plant's ash handling system.<sup>37</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

# D. Non-uniquely Associated Wastes

Non-uniquely associated and ancillary hazardous wastes may be generated by cleaning operations that generate up to 3,350 gallons of spent solvents each year; laboratory services that may generate 1,800 gallons of hazardous waste (F002, F003, F004, and D002) each year; and container storage, which could generate hazardous wastes from spills, and the associated clean up activities. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil (which has been analyzed and found to be non-hazardous).<sup>38</sup>

<sup>32</sup> <u>Ibid.</u>, pp. 36-37.

<sup>&</sup>lt;sup>33</sup> Versar, Inc, 1989, <u>Op. Cit.</u>, p. 3.

<sup>&</sup>lt;sup>34</sup> CDM Federal Programs Corporation, 1987, <u>Op. Cit.</u>, p. 7.

<sup>&</sup>lt;sup>35</sup> Versar, Inc., 1989, <u>Op. Cit.</u>, p. 3.

<sup>&</sup>lt;sup>36</sup> CDM Federal Programs Corporation, 1987, <u>Op. Cit.</u>, p. 7.

<sup>&</sup>lt;sup>37</sup> <u>Ibid</u>., p. 39.

<sup>&</sup>lt;sup>38</sup> <u>Ibid.</u>, pp. 73-76.

# E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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# COPPER

#### A. Commodity Summary

The physical properties of copper, including malleability and workability, corrosion resistance and durability, high electrical and thermal conductivity, and ability to alloy with other metals, have made it an important metal and production input to a number of diverse industries.<sup>1,2</sup> Copper deposits are found in a variety of geological environments, which are affected by the rock-forming processes that occurred at a particular location. These deposits can be grouped in the following broad classes: porphyry and related deposits, sediment-hosted copper deposits, volcanic-hosted massive sulfide deposits, veins and replacement bodies associated with metamorphic rocks, and deposits associated with ultramafic, mafic, ultrabasic, and carbonatite rocks. The most commonly mined type of copper deposit, porphyry copper, is found predominantly in areas along the western continental edges of North and South America, as well as in the southwestern United States, associated with large granite intrusions.<sup>3,4</sup>

Copper occurs in about 250 minerals, only a few of these, however, are commercially important.<sup>5</sup> Deposits considered to be economically recoverable at current market prices may contain as little as 0.5 percent of copper or less, depending on the mining method, total reserves, and the geologic setting of the deposit.<sup>6</sup> Most copper ores contain some amount of sulfur-bearing minerals. The weathering environment affecting the ore body following deposition is determined mainly by the availability of oxygen. Ores exposed to air tend to be oxidized, while those in oxygen poor environments remain as sulfides.<sup>7</sup>

The United States is the second largest copper producer in the world. Next to Chile, the United States had the largest reserves (45 million metric tons) and reserve base (90 million metric tons) of contained copper. In 1994, domestic mine production rose to slightly more than 1.8 million metric tons and was valued at about \$4.4 billion. The principal mining states, in descending order, Arizona, Utah, New Mexico, Michigan, and Montana, accounted for 98 percent of domestic production; copper also was recovered at mines in seven other states. Eight primary and five secondary smelters, nine electrolytic and six fire refineries, and 15 solvent extraction-electrowinning plants were operating at the end of 1994. Refined copper and direct melt scrap were consumed at about 35 brass mills; 15 wire rod mills; and 750 foundries, chemical plants, and miscellaneous consumers.<sup>8</sup> Exhibit 1 presents the names and locations of the mining, smelting, refining, and electrowinning facilities located in the United States. As available, Exhibit 1 also presents information on potential site factors indicating whether the facility is located in a sensitive environment.

<sup>5</sup> <u>Ibid</u>., p. 9.

<sup>6</sup> <u>Ibid</u>., p. 7.

<sup>7</sup> <u>Ibid</u>., p. 9.

<sup>&</sup>lt;sup>1</sup> "Copper," Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., Vol. VII, 1993, p. 381.

<sup>&</sup>lt;sup>2</sup> U.S. Environmental Protection Agency, <u>Technical Resources Document-Extraction and Beneficiation of Ores</u> and <u>Minerals: Volume 4 Copper</u>, Office of Solid Waste, 1993d, p. 3.

<sup>&</sup>lt;sup>3</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 384.

<sup>&</sup>lt;sup>4</sup> U.S. Environmental Protection Agency, 1993d, Op. Cit., p. 7.

<sup>&</sup>lt;sup>8</sup> Edelstein, Daniel L, from Minerals Commodities Summaries, U.S. Bureau of Mines, January 1995, pp. 50-51.

# Summary of Copper Mining, Smelting, Refining, and Electrowinning Facilities<sup>9</sup>

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
ASARCO	El Paso, TX	Smelting	
ASARCO	Amarillo, TX	Electrolytic Refining	
ASARCO	Ray, AZ	Electrowinning	
ASARCO	Hayden, AZ	Smelting and Electrowinning	
Burro Chief Copper Mine	Tyrone, NM	Extraction and Electrowinning	
Chino Mines Company	Hurley, NM	Smelting/Fire Refining	100 year floodplain, karst terrain 1,000 feet below surface, private wells within 1 mile <sup>10</sup>
Copper Range	White Pine, MI	Open Pit Mining, Smelting and Refining	fault area
Cyprus Pinos Altos Mine	Silver City, NM	Extraction	
Cyprus	Claypool, AZ	Smelting, Refining, and Electrowinning	
Cyprus Casa Grande Mine	Casa Grande, AZ	In-situ Extraction and Roasting	
Cyprus Miami Mining Corp.	Claypool, AZ	Heap Leaching	fault area, private wells within 1 mile
Cyprus Mineral Park Corp.	Kingman, AZ	Dump Leaching	
Cyprus Sierrita/Twin Buttes	Green Valley, AZ	Heap Leaching	
Cyprus Mining	Bagdad, AZ	Electrowinning	
Cyprus Bagdad Copper Mine	Bagdad, AZ	Heap Leaching and Milling	

<sup>&</sup>lt;sup>9</sup> ICF Incorporated, <u>Mining and Mineral Processing Facilities Database</u>, August 1992.

<sup>&</sup>lt;sup>10</sup> Phelps Dodge Corporation. Comment submitted in response to the <u>Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly</u> <u>Identified Mineral Processing Wastes</u>, January 25, 1996.

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
Flambeau Copper Mine	Wisconsin <sup>11</sup>	Extraction	
Gibson Mine	Mesa, AZ	Strip and In-situ Extraction	
Johnson Camp Mine	Tucson, AZ	Heap Leaching	
Kennecott	Garfield, UT	Mining	low pH and metals contamination of ground water found hydraulically down-gradient from mine operations <sup>12</sup>
Kennecott <sup>13</sup>	Magma, UT	Smelting and Refining	
Magma Mine (BHP Copper)	Superior, AZ	Undercutting and Filling (Mining)	
Magma (BHP Copper)	San Manuel, AZ	Smelting, Refining, and Electrowinning	public and private wells within 1 mile
Mineral Park Mine	Kingman, AZ	Extraction	
Mission Unit	Sahuarita, AZ	Extraction	
Montanore Mine	Libby, MT	Extraction	
Morenci Mine	Morenci, AZ	Heap Leaching	
Noranda	Casa Grande, AZ	Electrowinning	
Oracle Ridge Mine	San Manuel, AZ	Extraction	
Phelps Dodge	Morenci, AZ	Electrowinning	
Phelps Dodge	Playas, NM	Smelting	

<sup>12</sup> <u>Ibid</u>.

<sup>13</sup> <u>Ibid</u>.

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
Phelps Dodge	El Paso, TX	Refining	fault area, public and private wells within 1 mile
Phelps Dodge	Hurley, NM	Smelting and Electrowinning	
Pinos Altos Mine	Silver City, NM	Extraction	
Pinto Valley Operations	Miami, AZ	Extraction and Electrowinning	
Pinto Valley	Pinto Valley, AZ	Electrowinning	
Ray Complex	Hayden, AZ	Extraction	
San Manuel Div. Mine	San Manuel, AZ	Extraction	
San Pedro Mine	Truth or Consequence, NM	Extraction	
Silver Butte Mine	Riddle, OR	Extraction	
Silver Bell Unit	Marana, AZ	Extraction	
St. Cloud Mining Co.	Truth or Consequence, NM	Extraction	
Sunshine Mine	Kellog, ID	Extraction	
Tennessee Chemical	Copperhill, TN	Closed	
Tyrone Branch Mine	Tyrone, NM	Dump Leaching and Electrowinning	
Western World Copper Mine	Marysville, CA	Extraction	
Yerington Mine	Tucson, AZ	Extraction	

The majority of the copper produced in the United States is used in the electrical industry; it is used for a wide range of wiring applications (from power transmission lines to printed circuit boards), in microwave and electrical tubes, motors and generators, and many other specialized applications where its high electrical and thermal conductivity can be employed. While copper has been replaced in some applications by aluminum (e.g., for overhead power lines) and fiber optics (e.g., in telecommunications), its durability, strength, and resistance to fatigue assure its continued use in the electrical industry. These latter three characteristics also make copper and copper alloys a valued material in construction and containment (e.g., pipes and tanks), and in other activities where endurance and resistance to corrosion are required.<sup>14</sup>

Primary production of copper in the United States steadily increased in the early 1990s. Total apparent consumption rose from 2,170,000 metric tons in 1990 to 2,800,000 metric tons in 1994. Approximately 42 percent of the 1994 domestic consumption of copper went to building and construction industries, while 24 percent was used by the electrical and electronic products industries. Industrial machinery and equipment consumed 13 percent, transportation equipment consumed 12 percent, and consumer and general products consumed the remaining 9 percent.<sup>15</sup> Clearly, the development of new infrastructure in the United States and abroad would increase the worldwide demand for copper, but consumption per unit of new gross product would be less than that in the past because substitutes for copper are often used in a number of industries. For example, new telephone infrastructure is largely based on fiber optics technology rather than copper. Continued re-opening of mothballed facilities, expansion of existing facilities, and development of new mines could lead to copper supplies increasing faster than demand.<sup>16,17</sup>

# B. General Process Description

# 1. Discussion of the Typical Production Process

The two major processes employed in the United States to recover copper from ores are classified as either (1) pyrometallurgical methods, or (2) hydrometallurgical methods. Pyrometallurgical methods consist of conventional smelting technology, and are widely used. Hydrometallurgical methods involve leaching and recovery by precipitation or electrowinning, and are gaining in popularity. For example, in 1984 100,180 tons of copper were produced by solvent extraction and electrowinning (SX/EW), while in 1992 439,043 tons were produced by SX/EW.<sup>18</sup> Some within the industry believe that hydrometallurgical operations are only economically attractive for producing 30,000 metric tons of copper product per year or less.<sup>19,20</sup>

# 2. Generalized Flow Diagram

Exhibit 2 presents a flow diagram of the typical pyrometallurgical operations involved in the production of copper from ore. Exhibit 3 presents a flow diagram of the typical hydrometallurgical operations involved in the production of copper from ore.

<sup>15</sup> Ibid.

<sup>16</sup> <u>Ibid</u>.

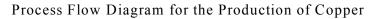
<sup>17</sup> U.S. Environmental Protection Agency, "Primary Copper Processing," <u>Report to Congress on Special Wastes</u> from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, p. 6-2.

<sup>18</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 412.

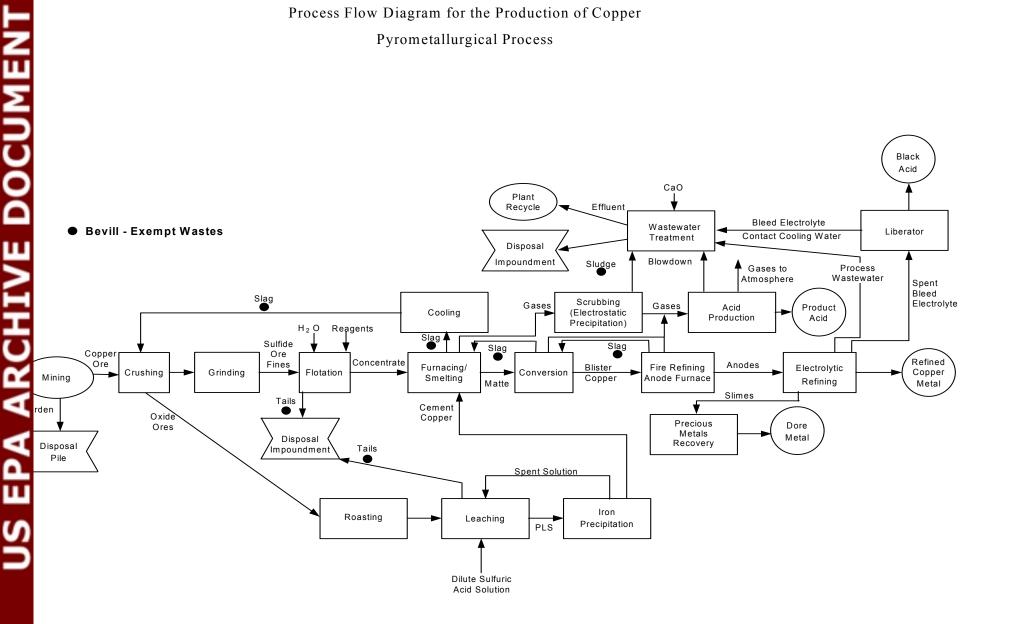
<sup>19</sup> <u>Ibid</u>., p. 408.

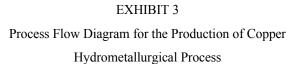
<sup>20</sup> Keith R. Suttill, "Pyromet or Hydromet?" Engineering and Mining Journal, 191, May 1990, p. 31.

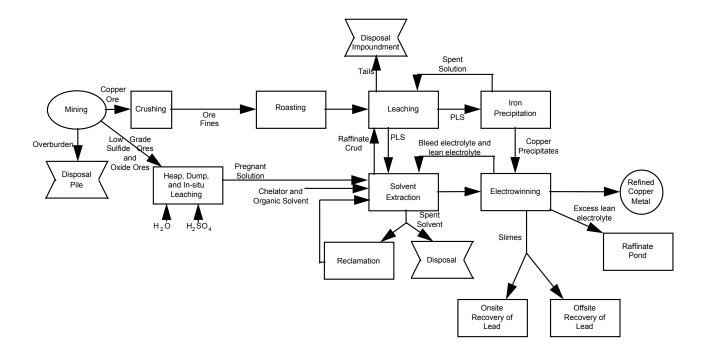
<sup>&</sup>lt;sup>14</sup> Edelstein, Daniel L, 1995, Op. Cit.



**Pyrometallurgical Process** 







# **Extraction and Beneficiation Operations**

Prior to pyrometallurgical operations, sulfide ore (which often contains less than one percent copper) is crushed and ground with water and placed in a concentrator.<sup>21</sup> The rock/water slurry is subjected to physical and chemical actions (i.e., air sparging and hydrophobic chemical reagents) inside a flotation tank. The chemical reagents assist the flotation process by acting as frothing and collector agents. Methylisobutyl carbonal (MIBC) is a typical frothing agent, and sodium xanthate, fuel oil, and VS M8 (a proprietary formulation) are typical collector agents. As a result of the physical and chemical actions, the copper value rises to the surface of the flotation unit as a froth.<sup>22</sup>

The material remaining on the bottom of the flotation tank (spent ore or "gangue"), is partially dewatered and then discharged to tailing ponds for disposal.<sup>23</sup> In cases in which the copper ore contains a large amount of clay minerals, "slime" (a mixture of clay minerals and copper values) often forms and is separated from the gangue for further copper recovery. The slime is reground and subjected to flotation to remove the copper value. Once the copper value is removed, the slime is ultimately managed/disposed with the gangue.<sup>24,25</sup>

The concentrate resulting from the flotation circuit contains approximately 30 percent copper and, in some instances, may also contain significant recoverable concentrations of molybdenum. If molybdenum is readily recoverable, as it is at Magma Copper (Arizona), the concentrate is sent to the molybdenum plant for recovery; otherwise, the concentrate is ready for subsequent pyrometallurgical operations.<sup>26,27</sup> Alternatively, the concentrate can be dewatered and the dry product may either be stored for further processing or shipped to another facility for processing. The collected water is usually recycled in the milling circuit.

All oxide ore and some low grade sulfide ores destined for hydrometallurgical beneficiation are not crushed, floated, or sent to a concentrator. These ores are instead leached with copper values recovered by solvent extraction and electrowinning operations.<sup>28,29</sup>

At a molybdenum recovery plant, such as the one at Magma Copper (Arizona), the copper concentrate contains approximately one percent molybdenum disulfide (which in itself is a saleable co-product). To isolate the molybdenum from the copper concentrate, the concentrate undergoes additional flotation steps. The copper concentrate is added to a rougher flotation cell where sodium cyanide is added to suppress the copper, thus causing the molybdenum to float to the surface. Some operations, however, including the Chino Mines facility, do not recover molybdenum disulfide using sodium cyanide. They instead use, sodium disulfide to suppress the copper and

<sup>21</sup> Phelps Dodge Corporation. Op. Cit.

<sup>22</sup> U.S. Environmental Protection Agency, <u>Trip Report -- Site Visit to Magma Copper and Cyprus Miami Copper</u> <u>Mines," Draft Memorandum</u>, Office of Solid Waste, April 1994b, p. 6.

<sup>23</sup> <u>Ibid</u>., p. 6.

<sup>24</sup> "Copper," 1993, <u>Op. Cit.</u>, pp. 388-92.

<sup>25</sup> U.S. Environmental Protection Agency, 1993d, <u>Op. Cit.</u>, p. 53.

<sup>26</sup> "Copper," 1993, <u>Op. Cit.</u>, pp. 388-92.

<sup>27</sup> U.S. Environmental Protection Agency, 1993d, <u>Op. Cit.</u>, p. 53.

<sup>28</sup> BHP Copper. Comment submitted in response to the <u>Supplemental Proposed Rule Applying Phase IV Land</u> <u>Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>, January 25, 1996.

<sup>29</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

float the molybdenum.<sup>30</sup> The copper concentrate falls to the bottom and the underflow is sent for drying and thickening prior to smelting. The molybdenum-containing overflow is sent to additional cleaner and recleaner circuits. At the last recleaner circuit, 70 percent of the overflow is filtered and dried, and the remaining 30 percent is returned to the filter at the beginning of the recleaner circuit. The filtered, dry molybdenum disulfide product (95 percent) is packed into 55-gallon drums and sold as molybdenite.<sup>31</sup>

# **Pyrometallurgical Processing**

Pyrometallurgical processes employ high-temperature chemical reactions to extract copper from its ores and concentrates. These processes generally are used with copper sulfides and in some cases high-grade oxides.<sup>32</sup> Depending on the copper mineral and the type of equipment, pyrometallurgical recovery may take as many as five steps: roasting, smelting, converting, fire refining, and electrorefining. The products from smelting, converting, fire refining are copper matte, blister copper, copper anodes, and refined copper, respectively.<sup>33</sup> Roasting dries, heats, and partially removes the sulfur and volatile contaminants from the concentrated ore to produce a calcine suitable for smelting.<sup>34</sup> Modern copper smelters generally have abandoned roasting as a separate step, and have combined this function with the smelting furnace. However, in older systems using multiple brick hearths, the copper concentrate moves from the top of the hearth towards the base, while air is injected counter-current to the concentrate. The roasted ore leaves through the bottom brick hearth and sulfur dioxide (2-6 percent) exits through the top.<sup>35</sup>

Smelting involves the application of heat to a charge of copper ore concentrate, scrap, and flux, to fuse the ore and allow the separation of copper from iron and other impurities. The smelter furnace produces two separate molten streams: copper-iron-sulfide matte, and slag, as well as sulfur dioxide gas.<sup>36</sup> The smelter slag, essentially a mixture of flux material, iron, and other impurities, is a RCRA special waste. The slags from some smelting furnaces are higher in copper content than the original ores taken from the mines, and may therefore be sent to a concentrator for copper recovery.<sup>37,38</sup> Tailings from flotation of copper slag are a second RCRA special waste. Reverberatory furnaces are being replaced by electric or flash furnaces because reverberatory furnaces are not as energy efficient, and they produce large volumes of low concentration SO<sub>2</sub> gas, which is difficult to use in sulfur recovery.<sup>39</sup> Moreover, the gases produced by electric furnace smelting are smaller in volume, lower in dust (less

<sup>30</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>31</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 7.

<sup>32</sup> Office of Technology Assessment, <u>Copper: Technology and Competitiveness</u>, OTA-E-67, Washington, DC: U.S. Government Printing Office, September 1988, p. 133.

<sup>33</sup> U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, p. 6-2.

<sup>34</sup> Office of Technology Assessment, 1988, <u>Op. Cit.</u>, p. 134.

<sup>35</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 394-95.

<sup>36</sup> Process upsets sometimes require the copper concentrate to be stored temporarily until the smelter is operational. In many cases, this temporary storage takes place in the pipeline. In other cases, such as at the Hidalgo Smelter, concentrate is shipped by rail car, then stored in an enclosed building prior to being fed by a conveyor belt to the smelter. (Phelps Dodge Corporation. <u>Op. Cit.</u>)

<sup>37</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 393.

<sup>38</sup> U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, p. 6-3.

<sup>39</sup> K. Yoshiki-Gravelsins, J. M. Toguri, and R. T. Choo, "Metals Production, Energy, and the Environment, Part II: Environmental Impact," Journal of Mines, 45, No. 8, August 1993, p. 23.

than 1 percent), and have a higher  $SO_2$  concentration, which allows better sulfur recovery in an acid plant.<sup>40</sup> Gases from smelting operations contain dust and sulfur dioxide. The gases are cleaned using a variety of particulate control technologies, including baghouses, scrubbers, settling chambers, and electrostatic precipitators.<sup>41</sup> The gases are then sent to the acid plant, which converts the sulfur dioxide-rich gases to sulfuric acid (a useable and/or saleable product).<sup>42</sup>

In the converter (the most common being the Peirce-Smith converter, followed by the Hoboken converter and the Mitsubishi continuous converter), a high silica flux and compressed air or oxygen are introduced into the molten copper matte. Most of the remaining iron combines with the silica to form converter slag, a RCRA special waste. After removing the slag, additional air or oxygen is blown in to oxidize the sulfur and convert the copper sulfide to blister copper that contains about 99 percent copper; the sulfur is removed in the form of SO<sub>2</sub> gas, which reports to an acid plant where it is converted to high grade sulfuric acid. Depending on the efficiency of the acid plant, differing amounts of SO<sub>2</sub> are emitted to the atmosphere. Some facilities have combined the smelting furnace and converter into one operation, such as the one used by Kennecott (i.e., the Kennecott-Outokumpo flash converting process).<sup>43,44</sup> In the interest of conserving energy and improving efficiency, many companies are now employing flash smelting (such as the Outokumpo, Inco, Mitsubishi, or Noranda processes) to produce matte feed.<sup>45</sup>

Oxygen and other impurities in blister copper must be removed before the copper can be fabricated or cast into anodes for electrolytic refining. Blister copper is fire refined in reverberatory or rotary furnaces known as anode furnaces. When co-located with a smelter or converter, the furnace may receive the blister copper in molten form so remelting is unnecessary. Air is blown in to oxidize some impurities; flux may be added to remove others. The residual sulfur is removed as sulfur dioxide. A slag is generated during anode furnace operation. This slag is also a component of the RCRA special waste. The final step in fire refining is the reduction of the copper and oxygen removal by feeding a reducing gas such as ammonia, reformed gas, or natural gas into the copper while it is still in the anode furnace. The molten copper then is cast into either anodes for further electrolytic refining or wire-rod forms.<sup>46,47</sup> Smelted copper typically retains metallic impurities at concentrations that can interfere with electrical uses. Anode copper may be suitable for non-electric uses such as decorative copper or cooking utensils, but wire bar is made specifically for electrical wire manufacturing and requires high grade electrowon or electrolytically refined copper.<sup>48</sup>

At the Cyprus Amax Minerals Company, during the addition of oxygen into the converter furnace while slag is present (slag blow), secondary copper materials may be added to recover copper and to cool the furnace charge. Once the iron has been removed, the converter furnace switches to "copper blow" (the addition of oxygen without the presence of slag), and at this point, very high copper content materials can be added to the furnace. For example, reverts (a mixture of converter slag and matte which is frozen to the walls and bottom of a transfer ladle) may be introduced at this point. Reverts are knocked loose and stored until they have cooled sufficiently to allow

<sup>40</sup> <u>Ibid</u>., p. 27.

<sup>47</sup> U.S. Environmental Protection Agency, 1990, Op. Cit., p. 6-4.

<sup>48</sup> BHP Copper. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>41</sup>Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>42</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 8.

<sup>&</sup>lt;sup>43</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 396.

<sup>&</sup>lt;sup>44</sup> U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, pp. 6-3 - 6-4.

<sup>&</sup>lt;sup>45</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 396.

<sup>&</sup>lt;sup>46</sup> <u>Ibid</u>., p. 399-400.

equipment to move them to the crushing and sizing area. The material is chipped and then fed back into the furnace for melting and then to the converters and eventually anode casting in order to continue copper production during times when the Isamelt furnace is down. Reverts are accumulated in more than one area and are surveyed for inventory control purposes and left undisturbed until ready to be reused in the furnaces. The matte is accumulated in a slag accumulation area located on the ground.<sup>49</sup>

Electrolytic refining (or electrorefining) purifies the copper anodes by virtually eliminating the oxygen, sulfur, and base metals that limit copper's useful properties. In electrorefining, the copper anodes produced from fire-refining are taken to a "tank house" where they are dissolved electrolytically in acidic copper sulfate solution (the electrolyte). The copper is electrolytically deposited on "starter" sheets of purified copper to ultimately produce copper cathodes (relatively pure copper with only trace contaminants -- less than a few parts per million) for sale and/or direct use. The concentration of copper and impurities in the electrolyte are monitored and controlled. As necessary, the electrolyte is purified and the resulting impurities (left on the bottom of the electrolytic cells -- often referred to as "anode slimes") are processed for recovery of precious metals (gold, silver, platinum, palladium), bismuth, selenium, and tellurium.<sup>50</sup> Electrorefining also produces aqueous waste streams (e.g., process wastewater, bleed electrolyte) that must be treated and discharged, reused, or disposed of in some manner. Many of the facilities use a wastewater treatment operation to treat these wastes. The solid residual from these treatment operations is a calcium sulfate sludge, which is yet another RCRA special waste generated by the primary copper sector.<sup>51</sup> The exemption from RCRA regulation for calcium sulfate sludge, which has a variable water content, does not depend on its water content.<sup>52</sup>

# Hydrometallurgical Beneficiation

Hydrometallurgical copper recovery is the extraction and recovery of copper from oxide ore and some low grade sulfide ores using aqueous solutions. Hydrometallurgical operations include the following: (1) acid extraction of copper from oxide ores; (2) oxidation and dissolution of sulfides in spent ore from mining, concentrator tailings, or *in situ* ore bodies (e.g., low grade oxide and sulfide mine wastes); and (3) dissolution of copper from concentrates to avoid conventional smelting.<sup>53</sup> In summary, the copper-bearing ore (and in some cases, the overburden) is leached, then the copper is recovered from the pregnant leachate through precipitation, or solvent extraction and electrowinning (SX/EW).<sup>54</sup>

The simplest form of hydrometallurgical beneficiation of low grade ore, practiced at large, open-pit copper mines is dump leaching. In dump leaching, the raw material is leached using a dilute sulfuric acid solution. At Phelps Dodge facilities, leaching is accomplished by applying raffinate (a weak aqueous acid solution) to the leach ore stockpiles by standard sprinkler irrigation spray heads or drip emitters.<sup>55</sup> There are several other types of leaching operations (progressing from least capital intensive and inefficient -- using the rock "as is" -- to most capital intensive and efficient -- using ground ore): *in situ*, heap or pile, dump, vat, and heat or agitation leaching. In some cases, roasting is employed prior to leaching in order to enhance the leachability of the material. In roasting, heat is

<sup>&</sup>lt;sup>49</sup> Cyprus Amax Minerals Company. Comment submitted in response to the <u>Second Supplemental Proposed Rule</u> <u>Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>, October 10, 1997.

<sup>&</sup>lt;sup>50</sup> "Copper," 1993, <u>Op. Cit.</u>, pp. 401-404.

<sup>&</sup>lt;sup>51</sup> U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, p. 6-4.

<sup>&</sup>lt;sup>52</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>53</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 408.

<sup>&</sup>lt;sup>54</sup> Office of Technology Assessment, 1988, <u>Op. Cit.</u>, p. 140.

<sup>&</sup>lt;sup>55</sup> U.S. Environmental Protection Agency Telephone Questionnaire. August 22, 1997. Facility Contact: Richard N. Mohr, Phelps Dodge Morenci, Inc.

applied to the ore, which enhances its amenability to leaching without destroying the physical structure of the ore particles. The roasted material is then subjected to leaching (as described above). The copper-rich leachate (referred to as "pregnant leachate solution") is subjected to further beneficiation while the waste material is either left in place (in the case of dump, *in situ*, heap, or pile leaching) or managed in tailing ponds (in the case of vat, heat, or agitation leaching).

Copper is removed from the pregnant leachate solution (PLS) through either iron precipitation (or cementation) or solvent extraction and electrowinning. In cementation, which was once the most popular method for recovering copper from the PLS, the leachate is combined with detinned iron in a scrap iron cone (such as the Kennecott-Precipitation Cone) or vibrating cementation mill, where the detinned iron replaces the copper in the solution. The copper precipitates are removed for subsequent hydrometallurgical refining (electrowinning) or pyrometallurgical processing.<sup>56,57</sup>

In solvent extraction (now, the most popular process), an organic chemical (chelator) that binds copper but not impurity metals is dissolved in an organic solvent (often kerosene<sup>58</sup>) and is mixed with the pregnant leachate solution. The copper-laden organic solution is separated from the leachate in a settling tank. A weak sulfuric acid (or lean) electrolyte<sup>59</sup> is then added to the pregnant organic mixture, which strips the copper into an electrolytic solution ready for electrowinning. The barren leachate (or raffinate) is sent back to the leaching system. Electrowinning is the recovery of copper from the loaded electrolyte solution produced by solvent extraction, yielding wire-grade<sup>60</sup> copper metal. When the iron concentration in the electrolyte stream<sup>61</sup> becomes too high, some solution is bled off and sent to the SX unit for further copper recovery. The copper-poor (or lean) electrolyte from electrowinning is returned to the SX plant. Excess lean electrolyte from the SX unit is returned to the raffinate pond to later be recycled into the leaching circuit. Filter clay is used to filter the electrolyte.<sup>62</sup> Impurities left on the bottom of the electrowinning cells are referred to as "muds or slimes." BHP Copper refers to the impurities left on the bottom of the electrowinning cells and send to lead smelting facilities for resource recovery.<sup>63</sup> Electrowinning is functionally equivalent to electrolytic refining.<sup>64,65</sup>

We note that at Magma Copper (Arizona), the pregnant leach solution (PLS) is collected in the PLS feed pond, where other inputs to the PLS feed pond include liquids from *in-situ* leaching, Gould Solution, and TNT filter cake. Gould Solution is produced from the electrolytic refining of copper foil at one facility in Chandler, AZ. The spent electrolyte solution (containing 100 g/L sulfuric acid and 60 g/L copper) is trucked to Magma Copper, where it

<sup>56</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 410.

<sup>57</sup> Office of Technology Assessment, 1988, Op. Cit., pp. 140-142.

<sup>58</sup> Phelps Dodge uses a petroleum distillate manufactured specifically for use in the solvent extraction process. This petroleum distillate consists of longer chain hydrocarbons with a lower volatile organic content than kerosene. (Phelps Dodge Corporation. <u>Op. Cit.</u>)

<sup>59</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>60</sup> <u>Ibid</u>.

<sup>61</sup> <u>Ibid</u>.

62 <u>Ibid</u>.

<sup>63</sup> BHP Copper. <u>Op. Cit.</u>

<sup>64</sup> "Copper," 1993, Op. Cit., pp. 412-13.

<sup>65</sup> Office of Technology Assessment, 1988, <u>Op. Cit.</u>, p. 142.

is added directly to the PLS feed pond. Magma Copper has proposed to accept filter cakes consisting of copper oxide mud from copper chloride etching solution generated during the production of circuit boards. This material (TNT filter cake) would be mixed with the PLS feed to the SX unit.<sup>66</sup> At the Phelps Dodge Morenci site, PLS which has been stripped of copper (acidic solution) from the SX process, copper-bearing bleed electrolyte and washdown water from the EW process, and fresh water are transferred by pipeline to lined impoundments for reuse in the leaching process. This "raffinate" is piped to the top of the leach stockpiles for reuse. In addition, water collected behind dams in Rocky Gulch and Gold Gulch is piped for reuse in the leaching process. All reagents used in the SX and EW processes are stored in above ground tanks.<sup>67</sup>

The Kennecott Corporation's new hydrometallurgical plant combines acid plant blowdown, refinery bleed solutions, and electrostatic precipitator (ESP) dusts in a series of chemical reactions to produce a metal concentrate, a sulfide cake, and non-hazardous tailings. The valued metals are returned to the smelter for recovery. Impurities such as bismuth, that would have otherwise compromised the quality of the copper product, can thereby be removed while extracting the maximum economic benefit in resource recovery from valuable metals contained in the dust.<sup>68</sup>

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

Additional pyrometallurgical technologies still under development include the solid matte oxygen converting (SMOC) process and continuous total pressure oxidation process. The SMOC process developed by Kennecott is a one-step smelting process designed to eliminate the hot matte and slag transfers between smelting and converting, thereby reducing their attendant fugitive emissions. In the total pressure oxidation process, chalcopyrite (CuFeS<sub>2</sub>) can be hydrothermally oxidized directly to digenite (CuS) inside a single, continuous, autoclave reactor. The enriched solid residue (super concentrate) is separated from the liquor, containing ferrous sulfate and sulfuric acid, and the upgraded concentrate can proceed directly to smelting. The acid solution can be used in heap or dump leaching.<sup>69</sup> Total pressure oxidization is especially well-suited for concentrates with a high copper to sulfur ratio.<sup>70</sup>

Magma has constructed a new flue dust leaching (FDL) facility to recover copper from several smelter byproduct streams. Feedstocks to the FDL facility were to include flash furnace dust (20-25 percent copper, 1.3 percent arsenic), converter flue dust (80 percent copper, 0.01 percent arsenic), acidic bleed solution from the Lurgi scrubbers (3.6 g/L copper, 0.4 g/L arsenic, 3.5 g/L acid pH 1.6). (Lurgi scrubbers are pollution control devices for smelter converter offgas.) These feedstocks were to be stored in bins or slurry tanks prior to entering a series of agitator leach vessels. Sulfuric acid (93 percent concentration) would be added to dissolve the copper into solution. The copper rich leachate was to be purified in a dedicated solvent extraction unit, where an extremely concentrated copper sulfate solution (one that could easily be crystallized into commercial grade copper sulfate crystals) would be generated. The crystals could be either sold "as is" or sent to the main solvent extraction circuit.<sup>71</sup> The remaining solids would be thickened, washed, and filtered. The resulting filter cake was to be sent back to the flash furnace for smelting. In a comment, Magma Copper wrote that this facility was originally designed to utilize BHP's existing SX plant, not the dedicated plant described above. After evaluating the high operating costs of the dedicated SX as well as the treatment plant, BHP determined that it could not economically operate the FDLP, and the plant has never

<sup>70</sup> J. A. King, D. A. Knight, and D. B. Dreisinger, "The Total Pressure Oxidation of Copper Concentrates," The Minerals, Metals and Materials Society, 1993, p. 735.

<sup>71</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 9.

<sup>&</sup>lt;sup>66</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 16.

<sup>&</sup>lt;sup>67</sup> U.S. Environmental Protection Agency Telephone Questionnaire. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>68</sup> Kennecott Corporation. Comment submitted in response to the <u>Second Supplemental Proposed Rule Applying</u> <u>Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>, May 12, 1997.

<sup>&</sup>lt;sup>69</sup> Robert W. Bartlet, "Copper Super-Concentrates--Processing, Economics, and Smelting," EPD Congress, 1992, pp. 652-653.

been operated.<sup>72</sup> Kennecott Utah Copper's modernized smelter includes a pneumatic conveying system that allows mineral-rich boiler and electrostatic precipitator (ESP) dusts to be re-introduced directly into the flash smelting and flash converting furnaces without any additional handling. This dust on average contains approximately 35% copper, as compared to less than 1% copper in mined ore and less than 30% in virgin copper concentrate. Additionally, this dust contains significant amounts of valuable precious metals.<sup>73</sup>

# 4. Beneficiation/Processing Boundaries

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

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

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

EPA determined that for this mineral commodity sector, depending on the specific process, the beneficiation/processing line occurs between flotation and furnacing or between iron precipitation and furnacing because furnacing (or smelting) significantly alters the physical/chemical structure of the beneficiated ore. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence also are considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below information about process waste streams associated with both extraction/beneficiation and mineral processing activities, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

### C. Process Waste Streams

As discussed above (and shown in Exhibits 2 and 3), the extraction, beneficiation, and processing of copper leads to the generation of numerous solid, liquid and gaseous wastes, which depending on the material, may be recycled or purified prior to disposal. The generation, treatment, and management of each of these wastes is discussed below.

<sup>&</sup>lt;sup>72</sup> BHP Copper. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>73</sup> U.S. Environmental Protection Agency, "Verbatim Comment Excerpts, Summary and Response Form, for Kennecott Utah Copper Corporation." Excerpt number COMM1054-8-1.

### 1. Extraction/Beneficiation Wastes

Wastes generated from the extraction and beneficiation of copper from copper-bearing ores are exempt from RCRA Subtitle C and the scope of BDAT determinations. Wastes from the extraction/beneficiation of copper-bearing ores are discussed below.

**Spent ore.** This waste from mining operations, along with overburden, is generated from the actual removal of copper ore from the ground and contains little or no recoverable copper values. Overburden and spent ore may be stockpiled for reclamation upon closure of the facility or to achieve contemporaneous reclamation of leach piles and rock piles.<sup>74</sup> These materials are typically hauled from the mine site and are disposed of in on-site spent ore dumps. At Magma Copper (Arizona), spent ore is left in place; at other facilities, however, the spent ore may be hauled to the surface and disposed.<sup>75</sup> In 1980, more than 282 million tons of spent ore were disposed.<sup>76</sup>

**Tailings (or gangue)**. This waste results from the flotation of ground ore/water slurry. The composition of tailings varies according to the characteristics of the ore; this waste is comprised of very fine host rock and nonmetallic minerals. Tailings are sent to tailings impoundments for disposal, but may first be dewatered in thickeners. For example, at Magma Copper (Arizona) tailings from the copper and molybdenum flotation processes are sent to a hydroseparator for dewatering. The hydroseparator underflow is sent to a thickener, where the solids (underflow) are sent to the repulper and the liquid stream (water overflow) is reused in the flotation circuit. Tailings generated during the flotation processes are excluded from RCRA Subtitle C regulation under the Bevill Amendment.<sup>77</sup> In 1985, the industry disposed of more than 189 million tons of gangue.<sup>78</sup>

**Slime**. A clay/copper material called slime is often generated during the flotation of copper ore containing a large amount of clay minerals. Slime is separated from the gangue and is reground and refloated to remove additional copper value. The slime is ultimately disposed of along with the tailings. There is no information on the quantity of slime generated annually.<sup>79</sup> The term also has another meaning in the industry, usually referring to the clay and silt fraction of the tailing that is separated from the coarser tailing materials by size classifiers (usually cyclones) at the tailing disposal site. This separation, which can be accomplished by gravity separation as the tailing slurry is deposited and flows toward the water decant area at the tailing ponds is encouraged in order to deposit the sandier materials near the tailing embankment to provide higher embankment stability than the finer materials would have created. The finer materials (slimes) are then deposited in the interior of the tailing impoundment.<sup>80</sup> We note that this "slime" is much different in composition than the "slimes or muds" generated by electrolytic refining (see below).

**Process wastewaters**. Various processing wastewaters result from conveyance, flotation, mixing, and dissolution operations. Process wastewaters may either be treated on site at wastewater treatment facilities or

<sup>&</sup>lt;sup>74</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>75</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 10.

<sup>&</sup>lt;sup>76</sup> U.S. Environmental Protection Agency, 1993d, <u>Op. Cit.</u>, pp. 50-51.

<sup>&</sup>lt;sup>77</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 10.

<sup>&</sup>lt;sup>78</sup> U.S. Environmental Protection Agency, 1993d, Op. Cit., p. 53-54.

<sup>&</sup>lt;sup>79</sup> "Copper," 1993, <u>Op. Cit.</u>, p. 388-92.

<sup>&</sup>lt;sup>80</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

discharged to tailings ponds, surface impoundments, or to receiving streams. Process wastewaters are believed not to be land stored and are fully recycled.<sup>81</sup>

**Solvent extraction/electrowinning**. These operations result in the generation of several liquid and semiliquid wastes. Often these materials are still either useful or rich in values and can be reused or recycled. The following waste streams are uniquely associated with copper beneficiation activities and, therefore, are subject to the Bevill Mining Waste Exclusion:

**Slimes or "muds"**. These materials result from the deposition of sediment in electrowinning cells. These materials often contain recoverable quantities of lead and are either processed on-site or are drummed and sent off-site for recovery.<sup>82</sup> Approximately 3,000 metric tons of slimes are generated annually.<sup>83</sup>

**Crud (often referred to as "gunk," "grungies," or "grumos")**. This waste is generated during solvent extraction. Crud is solid particles associated with oil/water dispersions of varied complexity and typically forms stable multi-phase emulsions. Crud is periodically removed from the system. The crud is centrifuged or otherwise treated to remove the organics, which are returned to the solvent extraction circuit for reuse. Site-specific management information is available for several companies. At the Chino Mines Company (Santa Rita, NM), the recovered organic is filtered using Filtrol No.1 montmorillonite clay<sup>84</sup> and then solids, mainly fine rock materials from the leach rock and particles of the clay used as a filter for the organic solution, are returned to the leach system. Any aqueous solution is drained off and returned to the raffinate pond and the leach circuit.<sup>85</sup> In some cases, the resulting solids contain sufficient quantities of precious metals to warrant recovery (off-site).<sup>86</sup> We note that at both the Magma Copper Company's San Manuel, AZ facility and the Cyprus Mines' Miami, AZ facility, crud is recycled into the raffinate pond which is linked to, and forms, an integral part of the SX/EW processing circuit.<sup>87,88</sup> Phelps Dodge Morenci generates 1,650 tons/year of copper bearing gunk. This gunk is smelted for flux values and to recover copper.<sup>89</sup> Entire sector production rates for crud are currently not available.

**Raffinate or barren leachate**. This waste is generated when the pregnant leachate is stripped and is recycled back to the leaching circuit. Approximately 70,036,000 metric tons of raffinate is generated

<sup>81</sup> Exhibit 1. Draft Technical Background Document Characterization of Mineral Processing Wastes and Materials, March 18, 1997.

82 "Copper," 1993, Op. Cit., pp. 401-404.

<sup>83</sup> U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Volume I, Office of Solid Waste, August 1992, p. I-3.

<sup>84</sup> Tom Burniston, James N. Greenshield, and Peter E. Tetlow, "Crud Control in Copper SX Plants," <u>Engineering</u> and <u>Mining Journal</u>, 193, No. 1, January 1992, pp. 32-33.

<sup>85</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>86</sup> U.S. Environmental Protection Agency, 1993d, Op. Cit., p. 54.

<sup>87</sup> RTI Survey 100750, <u>National Survey of Solid Wastes from Mineral Processing Facilities</u>, Magma Copper Co., San Manuel, AZ, 1989.

<sup>88</sup> Tom Burniston, James N. Greenshield, and Peter E. Tetlow, 1992, <u>Op. Cit.</u>, p. 34.

<sup>89</sup> U.S. Environmental Protection Agency Telephone Questionnaire. <u>Op. Cit.</u>

annually.<sup>90,91</sup> At the Phelps Dodge Corporation raffinate is recycled for its copper content and is reused in the leach system because of its acidity.<sup>92</sup>

**Spent kerosene**. Commonly used as the organic material in solvent extraction, spent kerosene is purified using filter clay. The resulting impurities or "grungies" are sent to the dump-leaching area, sent off-site for precious metals recovery, sent to the raffinate pond, or are disposed of with tailings.<sup>93</sup> The Phelps Dodge Corporation recycles the spent kerosene for reuse in the solvent extraction operation.<sup>94</sup>

# 2. Mineral Processing Wastes

Smelting and Refining operations generate numerous solid, liquid, and gaseous wastes, several of which are Bevill Exempt wastes including furnace slags, anode casting slags, and wastewater treatment sludges. Other wastes are described below.

**Spent bleed electrolyte**. Spent electrolyte results from electrolytic refining in electrolytic cells. Normally, spent electrolyte is purified in liberator cells. Liberator cells are similar to normal electrolytic cells, but they have lead anodes instead of copper anodes. The electrolyte is cascaded through the liberator cells, and an electric current is applied to strip the electrolyte of copper. Copper in the solution is deposited on copper starting sheets (cathodes). As the copper in the solution is depleted, the quality of the copper deposited is lowered. Copper liberator cathodes, which contain impurities, are returned to the smelter to be melted and cast into anodes. Purified electrolyte is recycled to the electrolytic cells. Any bleed electrolyte can be neutralized with mill tailings and disposed of intailing ponds or pumped to a raffinate pond, from which it is pumped to on-site copper leaching dumps. Sludge that settles to the floor of the liberator cell is returned to the smelter or sold.<sup>95,96</sup>

Site-specific management information is available for several companies. Cyprus Miami Mining Corp. in Claypool, AZ recycles the bleed electrolyte to the solvent extraction plant.<sup>97</sup> Magma Copper Company's San Manuel facility recycled the bleed electrolyte to the solvent extraction/electrowinning plant for copper recovery.<sup>98</sup> At one time Kennecott Utah Copper's Bingham Canyon, UT facility treated the bleed electrolyte in its wastewater treatment

<sup>97</sup> RTI Survey 100156, <u>National Survey of Solid Wastes from Mineral Processing Facilities</u>, Cyprus Miami Mining Corp., Clay Pool, AZ, 1989.

<sup>98</sup> RTI Survey 100750, 1989, Op. Cit.

<sup>&</sup>lt;sup>90</sup> The 1992 NIMPW Characterization Data Set indicates that 70,036,000 metric tons of raffinate are generated annually. We are currently trying to verify this number and will revise it in the near future (if appropriate).

<sup>&</sup>lt;sup>91</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-3.

<sup>&</sup>lt;sup>92</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>93</sup> U.S. Environmental Protection Agency, 1993d, <u>Op. Cit.</u>, pp. 114-115.

<sup>&</sup>lt;sup>94</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>95</sup> U.S. Environmental Protection Agency, <u>Revised Draft Wastes from Primary Copper Processing</u> <u>Characterization Report for Cyprus Miami Mining Corporation, Claypool, AZ</u>, Office of Solid Waste, May 1991, p. 5.

<sup>&</sup>lt;sup>96</sup> U.S. Environmental Protection Agency, <u>Draft Overview of Solid Waste Generation, Management, and</u> <u>Chemical Characteristics in the Primary Copper Smelting and Refining Industry</u>, Industrial Environmental Research Laboratory, Office of Research and Development, October 1984, p. 3-12.

plant.<sup>99</sup> It is now routed to the hydrometallurgical plant where it is used as reagent/raw material for metal recovery.<sup>100</sup>

At the Phelps Dodge Refinery in El Paso, electrolyte is withdrawn from tankhouse circulation and sent to the nickel sulfate plant for copper and nickel recovery. The process Phelps Dodge uses is similar to the above description except for the following steps. Liberator sludge is sent to the smelter for metal recovery and the copper-free solution is evaporated to concentrate the nickel salts. The precipitated nickel sulfate is separated from the concentrated sulfuric acid solution by centrifuging. While the nickel sulfate crystals are marketed, the concentrated spent sulfuric acid is disposed off site at a permitted deep-well injection facility.<sup>101</sup>

Approximately 307,000 metric tons of bleed electrolyte are generated annually. Bleed electrolyte exhibits the hazardous characteristics of toxicity (for arsenic, cadmium, chromium, lead, selenium, and silver) and corrosivity.<sup>102</sup> This partially recycled waste stream was formerly classified as a spent material. Additional data are included in Attachment 1. Spent bleed electrolyte is believed not to be land stored.<sup>103</sup>

**Tankhouse slimes**. Often referred to as "anode slimes", tankhouse slimes are the result of material deposition in electrolytic cells. Slimes contain the constituents in a copper anode that remain insoluble during the electrorefining process and ultimately settle to the bottom of the cells.<sup>104</sup> Generally, slimes generated from copper refining of various ores have the same values and impurities, including gold, silver, platinum group metals, copper, selenium, arsenic, tin, lead, and tellurium. However, their metals concentrations may vary widely, depending on the ore from which the copper anodes have been obtained. The raw slimes always have high copper contents, and the selenium content is also usually high. Therefore, normal slime treatment includes initial decopperization of the slimes, followed usually by deselenization. Traditionally, these slimes are then sent to smelting in a doré furnace, followed by refining.<sup>105</sup> A new method of metals recovery gaining popularity is wet chlorination, which uses chlorination and solvent extraction to recover these values.<sup>106</sup> These materials often contain valuable quantities of precious metals and are either processed on-site or are drummed and sent off-site for recovery. Approximately 4,000 metric tons of tankhouse slimes are generated annually.<sup>107</sup> Although EPA found no published information regarding waste characteristics, we used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium, silver, arsenic and lead. This partially recycled waste stream was formerly classified as a by-product.

The Phelps Dodge Corporation's refinery in El Paso processes tankhouse slimes in its slimes treatment plant. Treatment includes the removal of copper and tellurium, followed by deselenization through roasting. The

<sup>99</sup> RTI Survey 100834, <u>National Survey of Solid Wastes from Mineral Processing Facilities</u>, Kennecott Utah Copper, Bingham Canyon, UT, 1989.

<sup>100</sup> Kennecott Corporation. <u>Op. Cit.</u>

<sup>102</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-3.

<sup>103</sup> Exhibit 1. Op. Cit.

<sup>104</sup> James E. Hoffmann, "Advances in the Extractive Metal Metallurgy of Selected Rate and Precious Metals," Journal of Mines, 43, No. 4, 1991, pp. 22-23.

<sup>105</sup> M. Devia and A. Luraschi, "A Study of the Smelting and Refining of Anode Slimes to Doré Metal," <u>Copper 91</u> (<u>Cobre 91</u>), <u>Ottawa, Ontario, Canada, 18-21 Aug. 1991</u>, Pergamon Press, Inc., New York, 1992 p. 210.

<sup>106</sup> James E. Hoffmann, 1991, <u>Op. Cit.</u>, p. 23.

<sup>107</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-3.

<sup>&</sup>lt;sup>101</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

selenium-free calcine residue from the roasters is transferred to the precious metals plant, where it undergoes a wet chlorination leach and solvent extraction for precious metals recovery. Recovery of precious metals involves leaching with calcium nitrate to dissolve the contained silver, and electrowinning of the filtered silver nitrate solution to produce high purity silver crystals. These crystals are melted in a silver-induction furnace and cast into silver ingots. The silver-free calcine residue is leached. The residue is sent to the smelter for recycling and the liquor containing dissolved gold is delivered to the solvent extraction process. The resulting high purity gold sand, which is washed with dilute hydrochloric acid and alcohol, is melted in a gold induction furnace and cast into gold bars. A platinum-palladium cake is produced from the raffinate, and the residual precious metals (gold, platinum and palladium), rhodium, selenium and tellurium are removed by reduction with hydrazine. The hydrazine cake is returned to the autoclave at the slimes plant for recycling until the concentrations of platinum and palladium give the cake a red color, at which time it can be sold as platinum-palladium sponge.<sup>108</sup> Tankhouse slimes are believed not to be land stored.<sup>109</sup>

Acid plant blowdown. This waste originates in the gas cleaning section of the acid plant. It is generated from the water spraying of smelter converter gases and consists largely of smelter feed carryover solids. Blowdown has been reported to contain 14 percent sulfate, 15 percent total dissolved solids, 1 percent copper, 1 percent iron and 70 percent water.<sup>110</sup> Acid plant blowdown also may contain significant concentrations (i.e., >1,000 mg/L) of arsenic, cadmium, lead, molybdenum, and selenium (additional data are included in Attachment 1).<sup>111</sup> Approximately 4,847,000 metric tons of acid plant blowdown are generated annually. This waste exhibits the characteristics of toxicity (for arsenic, cadmium, chromium, lead, mercury, selenium, and silver) and corrosivity.<sup>112</sup> This partially recycled waste was formerly classified as a by-product.

Site-specific management information is available for several facilities. Four of the seven primary copper facilities generating acid plant blowdown (ASARCO Inc.'s Hayden, AZ and El Paso, TX plants; Cyprus Miami in Claypool, AZ; and Phelps Dodge Corporation in Hurley, NM) beneficially recycle all of the acid plant material for metals recovery, and thus do not generate K064. A fifth facility (Kennecott in Garfield, UT), currently generates calcium sulfate wastewater treatment plant sludge, a special mineral processing waste excluded from RCRA Subtitle C regulation under the Bevill Amendment, but is planning process changes that will result in the elimination of that waste stream in favor of metals recovery from acid plant blowdown. The two remaining primary copper facilities generating acid plant blowdown (Phelps Dodge in Hidalgo, NM; and BHP Copper (formerly Magma Copper) in San Manuel, AZ) do not generate a sludge that meets the K064 listing description. Phelps Dodge treats its acid plant blowdown with lime in a series of tanks, and discharges the resulting calcium sulfate wastewater treatment sludge to double-lined surface impoundments equipped with monitoring wells, subject to the requirements of a state discharge plan.<sup>113</sup>

Cyprus Miami Mining Corp. in Claypool, AZ recycles the solid fraction to the smelter and the liquid portion to the solvent extraction plant.<sup>114</sup> At the Phelps Dodge Hidalgo Smelter, radial flow scrubbers have been installed to minimize the volume of APB prior to neutralization of the APB with lime to create calcium sulfate

<sup>109</sup> Exhibit 1. Op. Cit.

<sup>110</sup> U.S. Environmental Protection Agency, 1991, Op. Cit., pp. 5-7.

<sup>111</sup> U.S. Environmental Protection Agency, <u>Study of Remanded Mineral Processing Wastes Draft Report</u>, Office of Solid Waste, April 1994c, p. 19.

<sup>112</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-3.

<sup>113</sup> National Mining Association. Comment submitted in response to the <u>Supplemental Proposed Rule Applying</u> <u>Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>, January 25, 1996.

<sup>114</sup> RTI Survey 100156, 1989, Op. Cit.

<sup>&</sup>lt;sup>108</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

sludge. The calcium sulfate sludge is sent to a series of double-lined ponds where the liquid phase is decanted and reused pursuant to New Mexico regulations.<sup>115</sup> Chino Mining Company in Hurley, NM neutralizes the blowdown with magnesium hydroxide in a settler. The solids are recycled to the smelter and the fluids are recycled to the concentrator.<sup>116</sup> At the Magma Copper Company's San Manuel, AZ facility, the blowdown is neutralized with alkaline tailings,<sup>117</sup> and the resulting mixture is sent to tailings dams.<sup>118</sup> Kennecott Utah Copper in Bingham Canyon, UT sends the blowdown to the hydrometallurgical plant where it is used as reagents/raw materials for metal recovery.<sup>119</sup>

Acid plant thickener sludge. This sludge results from the treatment of weak acid plant blowdown (see above). In the past, this waste stream generally was discharged to either a tailings pond or an evaporation pond. Recent site-specific information, addressing all Phelps Dodge facilities<sup>120</sup> and several others, however, indicates that this waste stream is no longer generated. Specifically, two facilities filter solids from the blowdown and blend the recovered solids with incoming copper ore for beneficiation/processing. The filtered blowdown is routed to an onsite electrowinning circuit for recovery of copper (and other metals). At a third facility, the blowdown is neutralized with ammonia, then filtered, and the resulting solids are blended with incoming ore. The majority of the filtrate is returned to the sulfuric acid plant for reuse as scrubber water, and the remaining portion of the filtrate is evaporated to recover ammonium sulfate product. At a fourth facility, the blowdown is neutralized with magnesium hydroxide, then filtered, and the resulting solids are blended with incoming ore. The filtrate is reused as make-up water in the flotation circuit. At a fifth facility, the blowdown is first neutralized with alkaline tailings and then discharged to a tailings pond (analysis of the neutralized blowdown indicates that it is not TC characteristic). At a sixth facility, the blowdown is neutralized with lime and then sent to a double-lined, Subtitle C evaporation pond. At a seventh facility, the blowdown is neutralized with lime, combined with other plant wastewaters, and then sent to an unlined evaporation pond (analysis of the combined wastewater indicates that it exhibits the TC characteristic for arsenic, lead, and selenium).<sup>121</sup> Additional data are included in Attachment 1.

**Waste contact cooling water**. This waste results from heat exchanging operations, such as those taking place at the smelter. The water used for anode cooling is reported to contain dissolved arsenic, copper, and zinc, and also to pick up aluminum and chlorides, probably from mold dressing compounds.<sup>122</sup> Site-specific management information is available for several companies. The Magma Copper Company's San Manuel, AZ facility recycles the copper anode cooling water to the concentrator.<sup>123</sup> At Kennecott's facilities, waste contact cooling water is routed to the KUCC process water system. The water is used for process water, and ultimately discharged to the tailings impoundment, where it is pumped back into the process water system.<sup>124</sup> At Cyprus Miami Mining Corp.,

<sup>122</sup> U.S. Department of Commerce, <u>Industrial Process Profiles for Environmental Use: Chapter 29 Primary Copper</u> <u>Industry</u>, Industrial Environmental Research Lab, July 1980. p. 89.

<sup>123</sup> RTI Survey 100750, 1989, Op. Cit.

<sup>&</sup>lt;sup>115</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>116</sup> RTI Survey 100495, <u>National Survey of Solid Wastes from Mineral Processing Facilities</u>, Chino Mining Co. Hurley, NM, 1989.

<sup>&</sup>lt;sup>117</sup> BHP Copper. Op. Cit.

<sup>&</sup>lt;sup>118</sup> RTI Survey 100750, 1989, Op. Cit.

<sup>&</sup>lt;sup>119</sup> Kennecott Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>120</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>121</sup> U.S. Environmental Protection Agency, 1994c, Op. Cit., pp. 3-4.

<sup>&</sup>lt;sup>124</sup> Kennecott Corporation. <u>Op. Cit.</u>

Claypool, AZ, contact cooling water is returned to the Industrial Water System.<sup>125</sup> According to the Phelps Dodge Corporation, waste contact cooling water may be clarified or distilled in a brine concentrator prior to reuse in the production process or as on-site irrigation water.<sup>126</sup> Approximately 13,000 metric tons of contact cooling water is generated annually.<sup>127</sup> Although EPA found no published information regarding waste characteristics, we used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for arsenic. This recycled waste stream was formerly classified as a spent material.

**WWTP liquid effluent**. Treated effluent from the wastewater treatment plant is either disposed of in the tailings surface impoundments or discharged through a NPDES permitted outflow, and therefore it is not included in the analysis. The Phelps Dodge Corporation reportedly recycles WWTP liquid effluent back into its operations.<sup>128</sup> Approximately 4,590,000 metric tons of WWTP liquid effluent is generated annually.<sup>129</sup> We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for lead. Additional data are included in Attachment 1.

**Process wastewaters**. Various processing wastewaters result from cooling and electrorefining operations. Water is used for many things, including seal water in crushers and pumps, and for dust suppression in low grade heat extraction from furnace cooling elements and acid plant coolers, sulfuric acid production, anode cooling, steam production, electricity production, potable drinking water, and conveyance of sanitary sewage.<sup>130</sup> Process wastewaters may either be treated on site at wastewater treatment facilities or discharged to tailings ponds, surface impoundments, or to receiving streams. At Claypool, process wastewater is limited to anode casting cooling water. It is mixed with cooling tower effluent and stored for later recycling back to the process.<sup>131</sup> At Magma Copper Company's San Manuel site, process wastewater from both the electrolytic refinery and the flash furnace is sent to an on-site tailings pond.<sup>132</sup> At Copper Range Co.'s White Pine facility, process wastewater consists of contact and non-contact cooling water. It is commingled with mill tailings and pumped to a tailings basin where the solids settle out. The water is then discharged through permitted outfalls.<sup>133</sup> Approximately 4,891,000 metric tons of process wastewaters are generated annually. This waste exhibits the hazardous characteristic of toxicity (for arsenic, cadmium, lead and mercury) and corrosivity.<sup>134</sup> We used best engineering judgement to determine that this waste may also exhibit the characteristics of toxicity for selenium. This recycled waste stream was formerly classified as a

<sup>&</sup>lt;sup>125</sup> U.S. Environmental Protection Agency, 1991, <u>Op. Cit.</u>, p. 3.

<sup>&</sup>lt;sup>126</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>127</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-4.

<sup>&</sup>lt;sup>128</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>129</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-4.

<sup>&</sup>lt;sup>130</sup> Christine P. Viecelli, "Comprehensive Water Management Program For a Primary Copper Smelter," <u>Residues</u> <u>and Effluents - Processing and Environmental Considerations</u>," The Minerals, Metals and Materials Society, 1991, p. 82.

<sup>&</sup>lt;sup>131</sup> U.S. Environmental Protection Agency, 1991, <u>Op. Cit.</u>, p. 5.

<sup>&</sup>lt;sup>132</sup> RTI Survey 100750, 1989, Op. Cit.

<sup>&</sup>lt;sup>133</sup> RTI Survey 101782, <u>National Survey of Solid Wastes from Mineral Processing Facilities</u>, Copper Range Co., White Pine, MI, 1989.

<sup>&</sup>lt;sup>134</sup> U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-4.

spent material. Additional data are included in Attachment 1. Hazardous process wastewaters are believed not to be land stored prior to reclamation.<sup>135</sup>

Scrubber blowdown. This waste results when low volumes of high total dissolved solids (TDS) materials are removed from the gas scrubbing system. At the Phelps Dodge Hidalgo smelter, electric furnace gases are cleaned in a scrubber. The resulting effluent is either neutralized and recycled, or utilized as acid plant scrubber liquor, and then neutralized with lime.<sup>136</sup> Chino Mining Company in Hurley, NM neutralizes the blowdown with magnesium hydroxide in a settler. The solids are recycled to the smelter and the fluids are recycled to the concentrator.<sup>137</sup> At Magma Copper company's San Manuel, AZ facility, Lurgi scrubber blowdown is usually recycled back through the concentrator. Only during mechanical failure, or insufficient mill capacity does the solution become mixed with acid plant blowdown and tailings for deposition on the tailings impoundments.<sup>138</sup> At Cyprus Mining Corporation, Casa Grande, AZ, scrubber blowdown resulting from tail gas cleaning operations using a double-contact alkali scrubber generates a slurry that is discharged to a 40-mil lined lagoon.<sup>139</sup> This waste exhibits the characteristic of toxicity for arsenic, cadmium, and selenium, and may also be toxic for mercury.<sup>140</sup> This partially recycled waste stream was formerly classified as a sludge. Although no published information regarding the 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 49,000 metric tons/yr, 490,000 metric tons/yr, and 4,900,000 metric tons/yr, respectively. Additional data are included in Attachment 1. Scrubber blowdown is believed not to be land stored.141

**Discarded furnace and converter brick**. This maintenance waste is periodically generated during rebuilding of the furnace and converters. At one facility, bricks are crushed and stockpiled for recycling to the sulfide mill where the copper is recovered through beneficiation. Furnace brick, at one location, was reported to contain 7 percent iron, 6 percent copper, 2 percent magnesium, and 1 percent phosphorus.<sup>142</sup> Approximately 3,000 metric tons of furnace brick is generated annually.<sup>143</sup> Revert (molten matte that is spilled during its transfer in the smelting process) also contains significant concentrations of copper and is returned to the crushing/grinding circuit.<sup>144</sup> At one facility, the converter bricks are re-processed through the smelter while the furnace bricks are discarded. Some bricks may contain chromium above hazardous characteristic levels.<sup>145</sup>

135 Exhibit 1. Op. Cit.

<sup>136</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>137</sup> RTI Survey 100495, 1989, Op. Cit.

<sup>138</sup> RTI Survey 100750, 1989, Op. Cit.

<sup>139</sup> ICF Incorporated, <u>Mineral Processing Waste Sampling Survey Trip Reports</u>, Prepared for U.S. Environmental Protection Agency, Office of Solid Waste, August 1989, p. 2.

<sup>140</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-4.

<sup>141</sup> Exhibit 1. Op. Cit.

<sup>142</sup> U.S. Environmental Protection Agency, 1991, <u>Op. Cit.</u>, p. 7.

<sup>143</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-4.

<sup>144</sup> U.S. Environmental Protection Agency, 1994b, Op. Cit., p. 11.

<sup>145</sup> U.S. Environmental Protection Agency, <u>Trip Report -- Site Visit to Magma Copper and Cyprus Miami Copper</u> <u>Mines," Draft Memorandum</u>, Office of Solid Waste, April 1994b. **APC dusts/sludges**. Generated during smelting operations, these materials may contain significant concentrations of copper. These dusts/sludges are typically fed back to the smelter.<sup>146</sup> Site-specific management information is available for several companies. At Kennecott Utah Copper, Bingham Canyon, UT, previously only some of the copper-containing flue dust was returned to the smelting vessel; the majority of the flue dust was stockpiled for future recycling.<sup>147</sup> KUCC no longer stockpiles flue dust for future recycling. Formerly, stockpiled material which could not be processed in the hydrometallurgical plant was disposed of at a properly permitted disposal facility. Flue dust that is generated in the current process is automatically reprocessed for recovery of mineral values in the hydrometallurgical plant.<sup>148</sup> All APC dusts generated at Phelps Dodge have recoverable values, and are recycled.<sup>149</sup>

Alternatively, bismuth can be recovered from air pollution control solids. Specifically, in copper smelting, a portion of the bismuth is volatilized in the copper converter and captured along with such elements as lead, arsenic, and antimony as a dust in a baghouse or cottrell system. The dust is then transferred to a lead smelting operation. A major portion of the bismuth, however, also remains with the metallic copper. Therefore, during electrolytic refining of the copper, the bismuth accumulates in the anode slime and can be reclaimed during recovery operations.<sup>150,151</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 100 metric tons/yr, 222,000 metric tons/yr, and 450,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for arsenic. This fully recycled waste stream was formerly classified as a sludge. APC dusts/sludges are believed not to be land stored and are fully recycled.<sup>152</sup>

**Surface impoundment waste liquids**. The liquids sent to surface impoundments frequently contain mixtures of tailings and process wastewater (such as slag concentrate filtrate), which may have been treated in a wastewater treatment plant. Often the solids are allowed to settle out, and the liquids are discharged through permitted outfalls. Approximately 615,000 metric tons of surface impoundment liquids are generated annually. This waste exhibits the hazardous characteristic of corrosivity.<sup>153</sup> We used best engineering judgement to determine that this waste may also exhibit the hazardous characteristic of toxicity for arsenic, lead, and selenium. Also, we used best engineering judgement to determine that this waste stream is partially recycled. This waste was formerly classified as a spent material. Additional data are included in Attachment 1.

**Chamber solids/scrubber sludge**. Approximately 31,000 metric tons of chamber solids and scrubber sludges are generated annually from smelting on refining processes.<sup>154</sup> Existing data and engineering judgment

<sup>146</sup> Gavin, P. Swayn, Ken R. Robilliard, and John M. Floyd, "Applying Ausmelt Processing to Complex Copper Smelter Dusts," Journal of Mines, 45, No. 8, 1993, p. 35.

<sup>147</sup> ICF Incorporated, 1989, <u>Op. Cit.</u>, p. 2.

<sup>150</sup> "Indium and Bismuth," <u>ASM International Materials Handbook</u>, Tenth Edition, Vol. 2: Properties and Selection: Non-ferrous Alloys and Special-Purpose Materials, 1990, p. 753.

<sup>151</sup> Funsho K. Ohebuoboh, "Bismuth-Production, Properties, and Applications," <u>Journal of Mines</u>, 44, No. 4, 1992. pp. 46-49.

<sup>152</sup> Exhibit 1. Op. Cit.

<sup>153</sup> Funsho K. Ohebuoboh, 1992, Op. Cit.

<sup>&</sup>lt;sup>148</sup> Kennecott Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>149</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>154</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-4

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

**Spent black sulfuric acid sludge.** This material is obtained from the vacuum evaporation of decopperized electrolyte. The black acid liquor may also be used in leaching operations or be sold to fertilizer manufactures.<sup>155</sup> Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

**WWTP sludge**. This sludge results from the neutralization of process waters using magnesium hydroxide or lime. This material is generated by the Phelps Dodge Hurley facility, which uses magnesium hydroxide, and the Phelps Dodge Hidalgo smelter, which uses lime.<sup>156,157</sup> Approximately 6,000 metric tons of solids and sludges are generated annually.<sup>158</sup> Although no published information regarding waste characteristics was found, we used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for cadmium and lead. This partially recycled waste stream was formerly classified as a sludge. Additional data are included in Attachment 1.

Attachment 2 contains a summary of the operational history and environmental contamination documented at several former copper production sites that are now on the Superfund National Priority List.

### D. Non-uniquely Associated Wastes

Non-uniquely associated hazardous wastes may be generated at on-site laboratories and include chemicals, liquid samples, and ceramics/crucibles which are disposed of off-site at commercial hazardous waste facilities. Other hazardous wastes may include spent paints and solvents (non-chlorinated solvents such as "140 Stoddard" and petroleum naphtha, and "Safety Kleen" solvents) generated from facility maintenance operations, and spent batteries. Waste oil also may be generated, and might be hazardous. Non-hazardous wastes are likely to include sanitary wastewater, power plant wastes (such as run-off from coal piles and ash), and refuse.

Finally, spent catalysts (vanadium pentoxide) are generated in the acid plant. Acid plants at copper smelters are ancillary operations that produce sulfuric acid from sulfur-rich smelter emissions. The spent vanadium pentoxide catalyst is not unique to copper smelter acid plants, and is either sent off-site for recycling for the silica values,<sup>159</sup> or disposed of either on- or off-site.<sup>160</sup>

# E. Summary of Comments Received by EPA

The Agency received information from nine public commenters on the MPSR's description of the copper sector. (COMM36, COMM38, COMM40, COMM46, COMM58, COMM67, COMM73, COMM1085, COMM1090) The Agency appreciates this information and has used it to update the summary of facilities, the general process description, and the process waste streams description as included in sections B, C and D above.

### **New Factual Information**

<sup>&</sup>lt;sup>155</sup> U.S. Environmental Protection Agency, 1984, Op. Cit., p. 3-12.

<sup>&</sup>lt;sup>156</sup> U.S. Environmental Protection Agency, 1992, Op. Cit., p. 13-74.

<sup>&</sup>lt;sup>157</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>158</sup> U.S. Environmental Protection Agency, 1992, Op. Cit.

<sup>&</sup>lt;sup>159</sup> Phelps Dodge Corporation. <u>Op. Cit.</u>

<sup>&</sup>lt;sup>160</sup> U.S. Environmental Protection Agency, 1994b, <u>Op. Cit.</u>, p. 12.

Three commenters provided new factual information that has been incorporated into sections B, C and D above. One commenter identified the following materials as being recycled back into their processing operations: raffinate, spent kerosene and WWTP effluent. (COMM38) One commenter stated that electrowinning produces lead containing slimes and not precious metals laden slimes. (COMM67) One commenter stated that the process wastewaters listed in the mineral processing section are actually beneficiation wastewaters. (COMM58) Seven commenters provided new process description information. (COMM38, COMM40, COMM58, COMM67, COMM46, COMM67, COMM40) One commenter provided a correction for the classification of scrubber blowdown. (COMM67) Two commenters provided information on their sites' locations. (COMM38, COMM40) One commenter corrected a description of the disposal of crud (COPMM38) Three commenters made the distinction between sulfide ores which are pyrometallurgically processed versus oxide and low-grade sulfide ores which are hydrometallurgically processed. (COMM38, COMM67) One commenter clarified that calcium sulfate sludge has a variable water content. (COMM38) One commenter included an alternate definition of slime. (COMM38) Two commenter stated that asbestos and PCBs are not hazardous wastes under RCRA. (COMM38) Two commenter added to the description of anode copper. (COMM67)

# Sector-specific Issues

Seven commenters asserted that slimes, muds, crud, raffinate, barren leachate solution and spent kerosene are uniquely associated. (COMM36, COMM38, COMM40, COMM46, COMM58, COMM67, COMM73) The Agency agrees with these commenters and has changed the MPSR accordingly. One commenter criticizes the generic nature of the process waste descriptions. The Agency acknowledges this fact and will modify the MPSR as necessary. (COMM67)

The Agency received comments on numerous issues on which the Agency decided no action was required. These issues include: the interpretation of the beneficiation/processing line (COMM40, COMM46); classifying wastes on a site specific basis (COMM67); the reinterpretation of existing regulatory interpretations (COMM67); report text about primary and secondary smelting that could be interpreted incorrectly (COMM67); the basis for determining beneficiation/processing line (COMM67); the Agency's use of best engineering judgment in making toxicity determination of waste streams (COMM38, COMM58, COMM67); the validity that WWTP effluent is toxic for lead (COMM38): surface impoundment wastes are not wastes since they are reused (COMM38): the aggregation of process wastewater streams in determining hazardous characteristics (COMM67); the classification of converter and anode slags (COMM38); relevance and basis for text in report regarding copper supply and demand (COMM38); the classification of tankhouse slimes as wastes since they contain valuable mineral resources (COMM38); the classification of waste contact cooling water as a waste discourages recycling (COMM38); the classification of APC dusts as wastes, since they are reclaimed in smelters (COMM38); the recycling of process related residues and sludges (COMM46); the classification of waste contact cooling water as a spent material (COMM67); the classification of reused sulfuric acid as a spent material (COMM67); the classification of APC sludge should be as a by-product (COMM67); the "Surface Impoundment Waste Liquids" section duplicates information in other sections (COMM67); the lack of identification of a waste referred to as "surface impoundment waste liquid" on page 940 in Appendix D of the MPSR (COMM67); the multiple grinding and flotation of the clay portion of ore is not recycling (COMM67); the Agency's distinction between tailings and slimes (COMM67); the term "ancillary" as applied to vanadium pentoxide catalyst (COMM67); the case histories presented in attachment 2 (COMM67); the inadequate description of materials under the chamber solids/scrubber sludge heading (COMM67); the importance of recycling water in the flotation circuit (COMM38); classification of converter and anode slag as wastes (COMM38); the term waste rock (COMM38); the environmental impacts of leaching (COMM67); converter slag, furnace brick, refinery bleed solution, wastewater sludge being reused within 48 hours of generation is unpractical or impossible (COMM36, COMM67, COMM1085, COMM1090); containers are use to transport slag but not for storage (COMM67); slags are not susceptible to weathering, blowing or erosion (COMM67, COMM40); continuous closed loop recycling of spent electrolyte (COMM46); the alternative feedstock restriction ignores the operation needs of copper smelters (COMM38); spent kerosene should not a waste (COMM67).

One commenter questioned how the generation rate of waste was used in determining the beneficiation/ processing line. (COMM67) The generation rate was applied to determine high volume/low toxicity wastes only after primary mineral processing was determined to occur. One commenter stated that slimes be reclassified as co-products and furnace and converter bricks be reclassified as in-process materials. (COMM67) Because slimes require significant processing to recover the precious metal values, they are not co-products. Bricks clearly are spent materials.

One commenter stated that the reuse of acid solution from the SMOC process might be a use constituting disposal. (COMM67) This is not a use constituting disposal if the reuse is a legitimate operation and meets the condition of recovering one or more of the following: metals, acid, water or cyanide.

One commenter cautions the Agency that ore should not be classified as having "high" or "low" value. (COMM67) The Agency disagrees with this commenter because many facilities have written to state that they use hydrometallurgical processes specifically on *low* grade sulfide ores. Without this terminology, it would be impossible to make this distinction.

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# **US EPA ARCHIVE DOCUMENT**

ATTACHMENT 1

	Total Con	stituent Analys	is - PPM		EP Toxic	ity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	6.20	145.04	356.00	5/5	10.00	139.73	361.00	3/3	-	-
Antimony	23.20	203.50	565.00	9/9	20.50	67.37	98.50	3/3	-	-
Arsenic	0.02	2,218.50	11,500.00	10/10	10.00	347.00	1,100.00	4/4	5.0	4
Barium	0.25	7.19	18.00	3/4	0.40	5.23	10.00	3/4	100.0	0
Beryllium	0.03	0.36	1.00	2/3	0.05	0.68	1.00	2/3	-	-
Boron	.			- 0/0	-	-	-	- 0/0	-	-
Cadmium	0.03	0.52	1.00	3/4	0.02	1.27	3.07	4/4	1.0	3
Chromium	0.84	12.59	38.00	4/4	0.80	5.55	10.00	4/4	5.0	2
Cobalt	1.90	39.15	124.00	4/4	1.69	55.56	126.00	3/3	-	-
Copper	10.00	26,787	120,380	14/14	485.00	10,991.25	22,200.00	4/4	-	-
Iron	54.30	386.54	1,360.00	8/8	89.40	443.85	1,390.00	4/4	-	0
Lead	0.25	19.68	90.60	6/6	0.25	3.20	5.00	3/4	5.0	2
Magnesium	9.13	196.76	503.00	4/4	14.40	195.53	505.00	3/3	-	-
Manganese	0.62	9.04	32.60	4/4	0.79	11.43	33.00	4/4	-	-
Mercury	0.0001	0.0050	0.0100	3/4	0.0001	0.0019	0.0062	2/4	0.2	0
Molybdenum	0.25	62.58	187.00	2/3	0.50	67.83	193.00	2/3	-	-
Nickel	10.00	6,357.30	33,050.00	10/10	10.00	200.67	365.00	3/3	-	-
Selenium	0.01	4.25	10.60	5/5	0.01	7.18	10.00	4/4	1.0	3
Silver	0.23	2.75	10.00	3/4	0.19	5.17	10.00	3/4	5.0	2
Thallium	1.25	17.92	50.00	2/3	2.50	34.17	50.00	2/3	-	-
Vanadium	0.25	3.58	10.00	2/3	0.50	6.83	10.00	2/3	-	-
Zinc	2.73	25.84	62.40	5/6	2.73	28.48	63.00	4/4	-	-
Sulfate	18,301	218,273	786,653	11/11					-	-
Fluoride	1.00	1.00	1.00	1/1					-	-
Chloride	32.50	121.63	285.00	6/6					-	-
TSS	95,650	224,330	308,000	5/5					-	-
pH *	1.00	1.93	2.72	4/4					2 <ph>12</ph>	3
Organics (TOC)	7.29	153.63	382.00	3/3					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT BLEED ELECTROLYTE - COPPER

	Total Cor	nstituent Analy	ysis - PPM		EP Toxic	ty Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	1.16	870.32	5,200.00	8/8	0.78	750.39	1,500.00	2/2	-	-
Antimony	0.26	36.44	140.00	2/4	0.17	2.58	5.00	1/2	-	-
Arsenic	0.05	855.76	5,800.00	10/15	0.04	884.35	12,800	12/15	5.0	10
Barium	0.05	1.38	5.90	7/12	0.05	2.54	10.90	8/15	100.0	0
Beryllium	0.005	0.07	0.13	1/2	0.01	0.25	0.50	0/2	-	-
Boron	-	· -	-	· 0/0				. 0/0	-	-
Cadmium	0.20	62.93	620.00	16/16	0.05	4.28	24.50	14/15	1.0	9
Chromium	0.10	3.62	21.00	14/14	0.00	0.41	5.00	11/15	5.0	1
Cobalt	0.02	3.35	9.00	4/5	0.05	5.03	10.00	1/2	-	-
Copper	1.80	3,151.86	40,000	20/20	1.89	144.53	1,190.00	9/9	-	-
Iron	7.90	2,402.62	10,000	12/12	0.22	103.82	1,010.00	10/10	-	-
Lead	0.20	1,061.28	17,900	19/19	0.04	2.83	6.74	13/15	5.0	3
Magnesium	2.10	638.49	2,070.00	10/10	60.60	1,015.30	1,970.00	2/2	-	-
Manganese	0.05	40.61	140.00	8/9	0.02	10.20	100.00	7/10	-	-
Mercury	0.00	0.32	1.50	6/11	0.0001	0.0426	0.3100	8/15	0.2	2
Molybdenum	0.50	70.68	390.00	5/6	5.91	15.86	25.80	2/2	-	-
Nickel	0.01	221.33	1,450.00	10/11	0.02	1.83	5.00	2/3	-	-
Selenium	0.00	78.97	1,000.00	6/13	0.01	1.21	7.63	11/15	1.0	3
Silver	0.00	11.52	124.00	6/11	0.01	0.41	5.00	6/15	5.0	1
Thallium	0.25	1.38	2.50	0/2	0.25	8.50	25.00	0/3	-	-
Vanadium	0.05	1.39	2.72	1/2	0.05	2.53	5.00	0/2	-	-
Zinc	5.10	1,737.16	10,000	13/13	3.16	100.70	467.00	10/10	-	-
Sulfate	766.00	23,198	135,570	12/12					-	-
Fluoride	20.60	761.02	1,780.00	6/6					-	-
Chloride	0.10	793.01	2,740.00	6/7					-	-
TSS	170.00	13,593.70	58,600.00	5/5					-	-
pH *	0.99	2.21	5.00	17/17					2 <ph>12</ph>	10
Organics (TOC)	1.39	436.30	1,300.00	3/3					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - ACID PLANT BLOWDOWN - COPPER

	Total Cor	nstituent Anal	ysis - PPM		EP Toxic	city Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	· -	-	0/0				- 0/0	-	-
Antimony	200.00	1,600.00	3,000.00	2/2				. 0/0	-	-
Arsenic	90.00	2,795.00	5,500.00	2/2	0.18	52.44	193.00	7/7	5.0	5
Barium	400.00	2,700.00	5,000.00	2/2	0.04	3.69	10.90	5/7	100.0	0
Beryllium	-	· -	-	0/0	45.00	45.00	45.00	1/1	-	-
Boron	-	· -	-	0/0				· 0/0		
Cadmium	250.00	1,875.00	3,500.00	2/2	0.16	7.97	24.50	6/6	1.0	4
Chromium	50.00	760.00	1,470.00	1/2	0.00	0.03	0.17	7/7	5.0	0
Cobalt	20.00	210.00	400.00	2/2				. 0/0	-	-
Copper	21,000	89,500	158,000	2/2				· 0/0	-	-
Iron	39,000	163,000	287,000	2/2	0.22	23.50	150.00	7/7	-	-
Lead	56,000	275,500	495,000	2/2	0.04	1.94	3.80	7/7	5.0	0
Magnesium	-	· -	-	0/0				. 0/0	-	-
Manganese	-	· -	-	0/0	0.03	0.36	1.03	4/5	-	-
Mercury	-	· -	-	0/0	0.0003	0.1038	0.3100	4/6	0.2	2
Molybdenum	50.00	625.00	1,200.00	2/2				- 0/0	-	-
Nickel	40.00	1,355.00	2,670.00	2/2				. 0/0	-	-
Selenium	5.00	307.50	610.00	1/2	0.03	0.24	0.61	7/7	1.0	0
Silver	67.30	217.00	366.70	2/2	0.02	0.04	0.10	2/5	5.0	0
Thallium	-	· -	-	0/0				. 0/0	-	-
Vanadium	-	· -	-	0/0				0/0	-	-
Zinc	2,230	13,315	24,400	2/2	3.16	193.64	500.00	7/7	-	-
Sulfate	-	· -	-	0/0					-	-
Fluoride	10.00	740.00	1,470.00	2/2					-	-
Chloride	620.00	9,310	18,000	2/2					-	-
TSS	-	· -	-	0/0					-	-
pH *	1.81	1.81	1.81	1/1					2 <ph>12</ph>	1
Organics (TOC)	-	-		0/0					-	-

# SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - ACID PLANT THICKENER SLUDGE - COPPER

	Total Co	nstituent Anal	ysis - PPM		EP Toxic	city Analysis	s - PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.798	0.798	0.798	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	0.002	0.151	0.300	2/2		-	-	- 0/0	1.0	0
Chromium	0.023	0.023	0.023	1/1		-	-	- 0/0	5.0	0
Cobalt				· 0/0		-	-	- 0/0	-	-
Copper	130.00	130.00	130.00	1/1		-	-	- 0/0	-	-
Iron				· 0/0		-	-	- 0/0	-	-
Lead	0.050	3.53	7.00	2/2		-	-	- 0/0	5.0	0
Magnesium	0.354	25.18	50.00	2/2		-	-	- 0/0	-	-
Manganese	0.060	0.060	0.060	1/1		-	-	- 0/0	-	-
Mercury				· 0/0		-	-	- 0/0	0.2	0
Molybdenum	0.011	0.011	0.011	1/1		-	-	- 0/0	-	-
Nickel	0.014	0.207	0.400	2/2		-	-	- 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	0.600	0.600	0.600	1/1		-	-	- 0/0	-	-
Sulfate	1889.00	2744.50	3600.00	2/2					-	-
Fluoride				· 0/0					-	-
Chloride				· 0/0					-	-
TSS	740.00	1794.00	2848.00	2/2					-	-
pH *	3.10	7.48	11.80	5/5					2 <ph>12</ph>	-
Organics (TOC)				· 0/0					-	-

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

	Total Cor	nstituent Anal	ysis - PPM		EP Toxic	tity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.050	1.23	7.71	7/7	0.05	1.02	4.91	5/5	-	-
Antimony	0.050	0.73	1.51	6/6	0.05	0.38	0.95	5/5	-	-
Arsenic	0.005	14.90	191.00	14/15	0.0003	4.75	23.20	11/12	5.0	3
Barium	0.005	27.57	318.60	12/12	0.0027	0.26	1.20	12/12	100.0	0
Beryllium	0.005	0.02	0.05	5/5	0.0050	0.01	0.01	5/5	-	-
Boron	-			- 0/0				- 0/0	-	-
Cadmium	0.0003	1.26	10.00	15/15	0.0050	7.31	32.00	12/12	1.0	5
Chromium	0.005	1.86	22.02	15/16	0.0001	0.12	0.53	12/12	5.0	0
Cobalt	0.010	0.15	0.50	6/6	0.0500	0.05	0.05	5/5	-	-
Copper	0.050	227.31	1,410.00	12/12	0.0500	159.88	664.00	7/7	-	-
Iron	0.090	957.33	8,466.00	8/9	0.0001	33.69	139.00	9/10	-	-
Lead	0.003	36.39	402.50	16/16	0.0020	1.39	7.30	12/12	5.0	1
Magnesium	0.221	485.67	3,643.00	8/8	3.3600	24.39	59.00	5/5	-	-
Manganese	0.050	8.03	63.07	8/8	0.0250	1.22	8.00	10/10	-	-
Mercury	0.0001	0.0010	0.0050	11/12	8.00E-07	0.1910	1.0600	5/11	0.2	2
Molybdenum	0.005	14.77	100.30	7/7	0.0500	0.51	2.33	1/5	-	-
Nickel	0.050	1.15	5.30	9/9	0.0500	0.15	0.40	3/6	-	-
Selenium	0.0005	0.55	7.00	15/15	0.0002	0.03	0.05	5/12	1.0	0
Silver	0.004	0.10	0.50	12/12	1.50E-05	0.03	0.05	11/12	5.0	0
Thallium	0.250	1.13	4.00	6/7	0.1000	0.32	0.81	6/6	-	-
Vanadium	0.050	0.18	0.50	5/5	0.0500	0.05	0.05	5/5	-	-
Zinc	0.01	8.72	42.00	11/11	0.0170	43.50	202.00	12/12	-	-
Sulfate	216.00	2,152.63	7,519.00	8/8					-	-
Fluoride	5.40	8.20	11.00	2/2					-	-
Chloride	28.40	363.39	1,862.00	7/7					-	-
TSS	1.50	55,080	270,800	13/13					-	-
pH *	1.35	6.37	8.50	28/28					2 <ph>12</ph>	3
Organics (TOC)	0.60	257.13	1,280.00	5/5					-	

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PROCESS WASTEWATER - COPPER

	Total Co	nstituent Anal	ysis - PPM		EP Toxic	tity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	1.84	1.84	1.84	1/1	1.63	1.63	1.63	1/1	-	-
Antimony	0.73	0.73	0.73	1/1	0.65	0.65	0.65	1/1	-	-
Arsenic	0.05	13.98	27.90	2/2	27.40	27.40	27.40	1/1	5.0	1
Barium	0.05	0.73	1.40	2/2	0.05	0.05	0.05	1/1	100.0	0
Beryllium	0.01	0.01	0.01	1/1	0.01	0.01	0.01	1/1	-	-
Boron			· -	0/0	-			0/0		
Cadmium	2.10	3.75	5.40	2/2	1.93	1.93	1.93	1/1	1.0	1
Chromium	0.17	0.28	0.40	2/2	0.17	0.17	0.17	1/1	5.0	0
Cobalt	0.05	0.05	0.05	1/1	0.05	0.05	0.05	1/1	-	-
Copper	4.90	4.90	4.90	1/1	3.05	3.05	3.05	1/1	-	-
Iron	11.50	11.50	11.50	1/1	9.50	9.50	9.50	1/1	-	-
Lead	4.90	11.60	18.30	2/2	4.88	4.88	4.88	1/1	5.0	0
Magnesium	15.80	15.80	15.80	1/1	14.80	14.80	14.80	1/1	-	-
Manganese	0.05	0.05	0.05	1/1	0.05	0.05	0.05	1/1	-	-
Mercury	0.01	0.49	0.98	2/2	0.022	0.022	0.022	1/1	0.2	0
Molybdenum	0.90	0.90	0.90	1/1	0.85	0.85	0.85	1/1	-	-
Nickel	0.47	0.47	0.47	1/1	0.44	0.44	0.44	1/1	-	-
Selenium	0.01	7.20	14.40	2/2	7.71	7.71	7.71	1/1	1.0	1
Silver	0.02	0.04	0.05	2/2	0.05	0.05	0.05	1/1	5.0	0
Thallium	0.25	0.25	0.25	1/1	0.25	0.25	0.25	1/1	-	-
Vanadium	0.05	0.05	0.05	1/1	0.05	0.05	0.05	1/1	-	-
Zinc	6.24	6.24	6.24	1/1	6.28	6.28	6.28	1/1	-	-
Sulfate			· -	0/0					-	-
Fluoride			· -	0/0					-	-
Chloride			· -	0/0					-	-
TSS			· -	0/0					-	-
pH *			· -	0/0					2 <ph>12</ph>	-
Organics (TOC)			-	0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SCRUBBER BLOWDOWN - COPPER

	Total Cor	stituent Analy	ysis - PPM		EP Toxic	tity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-			· 0/0	-	-
Antimony	2.20	2.45	2.70	2/2				- 0/0	-	-
Arsenic	0.06	33.23	150.00	5/5	0.25	0.25	0.25	2/2	5.0	0
Barium	0.001	0.001	0.001	1/1	5.00	5.00	5.00	2/2	100.0	0
Beryllium	-	-	-	0/0				- 0/0	-	-
Boron	-	-	-	0/0				· 0/0		
Cadmium	0.01	0.15	0.30	2/2	0.05	0.05	0.05	2/2	1.0	0
Chromium	0.02	1.61	4.00	3/3	0.25	0.25	0.25	2/2	5.0	0
Cobalt	-	-	-	0/0				· 0/0	-	-
Copper	0.01	25.41	90.00	7/7				- 0/0	-	-
Iron	0.63	48.21	88.00	3/3				· 0/0	-	-
Lead	0.03	2.11	7.00	4/4	0.25	0.25	0.25	2/2	5.0	0
Magnesium	0.10	2.77	4.20	3/3				- 0/0	-	-
Manganese	0.02	0.04	0.06	2/2				· 0/0	-	-
Mercury	0.0001	0.0001	0.0001	1/1	0.10	0.10	0.10	2/2	0.2	0
Molybdenum	0.72	1.76	2.80	2/2				· 0/0	-	-
Nickel	0.10	0.97	3.00	4/4				0/0	-	-
Selenium	0.02	3.08	9.00	3/3	0.05	0.05	0.05	2/2	1.0	0
Silver	0.02	0.02	0.02	1/1	0.25	0.25	0.25	2/2	5.0	0
Thallium	-	-	-	0/0				- 0/0	-	-
Vanadium	-	-	-	0/0				0/0	-	-
Zinc	0.11	0.57	1.00	3/3				- 0/0	-	-
Sulfate	1,250.00	6,908.25	18,842.00	4/4					-	-
Fluoride	17.00	17.00	17.00	1/1					-	-
Chloride	129.00	1,573.50	2,230.00	4/4					-	-
TSS	2,230.00	11,742.50	25,470.00	4/4					-	-
pH *	1.30	6.36	10.00	9/9					2 <ph>12</ph>	2
Organics (TOC)	-	-	-	0/0					-	-

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

	Total Co	nstituent Ana	lysis - PPM		EP To	oxicity Analys	sis - PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-		- 0/0		-	-	- 0/0	-	-
Antimony	-	-	-	- 0/0		-	-	- 0/0	-	-
Arsenic	-	-	-	- 0/0		-	-	- 0/0	5.0	0
Barium	-	-	-	- 0/0		-	-	- 0/0	100.0	0
Beryllium	-	-	-	- 0/0		-	-	- 0/0	-	-
Boron	-	-	-	- 0/0		-	-	- 0/0		
Cadmium	-	-	-	- 0/0		-	-	- 0/0	1.0	0
Chromium	-	-	-	- 0/0		-	-	- 0/0	5.0	0
Cobalt	-	-	-	· 0/0		-	-	- 0/0	-	-
Copper	50,000	225,000	400,000	2/2		-	-	- 0/0	-	-
Iron	150,000	150,000	150,000	1/1		-	-	- 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	-	-
Sulfate	-	-	-	- 0/0					-	-
Fluoride	-	-	-	- 0/0					-	-
Chloride	-	-	-	- 0/0					-	-
TSS	0	0	0	2/2					-	-
pH *	3.10	6.05	9.00	2/2					2 <ph>12</ph>	-
Organics (TOC)	-	-	-	- 0/0					-	0

# SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT SLUDGE - COPPER

**ATTACHMENT 2** 

MINING SITES ON THE NATIONAL PRIORITY LIST

# Mining Sites on the National Priority List

Name of Site:	Anaconda Smelter
Owner of Site:	Anaconda Copper Mining Company (merged with ARCO in 1977)
Location of Site:	Mill Creek, Montana (26 miles west of Butte)
Climate Data:	To be determined
Commodity Mined:	Copper
Facility History:	The Anaconda Copper Mining Company first began copper smelting operations in 1884 at the "Upper Works" smelter. The Upper Works consisted of a concentrator and smelter buildings, which housed roasters and reverberatory furnaces, all connected to masonry flues and two smokestacks. By 1887, the company had expanded and built an additional smelter 1 mile east of the Upper Works. The new smelter was known as the "Lower Works". By 1889, an electrolytic copper refinery had been built as well, and was located between the two smelters. Due to shortage of smelting capacity, a larger, more efficient copper smelter was completed in 1902, and known as "Smelter Hill" or "Washoe Smelter". The Upper and Lower Works were subsequently demolished in 1903. The Washoe Smelter operated from 1902 to 1980.
Waste(s) at Issue:	Copper ore processing has produced wastes that cover over 6,000 acres and contain elevated levels of arsenic, cadmium, copper, lead, and zinc. Wastes include 185 million cubic yards of tailings (pond); 27 million cubic yards of granulated slag (pile); and 0.25 million cubic yards of flue dust. Stack emissions have contaminated the soils near the smelter. Ongoing fugitive flue dust emissions (from piles) and fugitive dust emissions (from soil) have contaminated the community for over 100 years.
Disposal Sites:	This site has 12 Operable Units, but only two have been investigated: <u>Mill Creek Operable Unit</u> — Mill Creek is an unincorporated community located approximately 25 miles west-northwest of Butte, Montana. It covers 160 acres of land and consists of 37 household with less than 100 people. The contaminants of concern in this Operable Unit are arsenic, lead, and cadmium. Arsenic dust in the air, and arsenic, lead, and cadmium in the soil and drinking water present public health risks. <u>Flue Dust Operable Unit</u> — flue dust is a fine grained waste material which was formed in the smelter flue. The dust contains high concentrations of arsenic, cadmium, copper, lead, and other metals. The amount of flue dust stored onsite, as of December 1989, was estimated to exceed 316,000 tons. The other 10 Operable Units are as follows: <u>Smelter Hill</u> — former ore processing area. This Operable Unit has soil and ground water contamination by metals. <u>Old Works</u> — Wastes (tailings) are located in a 100-year floodplain along a 2.75 mile stretch of Warm Springs Creek. This area is the focus of a removal operation. In addition, waste piles and soils at the smelter site and surface water near the site will be sampled. <u>Arbiter</u> — a
	copper refining plant that produced cathode copper from sulfide ores using an ammonia leach process. Slurry wastes from this inactive plant contain arsenic, cadmium, lead, zinc, and are located in a pond near the plant. <u>Beryllium Disposal Areas</u> — a beryllium flake-metal pilot plant and a beryllium oxide pilot plant were operated on Smelter Hill between 1964 and 1968. Following closure, waste containing beryllium was disposed of in the Opportunity tailings pond. <u>Community soils</u> — nearby community soils contaminated by smelter emissions. <u>Slag</u> — slag is the material separated from the metal during refining process; it consists of 85% silica dioxide (sand) and 15% iron oxide.

	<u>Tailings/Alluvium</u> — tailings make up the largest volume of waste at this site and are deposited in both the Anaconda and Opportunity ponds. The Opportunity ponds stretch 3 miles across from east to west. <u>Regional Soils</u> — contaminated agricultural lands surrounding the site. <u>Regional Ground Water</u> — ground water which have been contaminated from sources such as the Opportunity ponds, slag piles, tailings, and contaminated soils. <u>Surface water and sediment</u> — tailings have migrated into streams near the site.
Soil Pathway:	It was discovered that the soil contamination (by arsenic, cadmium, and lead) in Mill Creek was widespread. The geometric mean concentration of arsenic in Mill Creek surface soils is 638 mg/kg; for cadmium it is 25 mg/kg; and for lead it is 508 mg/kg. At a depth of 18 inches, concentrations of arsenic are below 100 mg/kg and approach background levels at 42 inches below the surface. High concentrations of cadmium and lead are also found in the first 6 inches of the soil profile. However, lead and cadmium concentrations decrease more rapidly with depth than arsenic concentrations. Cadmium levels were found to be less than detection limits at a depth of 9 inches, and lead levels reached background levels below 6 inches.
Ground Water Pathway:	The water table underlying Mill Creek is 20 feet or deeper below the surface. Domestic well water is drawn from this aquifer. In 1986, sampling showed that seven household water supplies had detectable arsenic levels. Cadmium and lead levels were mostly at or below detection limits.
Surface Water Pathway:	Mill Creek is the major drainage system is the area of the Anaconda Smelter and The Mill Creek community. Mill Creek was sampled four times and results showed that arsenic was present in the creek. Total arsenic concentrations ranged form 12 to 32.2 ug/l. Zinc was also detected in the waters of Mill Creek. Until transport of contaminated soil into Mill Creek is controlled or remedied, it is estimated that recontamination of Mill Creek will occur at a rate of 1.5 mg/kg of soil per year.
Air Pathway:	In 1984, samples of airborne particulate matter were collected at four different locations near the smelter and tested for total suspended particulates, respirable particulates, and trace-metal content. Arsenic concentrations were found to be 0.1 mg/m <sup>3</sup> . The highest arsenic concentration found at the Mill Creek station was 0.681 mg/m <sup>3</sup> . Elevated levels of cadmium, lead, and arsenic were found in household dust samples as well. Residential dust showed an average concentration of 264 mg/kg arsenic, and indoor respirable arsenic concentrations were 0.019 ug/m <sup>3</sup> .
Environmental Issues:	The Anaconda Smelter site is located in the Upper Clark Fork Basin above Warm Springs Creek and the main stem of the Clark Fork River to the Bitterroot River below Missoula, Montana. In addition, the community of Mill Creek is immediately adjacent to this site. Therefore, contaminants from the Anaconda Smelter site (e.g., arsenic, lead) pose a potential risk to human health and the environment (e.g, aquatic life, drinking water).

# Mining Sites on the National Priority List

Name of Site:	Tex Tin Corporation
Owner of Site:	Tex Tin Corporation
Location of Site:	Texas City, TX (situated on 175 acres in an area of mixed land use)
Climate Data:	Not given
Commodity Processed:	Secondary copper smelting
Facility History:	Originally operated by the U.S. Government during World Ward II as its primary tin smelting operation, the site was then acquired by the Associated Metals and Minerals Corporation from the Wah Chang Corporation in 1970 and became know as the Gulf Chemical and Metallurgical Company (GC&M). Since 1985, the company has been known as the Tex Tin Corporation. At one time, the facility was operated as an iron recovery facility, but it is currently engaged in the secondary smelting of copper. The Tex Tin site was added to the NPL in August 1990.
Waste(s) at Issue:	Heavy metals (arsenic, tin, lead and nickel) found in onsite surface and ground water, and in ambient air sampled on and off the site.
Disposal Site:	In 1977, the Tex Tin had three metals reclamation circuits: nickel sulfate, ferric chloride, and tin. <u>Nickel sludge circuit</u> - The nickel sludge was stored in drums in the north end of the smelter building. After smelting, waste sludge was sold for other metals recovery. A small quantity removed during vessel cleaning was dumped with the slag from the tin process. <u>Ferric chloride circuit</u> - The company was sold iron sludge contaminated with the herbicide Amiben. The material was stored in two areas (not specified). Runoff would flow through the plant to the pond system. A small quantity removed from the settling tank was disposed of in Acid Pond B. <u>Tin ingots circuit</u> - The product was received in the form of ore sacks (imported from Bolivia) which were stored on pallets by Ponds A and B, tin residues in 55-gallon drums which were stored in the ore storage building, and tin ore which were piled along Highway 519. After primary smelting, rich slag was stored onsite. End slag was produced after the electrolyte process and GC&M planned to install a new rotary furnace for secondary tin smelting. In 1979, the nickel circuit had been discontinued. Ferric chloride production had also decreased which caused GC&M to cease buying Amiben-contaminated iron sludge for use in this circuit. GC&M also stopped disposing of the settling-tank sludge in the acid pond. A rotary furnace was added to the tin circuit which resulted in material dumped north of the acid pond. Waste areas identified at the site have included wastewater treatment ponds, a gypsum slurry pond, an acid pond which once contained ferric chloride and hydrochloric acid, several drained acid ponds, slag, sludge, and ore piles. One of the slag piles is contaminated with the herbicide Amiben. The facility also stored approximately 4,000 drums containing radioactive material. At one time, the facility stored piles of spent catalyst in the anticipation of building a plant to extract metals such as tungsten. An inactive, licensed, low-level radioactive landfill, co

Soil Pathway:	Possible soil contamination is not well characterized. In 1980, EPA conducted a Potential Hazardous Waste Site Inspection. Piles of tin slag, iron ore, and crushed empty barrels were noted in the rear of the plant. A reddish material (possibly iron) was noted in the drainage ditch located close to the area of the material piles. One soil sample was collected by the Texas Department of Health's Bureau of Radiation Control near the low-level radioactive landfill in December 1984. The four metals detected were found to be at significantly elevated concentrations and considered a health concern. They include: antimony (2,590 ppm), arsenic (720 ppm), copper (130 ppm), and lead (980 ppm). The level of copper in the soil was not sufficiently elevated to represent a health concern.
Ground Water Pathway:	The Chicot Aquifer underlies the site and extends from 60 feet to approximately 1,000 feet below the land surface. The flow is generally in a southeasterly direction towards Galveston Bay. Ground water in the vicinity of the acid pond was monitored from 1975 to 1980. The monitoring wells were screened at 37 to 47 feet below the ground surface. The contaminant concentrations detected were much higher from the downgradient wells' samples as compared to the upgradient well. Twelve metals were detected and determined to exceed drinking-water standards and long-term health advisories. The metals of concern and their maximum concentrations detected include: arsenic (0.198 ppm), barium (6.5 ppm), cadmium (7 ppm), chromium (0.25 ppm), copper (390 ppm), lead (200 ppm), manganese (357 ppm), mercury (0.011 ppm), nickel (7 ppm), silver (1.02 ppm), tin (100 ppm), zinc (140 ppm).
Surface Water Pathway:	Inspections by the Texas Water Quality Board concluded that dikes designed to prevent discharges from two old outfalls and the acid pond were seeping, allowing contaminated water to enter Wah Chang Ditch. The ditch is currently pumped into the Texas City Industrial Channel, which enters Galveston Bay. Twelve surface water samples were collected from various locations at the facility between 1975 to 1988. The constituent of concern and their maximum detected levels include: arsenic (0.94 ppm), chromium (81 ppm), copper (60 ppm), mercury (0.02 ppm), nickel (535 ppm), zinc (42.7 ppm).
Air Pathway:	In January 1986, air-quality monitoring samples were obtained along the site perimeter using high-volume particulate samplers. The conclusion reached after the sampling was that heavy metals and arsenic were being carried offsite by the wind. The maximum values of the detected contaminants were: arsenic (2.34 ug/m <sup>3</sup> ), cadmium (0.64 ug/m <sup>3</sup> ), chromium (0.40 ug/m <sup>3</sup> ), lead (4.42 ug/m <sup>3</sup> ), nickel (0.21 ug/m <sup>3</sup> ), and tin (103.6 ug/m <sup>3</sup> ).
Environmental Issues:	Commercial businesses, residential areas, and petrochemical complexes are all located within 0.25 miles of the site. The saline Swan Lake is located approximately 2 miles from the site and is used primarily for recreational fishing and crabbing. A principal concern is the potential environmental contamination of surface waters through the transport of heavy metals into Chicot Aquifer, and drainage of contaminated water into Galveston Bay. Most drinking water is supplied municipally, however, a 1985 survey identified a small beach house community located approximately one mile southwest of the Tex Tin facility that uses private water wells. The community, consisting of approximately 60 homes, is supplied by 25 wells. While most of the wells are more than 200 feet deep, at least three of the wells are less than 105 feet deep and are in the Chicot Aquifer. Possible human routes of exposure were noted as ingestion, inhalation, and dermal contact with contaminated media. Inhalation and incidental ingestion of airborne particles of Tex Tin emissions or entrained dust have also been cited as potential pathways of concern. In addition, low levels of radioactivity have been detected onsite in association with the tin, copper, and antimony slags and with the company roads that have been graded with tin slag. According to the Bureau of Radiation Control, the radiation levels are well below Federal occupational exposure limits, but are approaching the upper limits of the range of levels generally considered safe for the general public.

# Mining Sites on the National Priority List

Name of Site:	Torch Lake
Owner of Site:	Not applicable
Location of Site:	Keweenaw Peninsula of Upper Michigan (14 miles from Lake Superior)
Climate Data:	Not given
Commodity Mined:	Copper
Facility History:	For over 100 years, the area surrounding Torch Lake was the center of Michigan's copper mining, smelting, and milling activities. Over 10.5 billion pounds of copper were processed in the area between 1868 and 1968. An estimated 5 million tons of copper were produced in the Keweenaw Copper District of Michigan from the 1960's to 1968. More than half of this was processed along the shores of Torch Lake. Mining activities in the lake area peaked between the early 1900's and 1920. By 1986, only one small copper recovery plant was still operating. Torch Lake was listed on the NPL in June 1988.
Waste(s) at Issue:	At the mills, copper was processed and the recovered copper was sent to a smelter, while tailings were disposed of with process wastewaters into or on land around Torch Lake. In 1916, copper was recovered from previously discarded tailings in Torch Lake through an ammonia leaching process. Further technological advances initiated a flotation process using reagents consisting of 50 percent coal tar, 15 percent pyridine oil, 20 percent coal tar creosote, and 15 percent wood creosote. In 1926, xanthates were added to the reagents. Between 1868 and 1968, an estimated 200 million tons of tailings were pumped into the lake, reducing its volume by approximately 20 percent.
Disposal Site:	The Torch Lake site has three operable units (OUs). OU1 includes surface tailings, contents of buried and submerged drums along the western shore of the lake, and industrial chemicals. OU2 includes potentially contaminated media in and around the lake. OU3 includes other tailings sources in the mid-Keweenaw Peninsula, including the North Entry, the northern portion of Portage Lake, and tributary areas.
<b>Tailings:</b>	Mine tailings are divided into two categories. The first involves tailings resulting from crushing and gravitational separation processes. The resulting contaminants of concern are: arsenic, copper, lead, and zinc. The second category of tailings is a result of flotation reprocessing. The contaminants of concern associated with this category include: arsenic, copper, lead, zinc, and industrial chemicals (lime, pyridine oil, coal tar creosotes, wood creosote, pine oil, and xanthates). Surface and subsurface tailings samples were collected and analyzed. Fifty eight surface samples were collected from a 0- to 6-inch depth and density of 1 sample per 10 acres. Twelve subsurface samples were collected from a depth of 0 to 3 feet and at a density of 1 sample per 20 acres. The sampling analysis indicated that the concentration and distribution of metals appeared to be similar in both surface and subsurface samples. Copper concentrations were elevated above background soil concentrations (3,020 mg/kg surface and 5,540 mg/kg subsurface as compared to 100 mg/kg in native soils). In summary, however, neither organic or inorganic compound levels in tailings from OU1 were found to be dramatically higher than background soils. In 1989, the U.S. Bureau of Mines determined that leachate from 30 other sites and they concluded that very little metal is being released from the tailings.

Drums:	In 1989, buried and submerged drums in tailings piles were discovered and determined to have very low hazardous constituent concentrations as measured by EP Toxicity tests. PCBs and pesticides were not found above the detection limits in the samples. The eighth drum contained 4,000 ppm of trichloroethylene; and it is suspected that the contents of the drum are related to illegal dumping.
Soil Pathway:	A limited soil investigation found that traces of tailings and slag were evident. The contaminants of potential concern and their maximum values detected include: aluminum (7,600 mg/kg), arsenic (7 mg/kg), barium (101 mg/kg), chromium (20.1 mg/kg), copper (459 mg/kg), lead (329 mg/kg), manganese (357 mg/kg), mercury (0.47 mg/kg), nickel (33.7 mg/kg), and vanadium (26.30 mg/kg). Soil samples from residential locations generally had concentrations of inorganic compounds an order of magnitude higher than background concentrations. The EPA Technical Assistance Team (TAT) also collected samples from the east side of Torch Lake and determined that the metals detected in the samples were all within typical soil background concentrations and below maximum concentrations for EP Toxicity.
Ground Water Pathway:	The U.S. Geological Survey sampled well water in 1968 and 1977. Analysis of the 35 wells in Houghton County indicated that only 3 had specific conductance greater than 500 micromhos per centimeter. These results indicated Torch Lake as a high quality water source for general use. Many Torch Lake communities and seasonal residents get their water from municipal systems or from an independent supplier. In July 1989, EPA's TAT sampled seven private wells and two municipal wells. Only one location sampled had a concentration of either organic or inorganic compounds in excess of the Maximum Contaminant Levels (MCLs). The sample collected from the Lake Linden municipal well had an iron concentration of 0.33 ppm which is slightly greater than the Secondary MCL of 0.3 ppm for iron. Ground water contamination is to be discussed further in the ROD for OU2.
Surface Water Pathway:	Water enters Torch Lake from the Trap Rock River, and Hammell, Dover, McCallum, and Sawmill Creeks. The Trap Rock River is the largest discharger into Torch Lake, and the Trap Rock River Watershed covers approximately 58 percent of the Torch Lake Drainage Basin. An estimated 2,000 kilograms per year of dissolved copper is transported through Trap Rock River and its tributaries into Torch Lake. Contamination of the surface water is to be addressed in the ROD for OU2.
Air Pathway:	The Michigan Department of Resources (MDNR) collected air samples from four sampling locations (based on wind and population profiles) to monitor likely exposure points, emissions sources, and background conditions. Total Suspended Particulates (TSP) samples were collected for one month, for 24-hour periods every other day in 1989. Further analysis of the two samples indicating the highest concentration of TSP were further analyzed for arsenic, chromium, copper, nickel, lead, and zinc. The analysis indicated that mean ambient-air concentrations at the two sample stations exceeded background ambient-air concentrations for aluminum, arsenic, barium, copper, magnesium, iron, manganese, and TSP.
Environmental Issues:	A century of mining waste deposition into Torch Lake created environmental concerns in the 1970's. In 1971, a discharge of cupric ammonium carbonate leaching liquor from the Lake Linden Leaching Plant occurred and MDNR reported discoloration of several acres of lake bottom. Further investigations found 15 water quality parameters with acceptable background ranges. Heavy metal concentrations in lake sediments were within background ranges, except for arsenic, chromium, zinc, and copper, which were all at elevated levels. Plant and benthic invertebrate analysis did not indicate any water quality changes. Three months later, the spill was cited as the cause of temporary depletion of oxygen, elevated copper levels, increased pH, and increased carbon alkalinity in the lake

and bioassays indicated toxicity to some macroinvertebrates. Changes in the dominant predator fish species and observance of abnormalities in certain fish species prompted a fish consumption advisory in 1983 for Sauger and Walleye caught in the lake. In the same year, the lake was designated as a Great Lakes Area of Concern (AOC). In 1988, the Agency for Toxic Substances and Disease Registry (ATSCR) concluded that the site is a potential public health concern because of possible exposure to unknown etiological agents that may create adverse health effects over time. The mine tailings contaminating Torch Lake have not been determined to cause known health effects, and there is no indication that human exposure is currently occurring or has occurred in the past.