SCANDIUM

A. Commodity Summary

Although scandium was not mined domestically in 1993, scandium ore was intermittently recovered from tailings and concentrates as needed. By-product scandium concentrates previously produced in Utah and tailings previously generated by mining fluorite in Montana were available for processing to recover high purity scandium oxide. Although four processing companies, two in Colorado, one in Illinois, and one in New Jersey, produced refined scandium products in 1993, no domestic facility recovered scandium from uranium.[1] One company in Iowa had the technology to produce ultra-high purity (99.9999%) scandium oxide. Companies in Arizona, Illinois, and Iowa possessed capacity to produce ingot and distilled scandium metal products. Exhibit 1 presents the names and locations of facilities once involved in the production of scandium.

EXHIBIT 1

SUMMARY OF SCANDIUM FACILITIES

Baldwin Metals Processing Co.	Phoenix, AZ	Ingot and distilled scandium metal production.
Boulder Scientific Co.	Mead, CO	Refining. Processed scandium concentrates derived from thortveitite-bearing tailings from the mined-out Crystal Mountain fluorite mine near Darby, Montana.
Interpro (subsidiary of Concord Trading Corp.)	Golden, CO	Refining. Processed stocks of scandium concentrates previously generated by the Energy Fuels Nuclear uranium plant at Bingham Canyon, Utah.
Materials Preparation Center	Ames, IA	Scandium Oxide and Ingot Production (research organization).
Rhone Poulenc, Inc.	Phoenix, AZ	Ingot and distilled scandium metal production.
Kennecott	Garfield, UT	Scandium is available for refining in the form of a byproduct generated during processing of uranium at the copper mine.
Climax Mine	Climax, CO	Scandium is available for refining from the tungsten byproduct generated during the molybdenum operation.
APL Engineered Materials	Urbana, IL	Refining. Ingot and distilled scandium metal production.
Sausville Chemical Co.	Garfield, NJ	Refining. Processed scandium concentrates to produce scandium oxide, fluoride, nitrate, chloride, and acetate.

[1] Personal communication between Jocelyn Spielman, ICF Incorporated and James B. Hedrick, Scandium Specialist, U.S. Bureau of Mines, October 20, 1994.

Scandium used in the United States is primarily from domestic sources. Some minor amounts of scandium are recovered by recycling laser crystal rods. The principal uses for scandium are metallurgical research, high-intensity metal halide lamps, analytical standards, electronics, lasers, and research.[2]

Scandium is a soft silver metal which has a slightly yellow cast when exposed to air. Scandium readily reacts with acids and is not easily attacked by water. The metal does not tarnish in air, but at high temperatures (500 to 800 °C) scandium can be oxidized in air. Scandium is extremely electropositive, and therefore, its oxide is basic and acid soluble. Scandium exhibits a trivalent state in compounds and has no other observed valences. Scandium is chemically similar to rare earth elements; however, its ion size places it in geochemical equilibria with aluminum, magnesium, hafnium, and zirconium. Therefore, scandium is rarely found in the earth ores, but has been noted in minor amounts in gadolinite, xenotime, allanite, davidite, and others.[3]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Scandium is generally produced by small, bench-scale batch processes. Much initial recovery is from in-plant streams where solvent extraction is being used to recover other metals such as uranium. These crude materials are then worked up to high purity oxides and metals. The principal domestic scandium resource is fluorite tailings from the Crystal Mountain deposit near Darby, Montana. Tailings from the mined-out fluorite operations, which were generated from 1952 to 1971, contain thortveitite and associated scandium-enriched minerals. Resources are also contained in the tungsten, molybdenum, and titanium minerals from the Climax molybdenum deposit in Colorado, and in the kolbeckite (sterrettite), varsite, and crandallite at Fairfield, Utah.[4] Scandium is extracted from thortveitite by several methods.

2. Generalized Process Flow Diagram

Recovery From Thortveitite

As shown in the attached process flow diagrams, scandium can be recovered from thortveitite using several methods. Each method involves a distinct initial step (i.e., acid digestion, grinding, or chlorination) followed by a set of common recovery steps, including leaching, precipitation, and filtration.

Acid Digestion, Grinding, and Chlorination. Scandium is extracted from thortveitite by several methods. The method shown in Exhibit 2 involves digestion of thortveitite with concentrated hydrochloric or sulfuric acid, yielding a gelatinous silica residue that contains scandium. Another method, shown in Exhibit 3, begins by finely grinding thortveitite and then combining it with charcoal at 1,800 °C to form scandium carbide. This carbide is then further decomposed with hydrochloric acid, forming soluble scandium chloride. Exhibit 4 presents a third method that involves heating thortveitite in the presence of chlorine gas and carbon at 850 °C to form scandium chloride.

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[2] James B. Hedrick, "Scandium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 148-149.

[3] U.S. Environmental Protection Agency, "Scandium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, Office of Solid Waste, 1988, p. 3-20.

[4] James B. Hedrick, 1995, Op. Cit., pp. 148-149.

EXHIBIT 2

SCANDIUM FROM THORTVEITITE #1

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-20 - 3-30.)

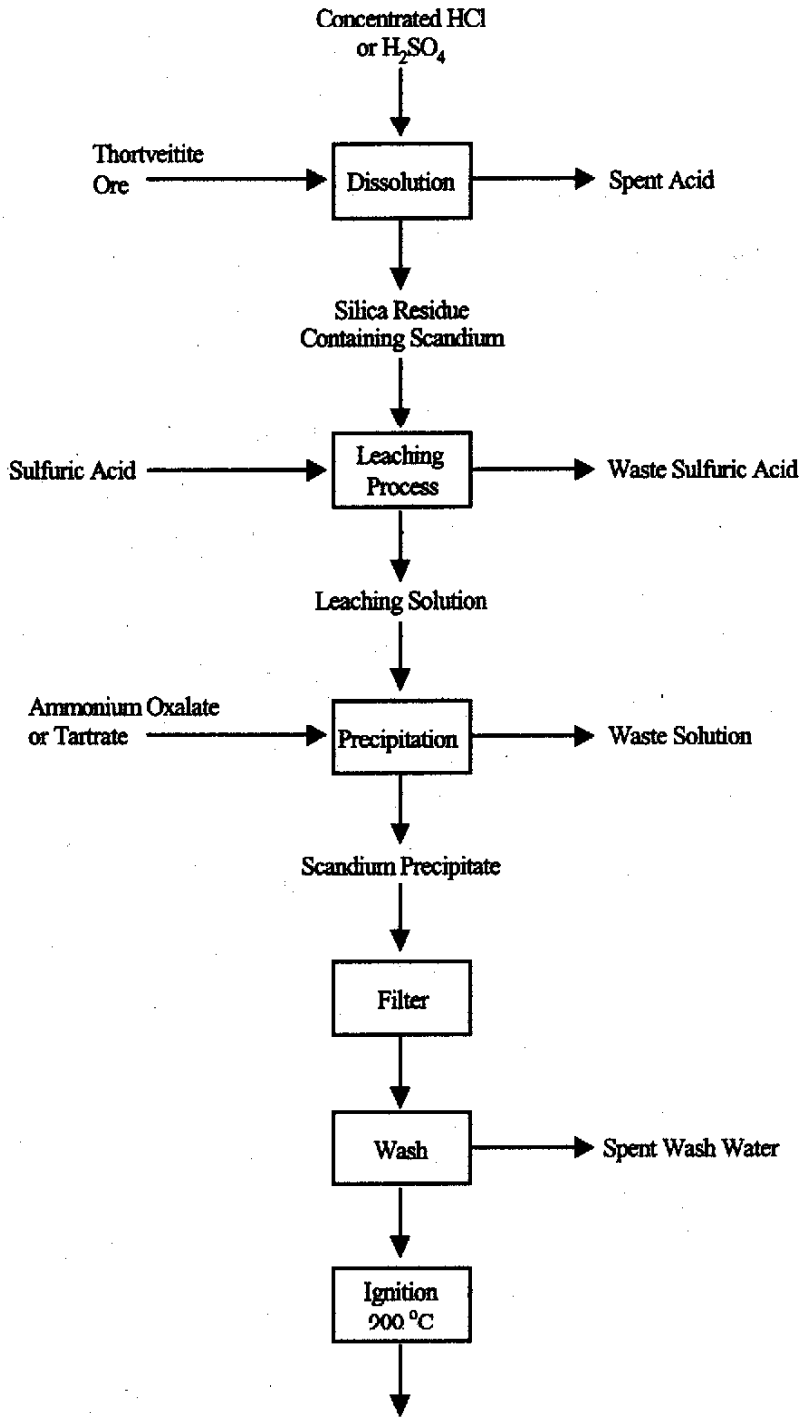


EXHIBIT 3

SCANDIUM FROM THORTVEITITE #2

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-20 - 3-30.)

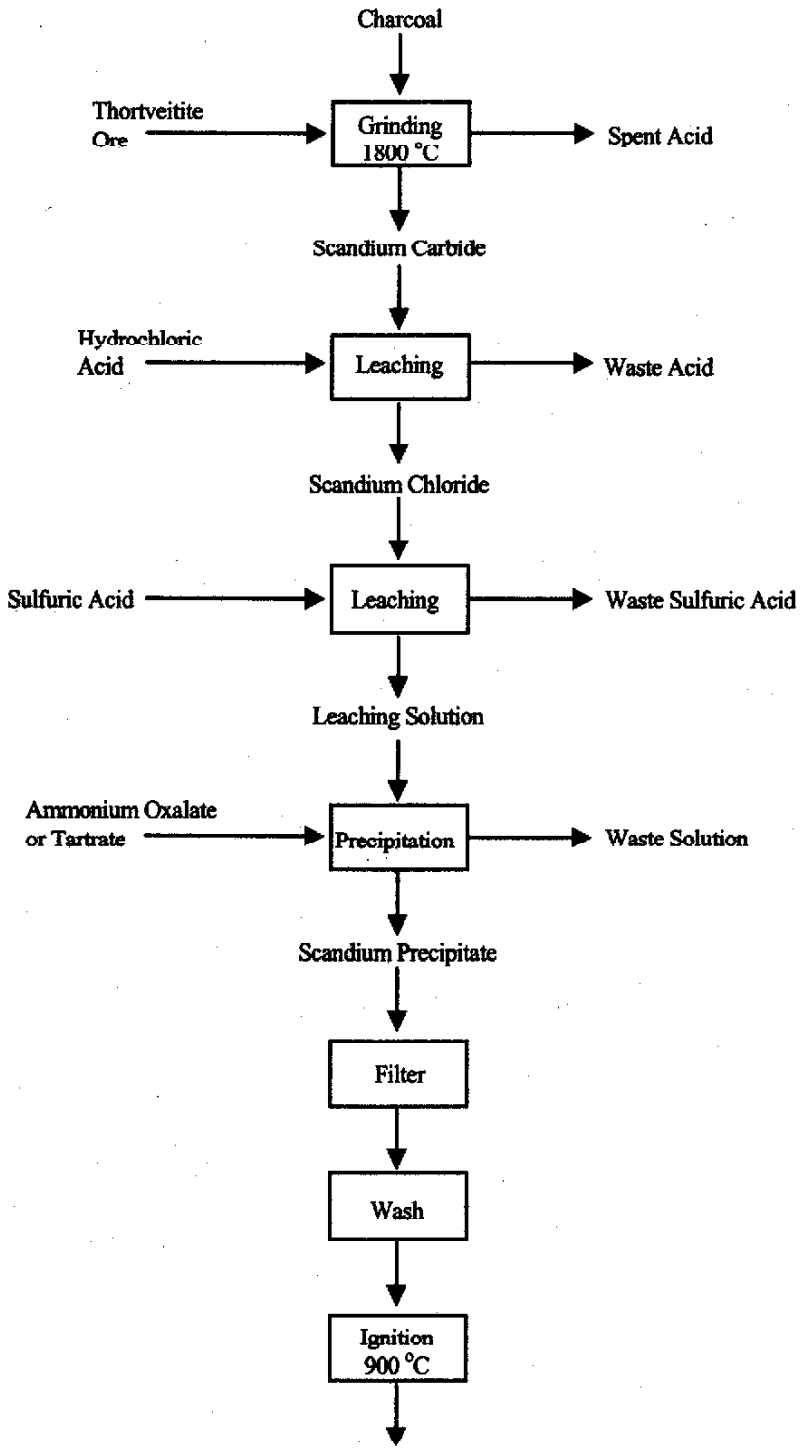


EXHIBIT 4

SCANDIUM FROM THORTVEITITE #3

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-20 - 3-30.)

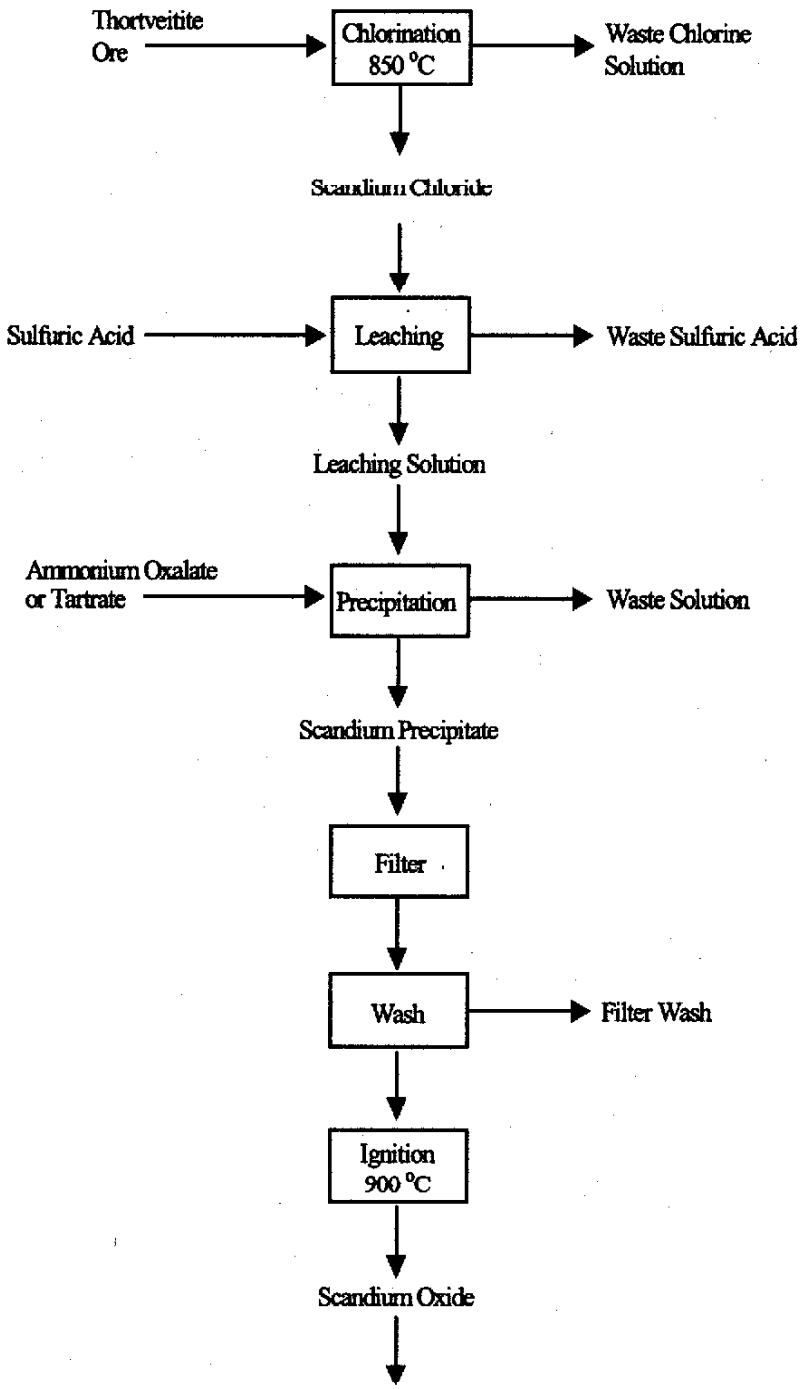
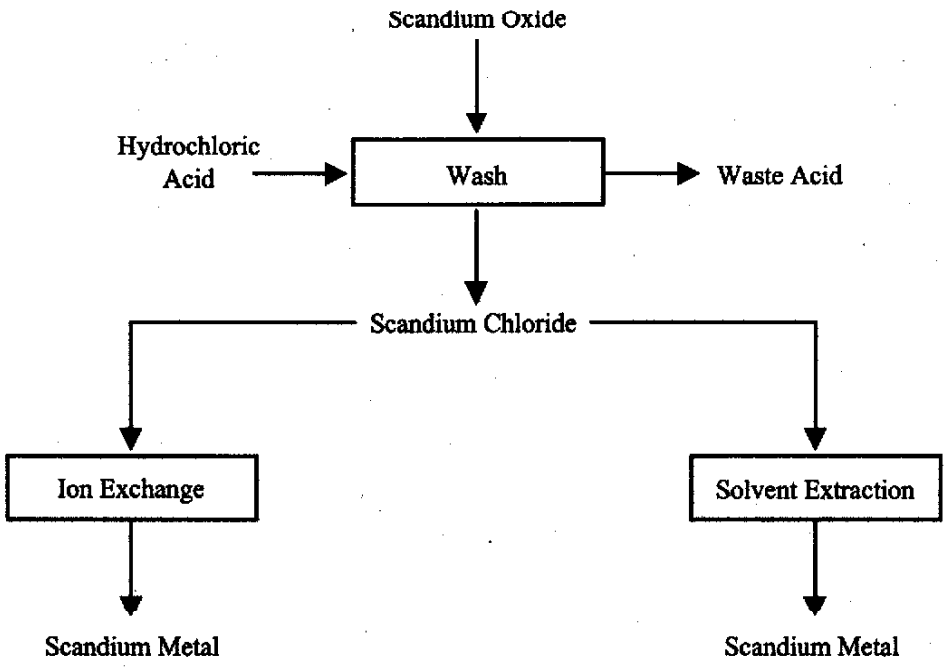


EXHIBIT 4 (Continued)

SCANDIUM FROM THORTVEITITE #3



In a fourth method, scandium can also be extracted from thortveitite using hydrofluoric acid in a similar method. Methods using magnesium or ammonium-hydrogen fluoride have also been used. Regardless of the method used, these initial recovery steps are followed by leaching, precipitation, filtration, washing, and ignition at 900 °C to form scandium oxide.[5]

Leaching, Precipitation, and Filtration. Scandium is obtained by leaching scandium chloride with sulfuric acid. Scandium is recovered from the leaching residues by adding ammonium oxalate or tartrate to the solution forming a scandium precipitate. This precipitate is filtered and washed, then decomposed by ignition at 900 °C, forming scandium oxide. The scandium oxide is then dissolved in hydrochloric acid to form scandium chloride.[6]

Purification. Scandium chloride is purified via distillation. Distillation removes a large quantity of metallic impurities, including iron, cadmium, magnesium, and chromium, along with carbon and nitrogen. Ion exchange or solvent extraction is also used for further purification.[7]

Recovery From Uranium (no longer used)

Alternatively, as shown in Exhibit 5, scandium was also once recovered from a byproduct generated during the processing of uranium at the copper mines in Garfield, Utah. The stripped solvent from uranium ore solvent extraction was acidified in stages. First the solvent was treated with hydrofluoric acid and filtered. Next, the resultant filter cake was treated with hydrochloric acid, followed by digestion and filtration. Oxalic acid was added to the resultant scandium, iron, and uranium filtrate to form scandium oxalate, which was calcined to yield scandium oxide. A second treatment with hydrochloric acid followed by extraction and stripping yielded scandium metal.

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

In addition to the methods described, the U.S. Bureau of Mines has investigated solvent extraction methods for recovering scandium from the leach filtrates of sulfated tantalum tailings.[8]

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

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[5] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-20.

[6] Ibid.

[7] Ibid.

[8] Michael D. Odekirk and Donna D. Harbuck, "Scandium Solvent Extraction from Liquors Produced by Leaching Sulfated Tantalum Tailings," EPD Congress, The Minerals, Metals & Materials Society, 1993, pp. 83-97.

EXHIBIT 5

SCANDIUM FROM URANIUM

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-20 - 3-30.)

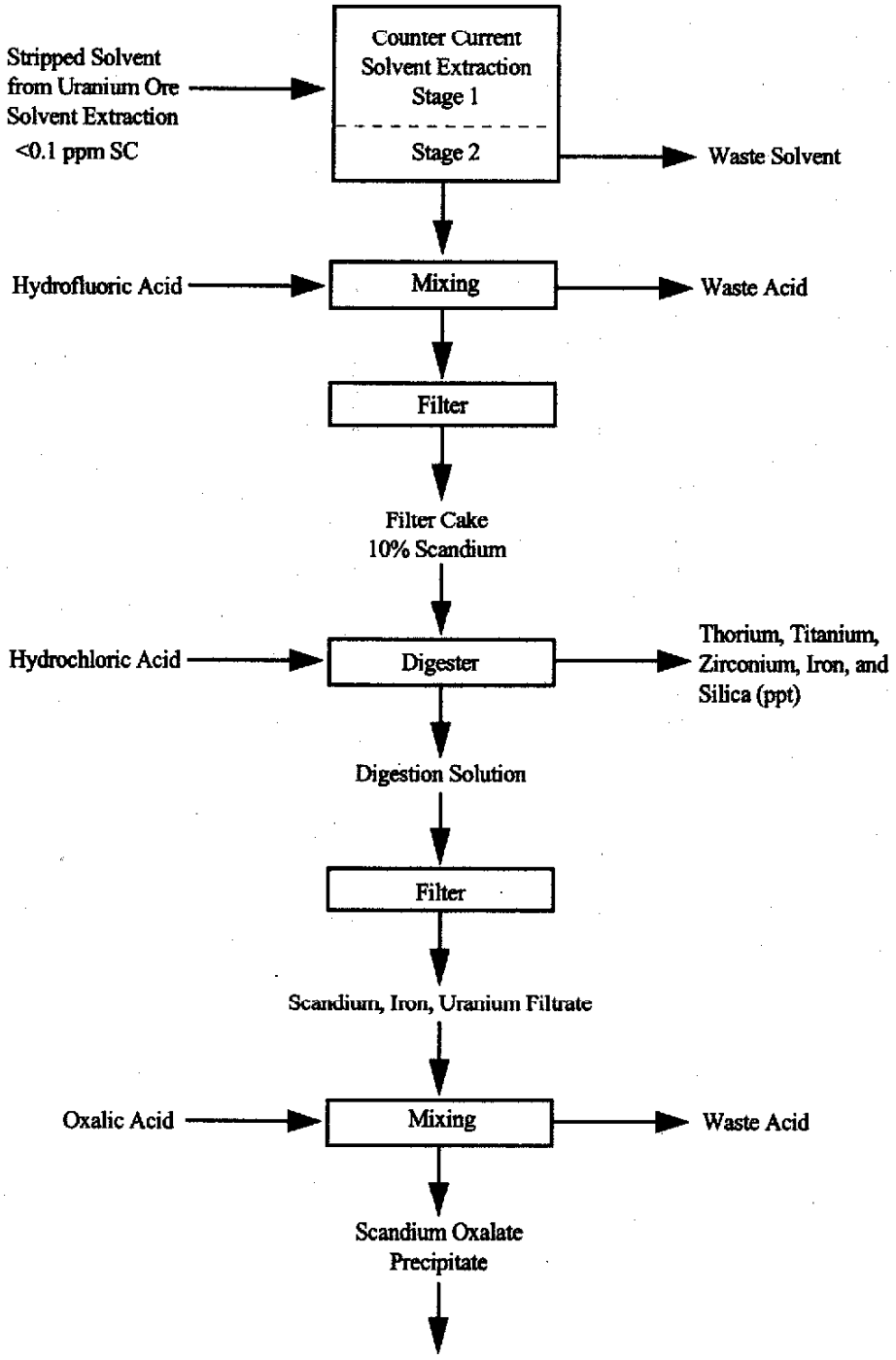
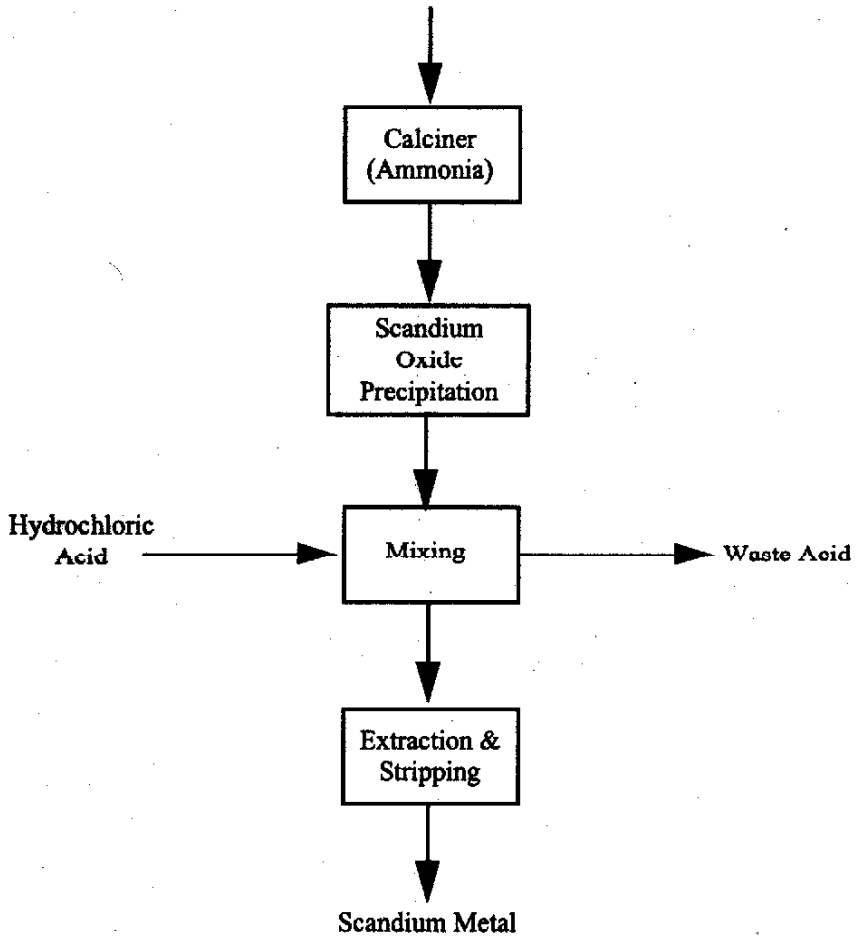


EXHIBIT 5 (Continued)

SCANDIUM FROM URANIUM



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 for scandium recovery from thortveitite occurs between ore preparation and digestion, grinding, or chlorination for thortveitite processes 1, 2, and 3, respectively. EPA identified these points in the process sequences as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the thortveitite ore occurs. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The wastes generated by recovery from uranium may have been radioactive, however, no further characterization, management, or generation data are available. Those wastes identified in Exhibit 5 include:

Waste Solvent
Waste Hydrofluoric Acid

2. Mineral Processing Wastes

Waste streams are more likely to be associated with the primary products that produced the crude scandium concentrate. Although it is difficult to predict the amount and nature of wastes resulting directly from scandium production because of the wide variety of sources that are available as scandium starting materials, the attached process flow diagrams identify wastes that are generated as a result of scandium production processes.[9]

For example, using Exhibits 2 through 4 the following wastes result from the production of scandium:

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

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

Spent solvents from solvent extraction. 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,

[9] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-20.

medium, and high annual waste generation rate of 700 metric tons/yr, 3,900 metric tons/yr, and 7,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of ignitability. This waste is classified as a spent material.

"Crud" from the bottom of the solvent extraction unit. 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.

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

Spent acids (e.g., hydrochloric and sulfuric). 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 700 metric tons/yr, 3,900 metric tons/yr, and 7,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

Waste solutions/solids from leaching and precipitation. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

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

As shown in Exhibit 5, the following wastes were generated when scandium was recovered through extraction from uranium ores. Since the process is no longer used, the Agency did not evaluate these materials further.

Digester precipitates
Waste Oxalic Acid
Waste Hydrochloric Acid

D. Non-uniquely Associated Wastes

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

E. Summary of Commented Received by EPA

EPA received no comments that address this specific sector.

BIBLIOGRAPHY

"Rare Earth Metals." From Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XIX. pp. 841.

Hedrick, James B. "Scandium." From Mineral Commodity Summaries. U.S. Bureau of Mines. 1995. pp. 148-149.

Hedrick, James B. "Rare Earths: The Lanthanides, Yttrium, and Scandium." From Mineral Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 1035-1047.

Odekirk, Michael D. and Harbuck, Donna D. "Scandium Solvent Extraction from Liquors Produced by Leaching Sulfated Tantalum Tailings." Salt Lake City Research Center. U.S. Bureau of Mines. EPD Congress. The Minerals, Metals & Materials Society. 1993. pp. 83-97.

Personal communication between Jocelyn Spielman, ICF Incorporated and James B. Hedrick, Scandium Specialist, U.S. Bureau of Mines. October 20, 1994.

U.S. Environmental Protection Agency. "Scandium." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste. 1988. pp. 3-20-3-30.

SELENIUM

A. Commodity Summary

Selenium is found in 75 different mineral species, however, pure selenium does not exist as an ore. For this reason, primary selenium is recovered from anode slimes generated in the electrolytic refining of copper. One facility, ASARCO - Amarillo, TX, processes this slime further to recover tellurium. For more information on tellurium recovery, see the tellurium report. According to the U.S. Bureau of Mines, three copper refineries, Asarco, Phelps Dodge, and Kennecott, accounted for all of the domestic production of primary selenium. The 1994 production was worth $3 million. End uses of selenium include:

- electronics, 35 percent;
- chemicals and pigments, 20 percent;
- glass manufacturing, 30 percent; and
- other, including agriculture and metallurgy, 15 percent.[1]

Exhibit 1 lists the names and locations of the facilities involved in the production of selenium.

EXHIBIT 1

SUMMARY OF SELENIUM PROCESSING FACILITIES

Facility Name	Location
ASARCO	Amarillo, TX
Kennecott (RTZ)	Garfield, UT
Phelps Dodge	El Paso, TX

B. Generalized Process Description

1. Discussion of Typical Production Processes

Generally, 30-80 percent of the selenium contained in copper anode slimes is recovered by commercial operations. Several methods of selenium recovery may be used. The two major processes for selenium recovery are smelting with soda ash and roasting with soda ash. Other methods include roasting with fluxes, during which the selenium is either volatilized as an oxide and recovered from the flue gas, or is incorporated in a soluble calcine that is subsequently leached for selenium. In some processes, the selenium is recovered both from the flue gas and from the calcine. At the process end points, selenium metal is precipitated from solutions of sodium selenite or selenious acid by sulfur dioxide.[2] Exhibits 2 through 4 present process flow diagrams for selenium production.

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[1] Stephen Jasinske, "Selenium," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 150-151.

[2] Neldon Jenson, "Selenium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 705-711.

EXHIBIT 2

SODA ROASTING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187 - 3-193.)

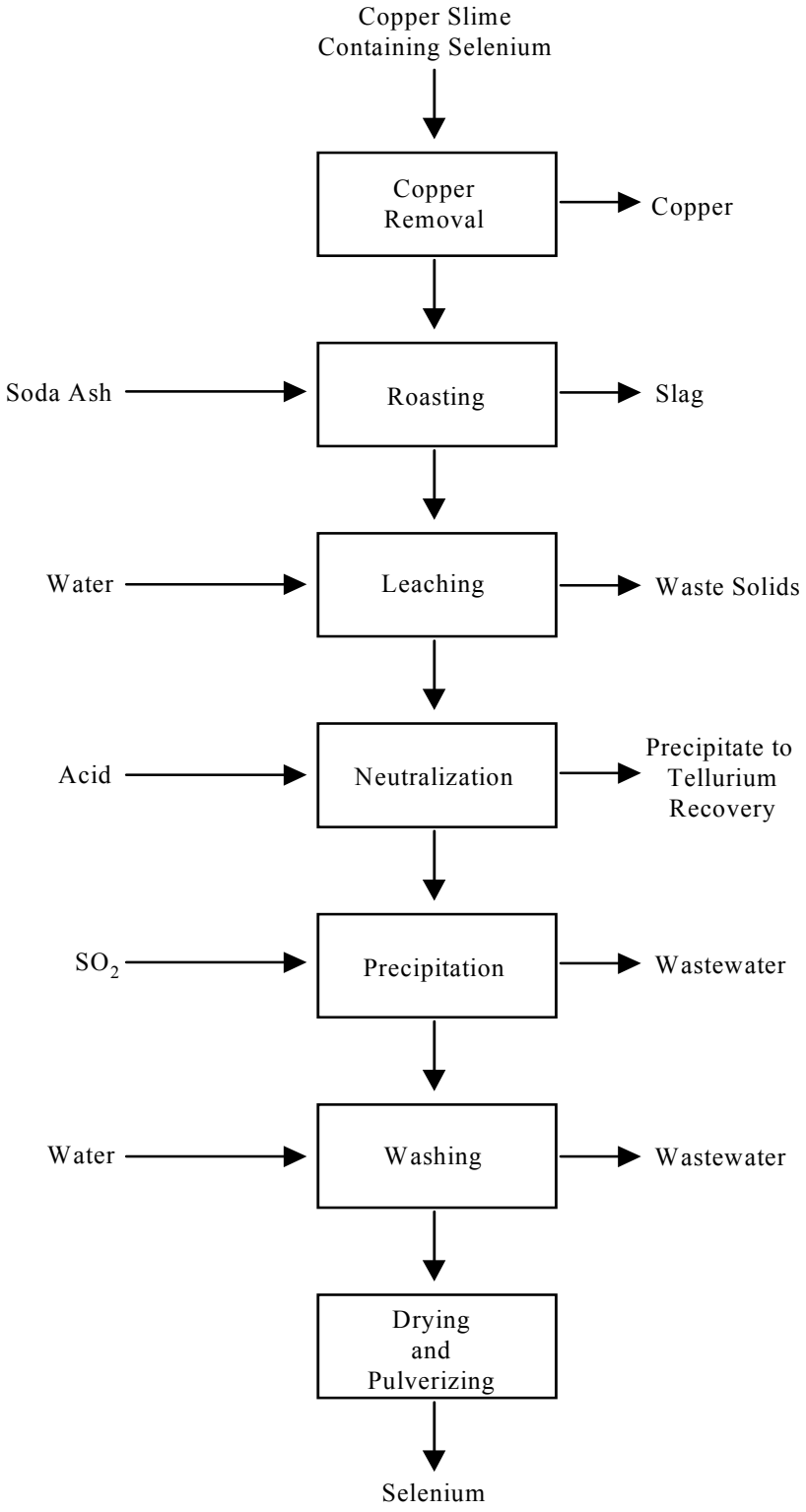


EXHIBIT 3

SODA SMELTING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187 - 3-193.)

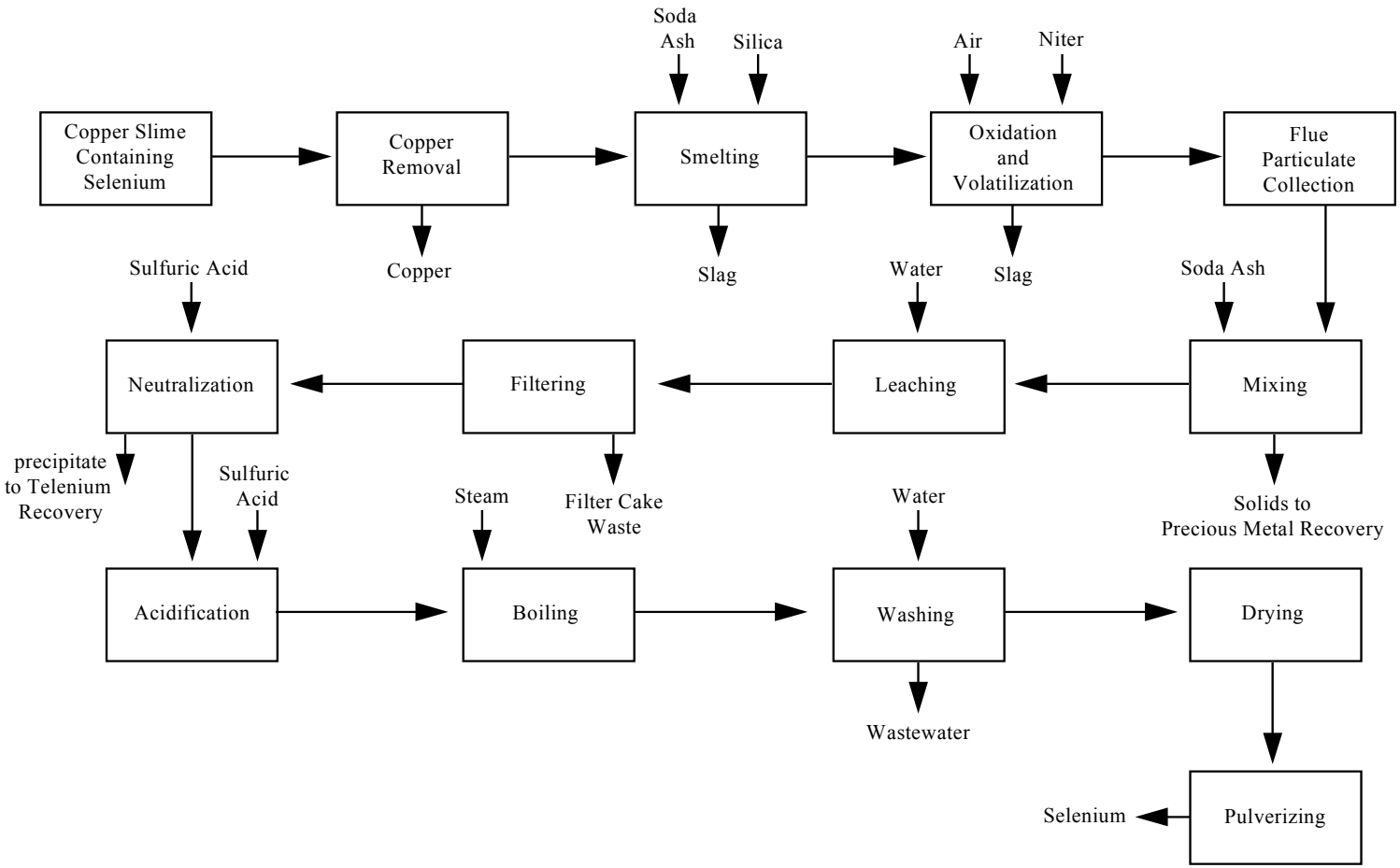
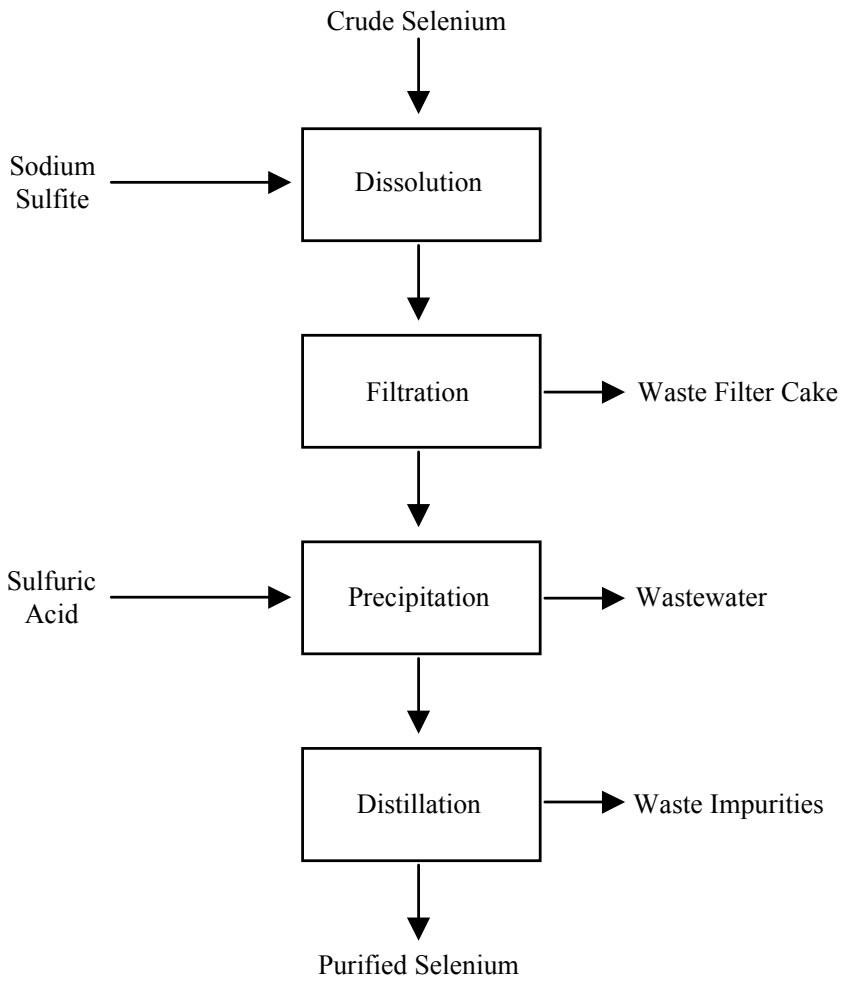


EXHIBIT 4

SELENIUM PURIFICATION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187 - 3-193.)



2. Generalized Process Flow

Roasting with Soda Ash

As shown in Exhibit 2, decopperized slime is roasted with soda ash to produce sodium selenite and sodium selenate. The selenium is then leached with water, neutralized to precipitate tellurium, and then sparged with SO_2 to precipitate selenium.[3]

Smelting with Soda Ash

As shown in Exhibit 3, decopperized slime is mixed with soda ash and silica and smelted in a furnace. Slag containing silica, iron, and several other metal impurities is generated as waste. The molten charge containing selenium is aerated to oxidize and volatilize the selenium, and the remaining solids are removed for precious metal recovery. The soda ash is leached with water and filtered to separate unwanted solid impurities, which are discarded as waste. The selenium-containing filtrate is neutralized to precipitate out tellurium, and is acidified to precipitate selenium. The selenium containing material formerly classified as sludge is then boiled, washed, dried, and pulverized to yield the selenium product.[4]

Selenium Purification

The selenium obtained from either smelting with soda ash or roasting with soda ash is then purified. As shown in Exhibit 4, the crude selenium is dissolved in sodium sulfite, and the resulting solution is filtered to remove unwanted solids as waste filter cake. The resulting filtrate is acidified with sulfuric acid to precipitate the selenium. The selenium precipitate is distilled to drive off impurities, producing a high purity selenium for commercial and industrial use.

Kennecott Utah Copper Corporation (KUCC)

One company now recovers selenium via a hydrometallurgical process. Liquid from its gold recovery circuit is treated with SO_2 to precipitate crude selenium. The crude selenium is retorted (distilled) in an electric melting furnace. The offgas from the selenium retort is cooled to collect the selenium. After retorting and condensation, the pure selenium is crushed, sized, and packaged for shipment.[5]

High purity selenium is currently produced from crude coked selenium. After wet grinding, pulping, and decantation washing with hot water to (remove impurities such as arsenic), the high purity circuit feed is leached with hot sodium sulfite solution. Selenium dissolves to form a compound similar to sodium thiosulfate. After leaching, the slurry settles and the solution is decanted through a clarifier press to the precipitation tanks. Selenium is precipitated by acidification of this solution with concentrated H_2SO_4. The solutions are kept cool during acidification to obtain red amorphous selenium. After precipitation, the slurry is settled and most of the solution decanted to waste. Settled slurry is repulped with water and heated with steam. Heating converts the red selenium to a gray crystalline powder. The slurry is then centrifuged in a perforated bowl centrifuge and the solids washed by displacement with copious amounts of water.

Centrifuge cake is charged into the first stage of the three stage distillation circuit. Condensed selenium from these stills is collected in fractionating trays. Samples for spectrographic analysis of 19 elements are taken through the run. Early fractions are high in tellurium and other high-boiling-point impurities. Impure fractions are

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[3] Ibid.

[4] U.S. Environmental Protection Agency, "Selenium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-187--193.

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

rejected to sulfite leaching or redistillation in the first-stage stills. Acceptable fractions from the first-stage stills are advanced to second-stage distillation in a silicon carbide retort. Condensed selenium from this stage is passed through a shotter (pelletizer) and quenched with water. Seven fractions are normally made and a sample of each is analyzed spectrographically for 19 impurity elements. First and last fractions, as well as others showing abnormal impurity levels, are recycled to an appropriate part of the purification circuit. Acceptable fractions are advanced to third-stage distillation. Condensed selenium shot from third-stage distillation is again collected in seven fractions, each of which is analyzed spectrographically. Reject fractions are recycled back to an appropriate part of the circuit. Acceptable selenium shot from third-stage distillation is made up into lots and blended. Samples from the blended material are analyzed again spectrographically and chemical analysis is made for halogens, sodium sulfur, and nonvolatile material. Finally, acceptable lots are packaged for sale or stored for doped selenium production.[6]

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

None identified.

4. Beneficiation/Processing Boundaries

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

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Not applicable.

2. Mineral Processing Wastes

Selenium is recovered from anode slimes generated from the electrolytic refining of copper. Because of this, all wastes from selenium production generated after the production of the copper anode slimes are mineral processing wastes. Listed below are possible waste streams from selenium production.

Plant process wastewater (PWW). This waste may exhibit the characteristic of toxicity for lead. In addition, this waste may also exhibit the characteristic of corrosivity since it is expected to have a pH of 0.8 to 1.9. The 1991 generation rate for the sector was 66,000 metric tons per year.[7] Waste characterization data are presented in Attachment 1. This waste may be recycled and formerly was classified as a spent material.

Slag. This waste may contain silica, iron, and other metal 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, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium. Slag may be recycled and formerly was classified as a byproduct.

Spent 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 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium. This waste may be recycled and formerly was classified as a byproduct.

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[6] Ibid.

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

Tellurium slime wastes are sent to tellurium product recovery. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium. This waste formerly was classified as a byproduct.

Waste solids. 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 50 metric tons/yr, 500 metric tons/yr, and 5,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium.

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received by EPA

New Factual Information

One commenter provided new information about its facility's selenium recovery process (COMM 40). This new information has been included in the sector report.

Sector-specific Issues

None.

BIBLIOGRAPHY

Jasinski, Stephen. "Selenium." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 150-151.

Jenson, Neldon. "Selenium." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 705-711.

Lansche, Arnold M. "Selenium and Tellurium - A Materials Survey." U.S. Bureau of Mines. Information Circular 8340. 1967. pp. 32-34.

"Selenium and Selenium Compounds." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XX. 1982. pp. 575-599.

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

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. Vol. II. August, 1992. pp. 32-2 - 32-6.

U.S. Environmental Protection Agency. "Selenium." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp. 3-187 - 3-193.

ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PLANT PROCESS WASTEWATER (ACID PLANT BLOWDOWN) - SELENIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.50	0.50	0.50	0/1	0.32	0.32	0.32	1/1	-	-
Antimony	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	-	-
Arsenic	0.50	1.45	2.40	1/2	0.95	0.95	0.95	1/1	5.0	0
Barium	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	100.0	0
Beryllium	2.000	0.050	0.050	0/1	0.0050	0.0050	0.0050	0/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.017	0.034	0.050	1/2	0.043	0.043	0.043	1/1	1.0	0
Chromium	0.50	0.50	0.50	0/1	0.11	0.11	0.11	1/1	5.0	0
Cobalt	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	-	-
Copper	0.090	0.30	0.50	1/2	0.050	0.050	0.050	0/1	-	-
Iron	1.63	1.63	1.63	1/1	1.50	1.50	1.50	1/1	-	-
Lead	1.42	9.16	16.90	2/2	12.00	12.00	12.00	1/1	5.0	1
Magnesium	14.90	14.90	14.90	1/1	14.10	14.10	14.10	1/1	-	-
Manganese	1.06	1.06	1.06	1/1	0.98	0.98	0.98	1/1	-	-
Mercury	0.00072	0.00072	0.00072	1/1	0.00088	0.00088	0.00088	1/1	0.2	0
Molybdenum	23.30	88.43	130	3/3	20.90	20.90	20.90	1/1	-	-
Nickel	0.10	0.30	0.50	1/2	0.050	0.050	0.050	0/1	-	-
Selenium	0.50	2.05	3.60	1/2	0.90	0.90	0.90	1/1	1.0	0
Silver	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	5.0	0
Thallium	2.50	2.50	2.50	0/1	0.25	0.25	0.25	0/1	-	-
Vanadium	0.50	0.50	0.50	0/1	0.050	0.050	0.050	0/1	-	-
Zinc	0.50	0.50	0.50	0/1	0.21	0.21	0.21	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	27,000	27,400	27,800	2/2	-	-	-	0/0	-	-
Fluoride	40.00	80.00	120	2/2	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	158	158	158	1/1	-	-	-	0/0	-	-
TSS	25	20,313	40,600	2/2	-	-	-	0/0	-	-
pH *	0.80	1.35	1.90	2/2					2<pH>12	2
Organics (TOC)	25.20	26.35	27.50	2/2					-	-

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

SILICON AND FERROSILICON

A. Commodity Summary

Most ferrosilicon is used as an alloying element in the ferrous foundry and steel industries. Aluminum producers and the chemical industry were the main consumers of silicon metal. Ferrosilicon was produced by six companies in seven plants in the United States in 1992, and silicon metal was produced by six companies in eight plants.[1] Exhibit 1 lists these facilities and their locations. There are two standard grades of ferrosilicon, with one grade approximately 50 percent silicon and the other 75 percent silicon by weight.[2] The purity of silicon metal generally ranges from 96 to 99 percent.

EXHIBIT 1

SUMMARY OF FERROSILICON AND SILICON SMELTING AND REFINING FACILITIES (IN 1992)[a]

Facility Name	Location	Products
American Alloys Inc.	New Haven, WA	FeSi and Si
Applied Industrial Minerals Corp.	Bridgeport, AL	FeSi
Dow Corning Corp.	Springfield, OR	Si
Elkem Metals Co.	Alloy, WV	Si
Elkem Metals Co.	Ashtabula, OH	FeSi
Globe Metallurgical Inc.	Beverly, OH	FeSi and Si
Globe Metallurgical Inc.	Selma, AL	Si
Keokuk Ferro-Sil Inc	Keokuk, IA	FeSi
Silicon Metaltech Inc.	Wenatchee, WA	Si
Simetco Inc.	Montgomery, AL	Si
SKW Alloys Inc	Calvert City, KY	FeSi
SKW Alloys Inc	Niagara Falls, NY	FeSi and Si

[a] - Cunningham, L. D., "Silicon." Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. p. 1191.

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[1] L.D. Cunningham, "Silicon," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 152.

[2] L.D. Cunningham, "Silicon," from Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. p. 1183.

B. Generalized Process Description

1. Discussion of Typical Production Processes

In the United States all primary production of ferrosilicon and silicon metal is by the reduction of silica (SiO_2) to silicon (Si) in submerged arc electric furnaces. High purity silicon is made from metallurgical grade silicon, and is, therefore, secondary processing which is outside the scope of this report.

2. Generalized Process Flow Diagram

Exhibits 2 and 3 are typical production flow diagrams illustrating the production of silicon and ferrosilicon. As shown in the exhibits, the feed silica is washed, sized, and crushed. The silica is then mixed with a reducing agent, and either coal, coke, or charcoal. Wood chips are added for porosity. The mixture is fed into the furnace, and when ferrosilicon is being produced, iron or steel scrap is added.[3] The furnace is tapped periodically and the molten ferrosilicon or silicon metal is drawn out and cast into ingots. The ingots are allowed to cool, then are crushed to produce the final product.[4]

High purity silicon used in the electronics industry is made from silicon metal, and is therefore beyond the scope of this report. However, a brief overview of the production process is included for completeness. Naturally occurring quartz is converted to metallurgical grade silicon by heating it with coke in an electric furnace. The low grade silicon is then converted to high grade halide or halosilane which is then reduced with a high purity reagent.[5]

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

Research is being conducted in Austria on the production of ferrosilicon from lump quartz and charcoal using a plasma reactor. Other input substitutions also are being investigated, including using sand as a replacement for quartz, and taconite tailings instead of iron or steel. In addition, the use of plasma reactors in smelting silicon is being investigated in Austria.[6,7]

4. Beneficiation/Processing Boundaries

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

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[3] U.S. Environmental Protection Agency, "Silicon and Ferrosilicon," from 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes, 1988, pp. 3-194 - 3-195.

[4] L.D. Cunningham, 1992, Op. Cit., p. 1184.

[5] "Silicon and Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XX, 1982, p. 836.

[6] Goodwill, J. E., "Plasma Melting and Processing - World Developments," 48th Electric Furnace Conference Proceedings, New Orleans, LA, December 11-14th 1990, p. 280.

[7] Goodwill, J. E., "Developing Plasma Applications for Metal Production in the USA," Ironmaking and Steelmaking, Vol. XVII, No. 5, 1990, pp. 350-354.

EXHIBIT 2

SILICON PRODUCTION

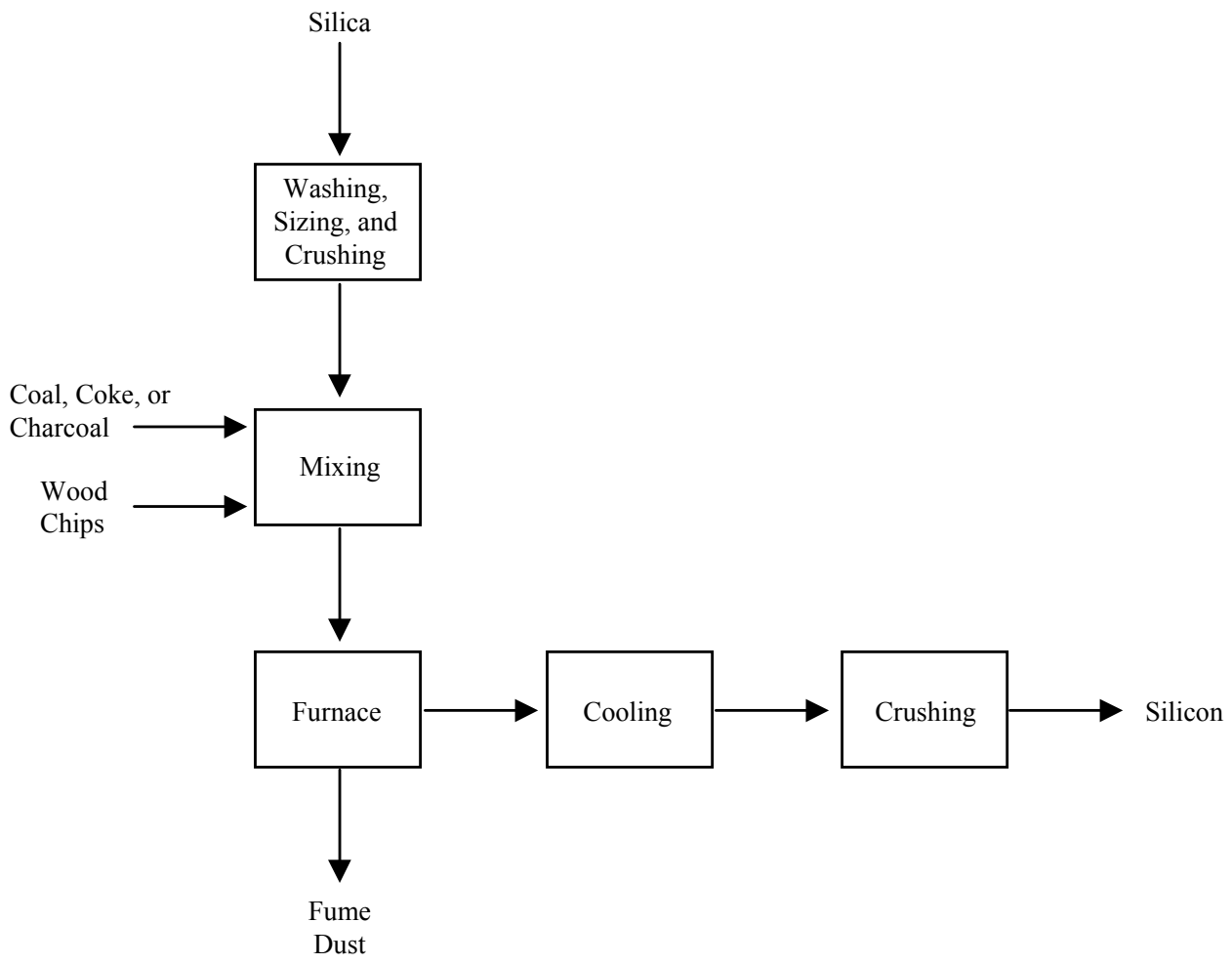
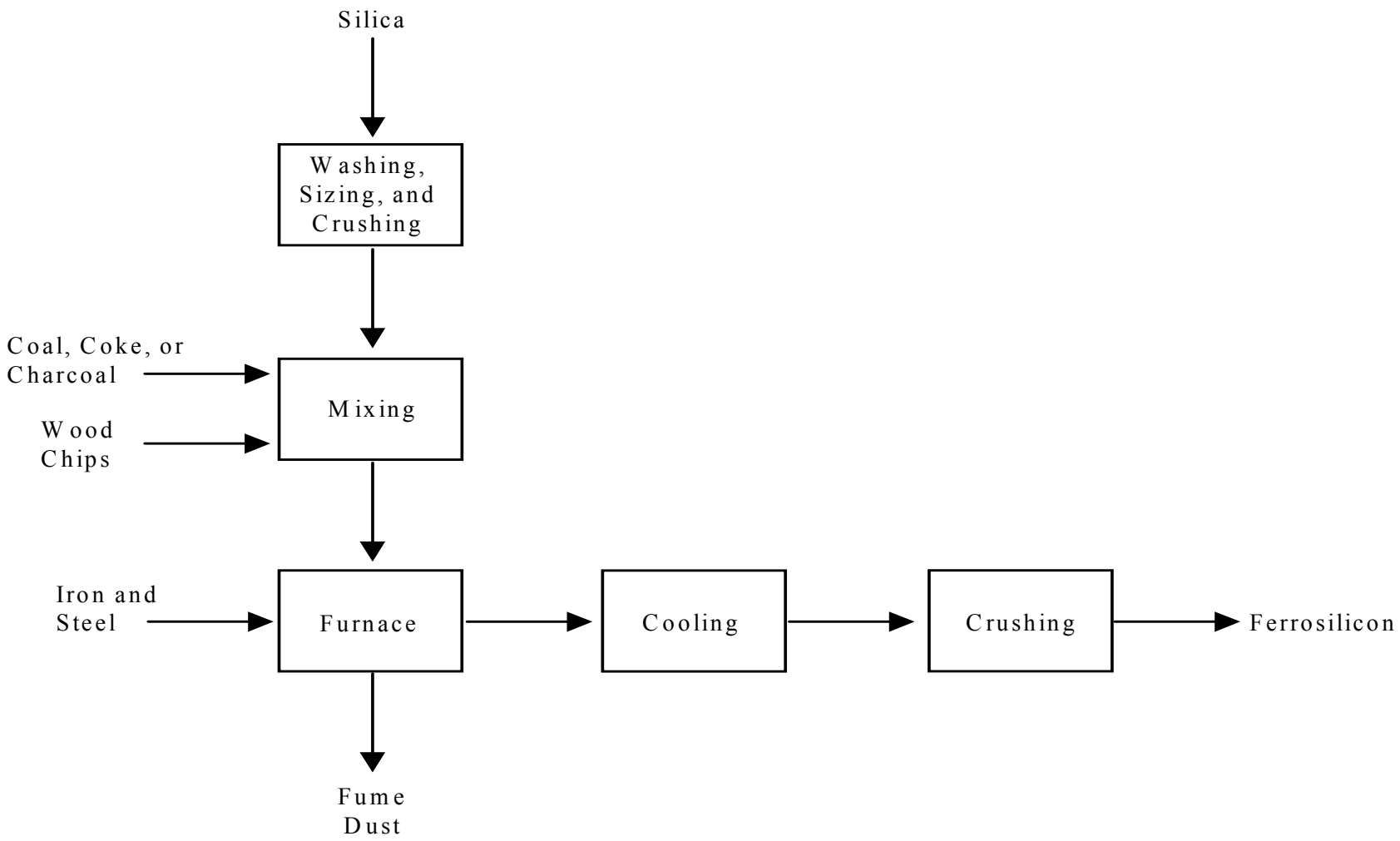


EXHIBIT 3

FERROSILICON PRODUCTION



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

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between ore crushing and charging to the furnace because silica is thermally reduced to silicon or ferrosilicon in the furnace. 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

The following wastes may result from beneficiation activities: gangue, spent wash water, and tailings. No information on waste characteristics, waste generation, or waste management for these waste streams was available in the sources listed in the bibliography.

2. Mineral Processing Wastes

Dross. The waste to product ratio for dross is approximately 1:99. Dross from the production of silicon metal can be used to produce ferrosilicon. Ferrosilicon dross can be used to produce silicomanganese. Dross can also be sold as an aggregate.[8] Dross is recycled and is not believed to be a solid waste.[9] 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.

Slag. 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.

APC Dust/Sludge. The furnaces are generally equipped with fume collection systems and baghouses to reduce air pollution by capturing emissions from the furnace.[10] Originally, the baghouse dust (microsilica) was considered of little or no value. However, microsilica is now used as an additive in a number of different products,

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[8] Personal communication between ICF Incorporated and Joseph Gamboji, U.S. Bureau of Mines, June 28, 1989.

[9] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Volume I, Office of Solid Waste, August 1992, pp. I-4 and I-6.

[10] "Silicon and Ferrosilicon," Op. Cit., p. 3-195.

including high-strength concrete.[11] 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 at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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[11] L.D. Cunningham, 1992, Op. Cit., p. 1184.

BIBLIOGRAPHY

Alsobrook, A.F. "Silica: Specialty Minerals." From Industrial Minerals and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 893-911.

Cunningham, L. D. "Silicon." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 152-153.

Cunningham, L. D. "Silicon." From Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 1183-1198.

Goodwill, J.E. "Developing Plasma Applications for Metal Production in the USA." Ironmaking and Steelmaking. Vol. XVII. No. 5. 1990. pp. 350-354.

Goodwill, J. E. "Plasma Melting and Processing - World Developments." 48th Electric Furnace Conference Proceedings. New Orleans, LA. December 11-14th 1990. pp. 279-281.

Neuharth, C.R. "Ultra-High-Purity Silicon for Infrared Detectors: A Materials Perspective." U.S. Bureau of Mines Information Circular 9237. 1989. pp. 1-13.

Personal communication between ICF Incorporated and Joseph Gamboji, U.S. Bureau of Mines, June 28, 1989.

"Silicon and Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed. Vol. XX. 1982. pp. 826-848.

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

U.S. Environmental Protection Agency. "Silicon and Ferrosilicon." From 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes. 1988. pp. 3-194 - 3-198.

SODA ASH

A. Commodity Summary

Six companies in Wyoming and California comprise the United States soda ash industry, which is the largest in the world. The total estimated value of domestic soda ash produced in 1994 was $650 million. According the U.S. Bureau of Mines, the six producers had a combined nameplate capacity of 11 million tons per year and operated at 83% of that capacity in 1994. Soda ash is used in many products:

- glass, 49%
- soap and detergents, 13%
- flue gas desulfurization, 3%
- chemicals, 23%
- distributors, 5%
- pulp and paper, 2%[1]

Soda ash is the common name for sodium carbonate. This alkali compound is the eleventh largest inorganic chemical, in terms of production, of all domestic inorganic and organic chemicals, excluding petrochemical feedstocks. Natural soda ash is produced from trona ore, sodium carbonate-bearing brines, or surface mineralization. All of the active facilities produce natural soda ash from sodium carbonate-rich brines or from underground mining of trona ore.[2] Synthetic soda ash can be made by one of several chemical reactions that use common raw materials for feedstocks, such as limestone, salt, and coal. Other technologies produce soda ash as a byproduct.[3] Exhibit 1 presents the names and locations of the facilities involved in the production of soda ash.

EXHIBIT 1

SUMMARY OF SODA ASH PROCESSING FACILITIES

Facility Name	Location
FMC Corporation	Green River, WY
General Chemical Partners	Green River, WY
North American Chemical Company	Argus,CA Westend, CA
Rhone-Poulenc Mine	Green River, WY
Tenneco	Green River, WY
TG Soda Ash Mine	Green River, WY

[1] Dennis Kostick, "Soda Ash," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 156-157.

[2] Dennis S. Kostick, "Soda Ash and Sodium Sulfate," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 1237-1250.

[3] Dennis Kostick, "Soda Ash," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 929-955.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Soda ash from Wyoming trona is mined, crushed, dried, dissolved, filtered, recrystallized, and redried. In California, soda ash from sodium carbonate-bearing brines in solution is mined, carbonated, filtered, dried, decomposed, bleached, and recrystallized to dense soda ash. These processes are described in more detail below.

2. Generalized Process Flow Diagram

All the Wyoming trona mines use room and pillar mining with multiple entry systems. Most use a combination of one or more types of mining: conventional, continuous, longwall, shortwall, or solution.[4] The FMC Corporation is the only natural soda ash producer that uses longwall mining to augment its mining technology. Shortwall mining is used exclusively by TG Soda Ash, Inc. Since the late 1980's, most Wyoming soda ash companies have installed continuous hauling systems to replace shuttle cars. FMC Corporation has been discharging tailings and spent solutions from solution mining to its tailing ponds since about 1953. Since then, sodium carbonate decahydrate crystals have been collecting on the bottom of these ponds at a rate of 20 to 30 cm per year. In 1985, FMC began using a bucket wheel dredge to extract almost 160 kt of crystals annually from the 485 hectare pond. The crystals are slurried, dewatered, melted, and processed into soda ash in the refinery. Other producers have similar ponds where sodium carbonate decahydrate has collected since the plants were built. Because of environmental considerations and the cost of constructing and maintaining tailing ponds, all the producers now inject waste tailings underground. This will reduce the future buildup of sodium decahydrate in the tailing ponds. In addition, several of the Wyoming soda ash producers are selling their spent purge liquors that contain dissolved sodium carbonate in solution to local power utility companies for pH control of process water.[5] Trona ore must be further refined to yield a 99% pure soda ash product.

Sodium sulfate, sodium chloride, potassium chloride, and borax must be physically and chemically removed from sodium carbonate bearing brines in order to process the sodium carbonate content into refined soda ash. The Wyoming facilities use one of two processes to refine soda ash from trona ore: (1) the monohydrate process or (2) the sesquicarbonate process. The two processes are essentially the same, differing only in the sequencing of procedures. The monohydrate method is the primary process used today to make soda ash. In addition to these two processes, the North American facilities at Searles Lake produce soda ash via another operation.[6]

Monohydrate Process

In the monohydrate process, trona is crushed and calcined in rotary gas-fired calciners operating at 150-300°C. Calcining removes water and carbon dioxide from the ore, and leaves an impure product containing 85% soda ash and 15% insolubles. The thermal decomposition of trona involves the following reaction:

$$2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O \text{ (trona)} + \text{heat} \rightarrow 3Na_2CO_3 + CO_2 + 5H_2O$$

The calcinate is dissolved with hot water and sent to evaporative, multiple-effect crystallizers or mechanical vapor recompression crystallizers where sodium carbonate monohydrate crystals precipitate at 40-100°C. This is below the transition temperature of monohydrate to anhydrous soda ash. The insoluble portion of the ore containing shale and shortite are collected by clarifiers, filtered, and washed to recover any additional alkali before they are piped as a slurry to tailing ponds or injected underground. Some companies pass the liquor through activated carbon beds prior to crystallization to remove trace organics solubilized from the oil shale so that the organics do no interfere with

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[4] Ibid.

[5] Ibid.

[6] Ibid.

crystal growth rate. The crystals are sent from the crystallizers to hydroclones and dewatered in centrifuges. The centrifuge cake is conveyed to steam tube dryers where the crystals are dehydrated into anhydrous soda ash at 150°C, screened, and sent to storage or shipment. The final product made by the monohydrate process is dense soda ash.[7] Exhibit 2 presents a process flow diagram for the monohydrate process.

Sesquicarbonate Process

The sesquicarbonate process, the second process used to process Wyoming trona, produces light to intermediate grades of soda ash crystals. The trona is crushed, dissolved in hot mother liquor, clarified, filtered, and passed to cooling crystallizers where crystals of sodium sesquicarbonate precipitate. Activated carbon is added to filters to control the organics that interfere with crystal growth. The sodium sesquicarbonate is hydrocloned, centrifuged, and calcined using gas or indirect steam heat. Dense soda ash can be made by calcining the sodium sesquicarbonate at 350°C.[8] Exhibit 3 presents a process flow diagram of the sesquicarbonate process.

Searles Lake Process

At the North American Chemical Company facility at Searles Lake, complex brines are first treated with carbon dioxide gas in carbonation towers to convert the sodium carbonate in solution to sodium bicarbonate, which will precipitate under these conditions. The sodium bicarbonate is separated from the remainder of the brine by settling and filtration and is then calcined to convert the product back to soda ash. The decarbonated brine is cooled to recover borax and Glauber's salt. A second dissolving, precipitating with carbon dioxide, filtering, and calcining the light soda ash to dense soda ash, results in a refined product of better than 99% sodium carbonate.[9] Exhibit 4 presents the Searles Lake process.

Sodium Bicarbonate

Sodium bicarbonate, baking soda, is manufactured by percolating carbon dioxide gas through a carbonation tower containing a saturated soda ash solution. The sodium bicarbonate precipitate is collected, filtered, centrifuged, dried, screened, and packaged. Three of the five sodium bicarbonate producers are also soda ash producers.[10]

Sodium Hydroxide

Sodium hydroxide, or chemical caustic soda, is made from lime and soda ash by the following reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCo_3 + 2NaOH$$

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[7] Ibid.

[8] Ibid.

[9] U.S. Bureau of Mines, 1992, Op. Cit., pp. 1237-1250.

[10] Dennis Kostick, 1994, Op. Cit., pp. 929-955.

EXHIBIT 2

THE MONOHYDRATE PROCESS

(Adapted from: Soda Ash: Mineral Processing Waste Generation Profile.)

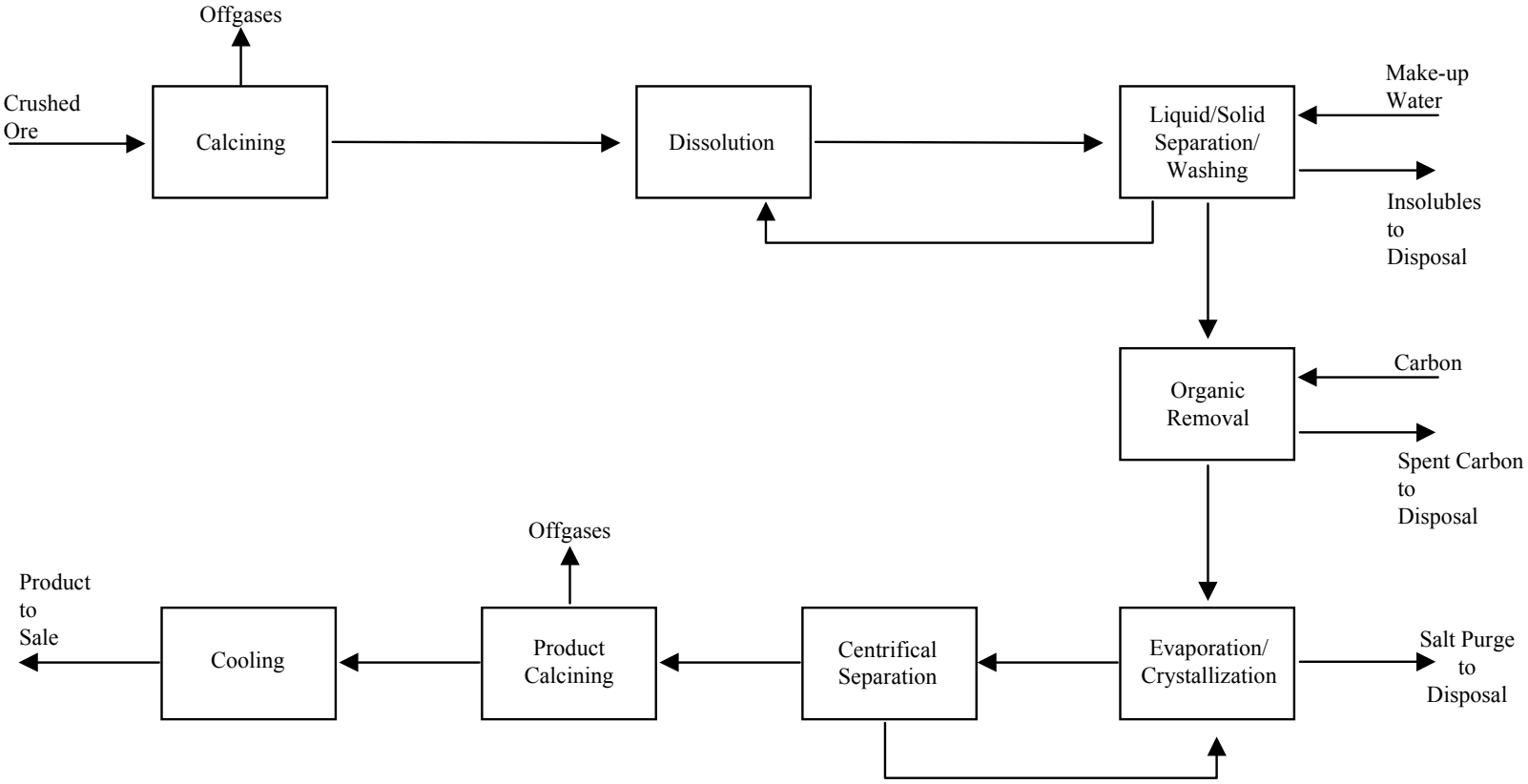


EXHIBIT 3

THE SESQUICARBONATE PROCESS

(Adapted from: Soda Ash: Mineral Processing Waste Generation Profile.)

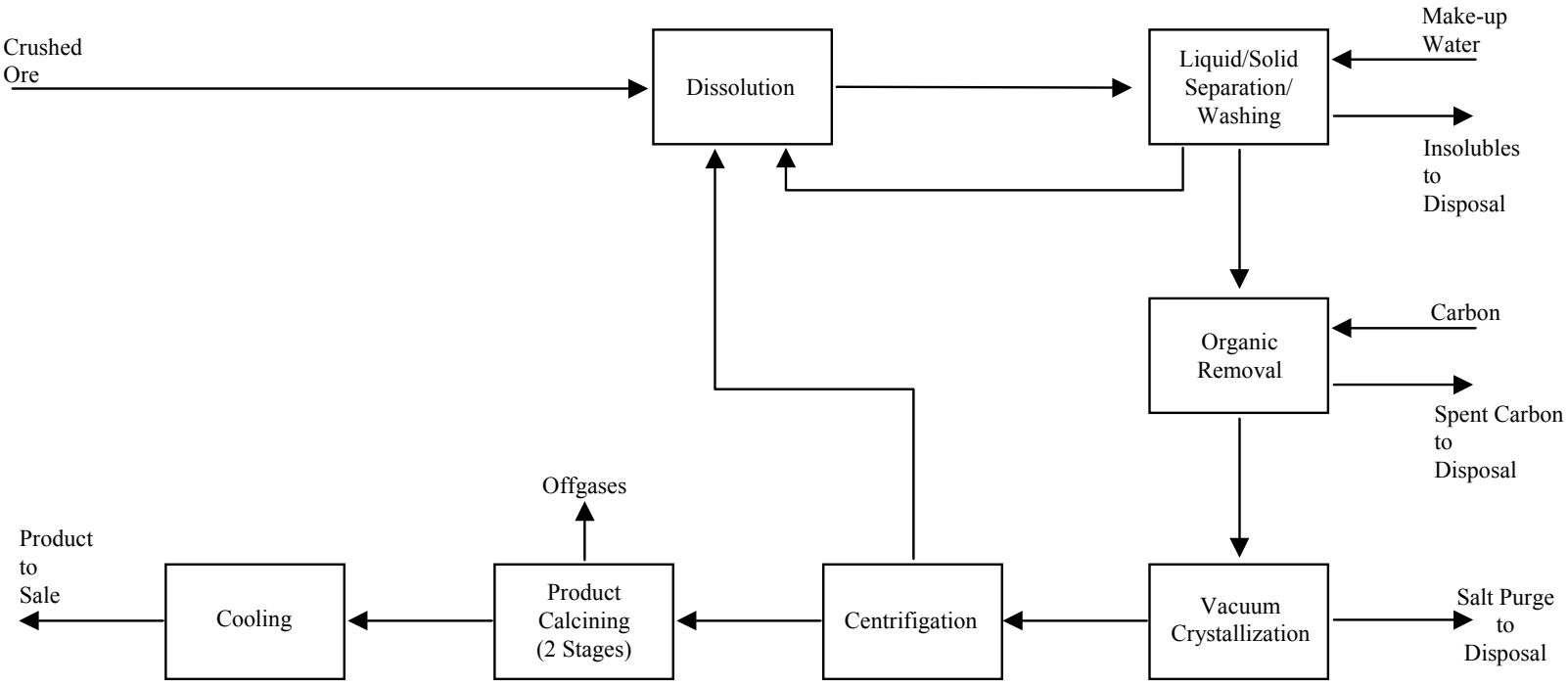
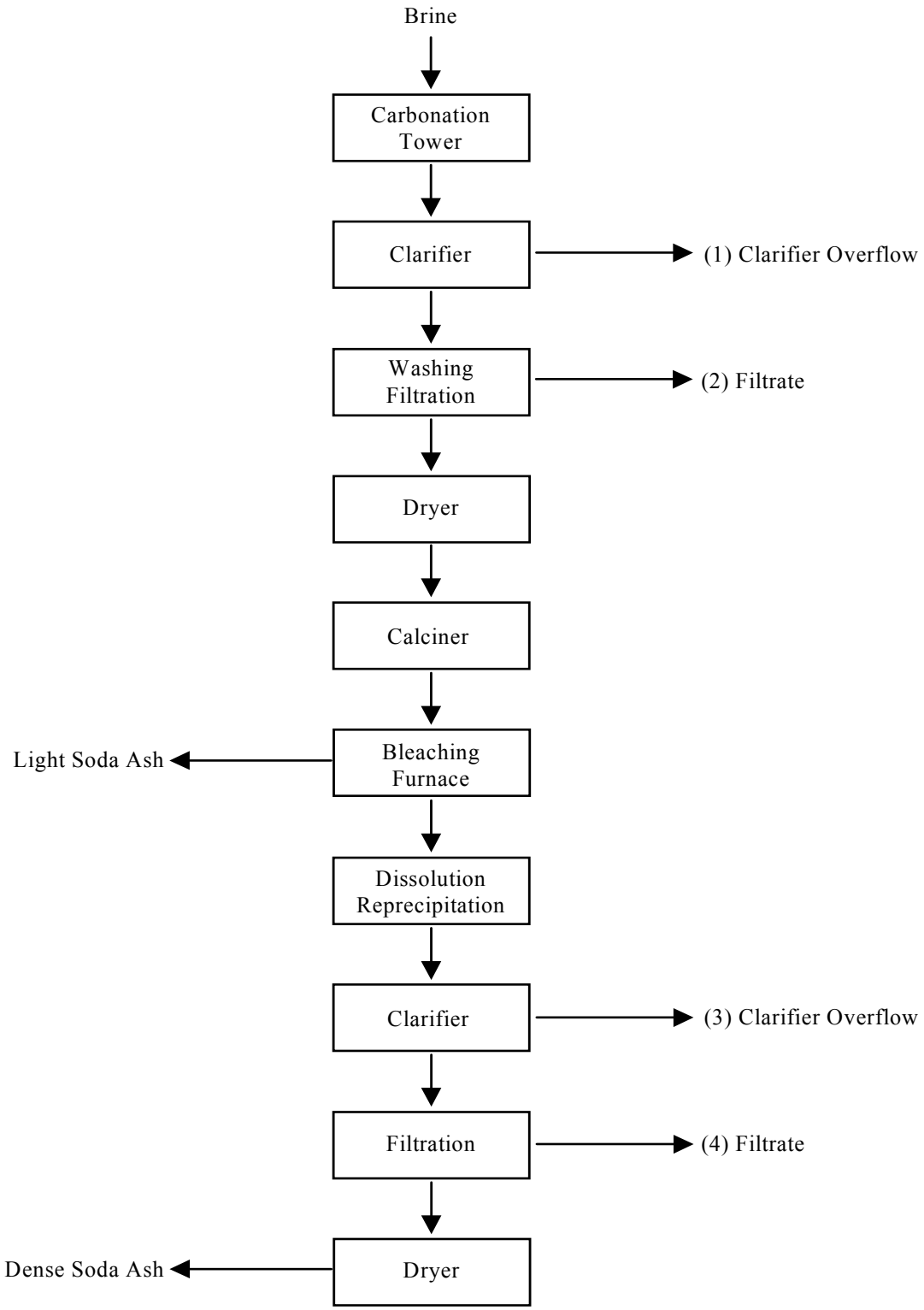


EXHIBIT 4

THE SEARLES LAKE PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-43 - 2-46.)



The lime is slaked and added to dissolved soda ash to produce chemical caustic soda. Calcium carbonate is precipitated from the reaction, calcined back to lime, and recycled. FMC uses about half of its caustic soda to produce captive sodium cyanide for precious metal recovery at its gold operation. [11]

Sodium Sesquicarbonate

Sodium sesquicarbonate is a hydrated compound containing soda ash and sodium bicarbonate. Trona ore is first crushed and dissolved to separate the insoluble impurities. The sodium compounds in solution are then clarified, filtered, crystallized, centrifuged, calcined, and recovered as long needle-shaped monoclinic crystals of sodium sesquicarbonate. FMC has a 50 ktpy sodium sesquicarbonate facility that sells mainly to the detergent industry. [12]

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

None identified.

4. Beneficiation/Processing Boundaries

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

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Extraction and beneficiation wastes include **overburden**, **tailings**, and **spent dissolution wastes**. The trona ore dissolution wastes are sent to tailings ponds. Waste tailings are injected underground.

Monohydrate Process Waste Streams

Ore insolubles. About 110 to 150 kg per kkg of ore insolubles are generated. These insolubles are transported to evaporation ponds for disposal.[13]

Filter aid and **carbon absorbent.** The waste generation for these wastes ranges from about 0.5 to 2 kg per kkg of product. Spent carbon absorbent and spent filter aids are sent to on-site evaporation ponds for disposal.[14]

Scrubber water. Scrubber liquor is recycled to the process for recovery of additional product.[15]

Particulates from crushing and calcination are generated. The calciner offgases contain carbon dioxide. Airborne particulate emissions from crushing are about 1.5 kg per kkg of product. From calcination, emissions are about 95 kg per kkg or product. The particulates from crushing and conveying are collected in bags and recycled to the ore bin which feeds the calciners. Residual emissions from the bag collectors are 0.015 kg per kkg of product. Particulates from the calciner consist of raw sodium carbonate dust. These particulates are passed through dry

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[11] Ibid.

[12] Ibid.

[13] Ibid.

[14] Ibid.

[15] Ibid.

cyclones and electrostatic precipitators in series. The overall removal efficiency is 99.5%, resulting in residual particulates of 0.28 kg per kkg of product. Collected particulate is periodically recycled to the calciner.[16]

At the Tenneco Corporation facility in Green River, WY, tailings generated from the calcining process are discharged to the tailings tank. The tailings tank also receives fly ash and bottom ash generated from using coal to fire the calcining kiln and the steam boiler. This waste is treated in a thickening tank by adding anionic and cationic flocculants to the tailings to increase the solids content from approximately 10 to 50% solids. The waste is then disposed of in one of two waste management units, (1) the tailings pond, or (2) the mine void. The mine void is located in an old mine shaft approximately 800 feet below ground. Tailings which will be disposed of in the mine void are first accumulated in a holding tank adjacent to the mine shaft. The tailings are gravity fed into the mine when the holding tank fills. Tailing supernatant that accumulates in the mine is collected in a sump and periodically pumped and disposed of in the tailings pond. Eighty percent of the time thickened tailings are disposed of in the mine void and the remainder of the time thickened tailings are disposed of directly in the tailings pond.[17]

Airborne emissions from product drying, cooling, and packaging are generated from the monohydrate process. These wastes are controlled by the use of baghouses and wet scrubbers, with the recovered materials being recycled to the process. Emissions from the sodium carbonate drier are generated at about 2 kg per kkg of product. After wet scrubbing, residual emission is 0.02 kg per kkg of product. Product cooling generates about 0.7 kg of emissions per kkg of product. After bag dust collection, the residual emission is 0.005 kg per kkg of product. Product screening, storing, and packaging generates 1.4 kg of emissions per kkg of product. After bag dust collection, residual emission is 0.005 kg per kkg of product.[18]

Purge liquor. Purge liquor from calcining is often sold as a sulfur neutralizer or dust suppressant. At the California facility, purge liquor is produced in the brine operation and is sent back into the lake.

Mother liquor is a possible waste stream from centrifugation. This waste stream is recycled.

Trona ore processing waste is generated from the purification of calcined material.

At the Stauffer Chemical Company facility in Green River, WY, trona ore processing waste is generated at each of five calcining rakes after dissolution and purification. Waste from trona ore processing is pumped to a tank and combined with sluice water from a tailings pond so the waste can be pumped to one of the three on-site surface impoundments designated to receive the waste. The waste sent to the three impoundments contains approximately 10% sodium carbonate. As water evaporates the sodium carbonate dries forming sodium decahydrate.[19]

At General Chemical in Green River, WY, 1,451,488 metric tons of this waste was generated in 1988. This waste was characterized by a pH of 11.5. The waste is either sold or sent to an unlined surface impoundment.[20]

At the Tg Soda Ash facility in Green River, WY, 580 million gallons of this waste were reported in 1988. This waste reportedly had a pH of 11.5. The waste was sent to a surface impoundment lined with in-situ clay for solids precipitation and dewatering.[21]

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[16] Ibid.

[17] U.S. Environmental Protection Agency, Mineral Processing Waste Sampling Survey Trip Reports, Tenneco Corporation, Green River, WY, August 1989.

[18] Ibid.

[19] Ibid.

[20] RTI survey for General Chemical Partners, Green River, WY, 1988, ID# 100388.

[21] RTI Survey for Tg Soda Ash, Green River, WY, 1988, ID# 100206.

Sesquicarbonate Process Waste Streams

Trona ore particulates are generated from crushing, drying, and calcination. About 1.5 kg per kkg of trona ore particulates are generated from crushing. About 2 kg per kkg of particulates are generated by drying operations. Approximately 95 kg per kkg of particulates are produced by calcination. Particulate emissions from drying and packaging are controlled by wet scrubbers and dry bag collectors, respectively. Emissions after control average 0.02 kg per kkg from the driers and 0.02 kg per kkg from the product packaging operations. Solids recovered from the dry bag collectors are recycled to product storage. Emissions from ore calcination are also collected and recycled.[22]

Scrubber water is generated from air pollution control devices. This is recycled to recover additional product.[23]

Ore residues. About 110 to 150 kg per kkg or ore residues, chiefly shale, are generated in the initial steps.[24]

Spent carbon and filter wastes from carbon absorption and filtration range from 0.5 to 2.0 kg per kkg per product. Waste filter aids and carbon absorbents are washed to the evaporation ponds for final disposal. Solid wastes from initial ore leaching are slurried to tailings ponds to settle out suspended materials and then to the final disposal ponds which serve as evaporation ponds from which there is no discharge.[25]

Suspended particulate matter is generated by the use of wet scrubbers for air pollution control, resulting in wastewater containing 2 kg per kkg of suspended particulates.[26]

Purge liquor from calcining. This waste is often sold as a sulfur neutralizer or dust suppressant.

Mother liquor from centrifugation. This waste stream is often recycled.

Searles Lake Process Waste Streams

Calciner offgases. About 170 kg of water vapor and 415 kg of carbon dioxide per kkg of soda ash are generated by calcination of the sodium bicarbonate intermediate. These offgases are cooled to recover water for other on-site uses and for use in product purification. After water removal, the carbon dioxide in recycled to the initial process calcination step.[27]

Particulate emissions from driers. These emissions are controlled by dry collectors, and the recovered solids are recycled to the process. Residual airborne particulate emissions are less than 1 kg per kkg of product.[28]

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[22] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Volume III, August 1980, Chapter 13.

[23] Ibid.

[24] Ibid.

[25] Ibid.

[26] Ibid.

[27] Ibid.

[28] Ibid.

Spent brine. Spent brine from the initial carbonation and filtration steps contains about 16,000 kg per kkg of product of unrecovered sodium carbonate and other raw brine constituents. The spent brine contains about 65% water, 16% sodium chloride, and 19% of other constituents including sodium sulfate, borax, and potassium chloride. This waste stream is combined with other waterborne waste streams and returned to the brine source.[29]

Waste mother liquor. This waste stream is generated from product recrystallization and contains principally unrecovered sodium carbonates, along with smaller amounts of other raw brine constituents such as sodium sulfate, borax, and potassium chloride. This waste stream is combined with other waterborne waste streams and returned to the brine source.[30]

2. Mineral Processing Wastes

None identified.

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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[29] Ibid.

[30] Ibid.

BIBLIOGRAPHY

"Alkali and Chlorine Products." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. 1992. Vol. I. pp. 876.

Kostick, Dennis S. "Soda Ash." From Industrial Minerals and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 929-955.

Kostick, Dennis. "Soda Ash." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 156-157.

Kostick, Dennis. "Soda Ash and Sodium Sulfate." From Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 1237-1250.

Kostick, Dennis. "Soda Ash." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 741-755.

RTI survey for General Chemical Partners, Green River WY. 1988. ID# 100388.

RTI Survey for Tg Soda Ash, Green River, WY. 1988. ID# 100206.

U.S. Environmental Protection Agency. Mineral Processing Waste Sampling Survey Trip Reports. Tenneco Corporation, Green River, WY. August 1989.

U.S Environmental Protection Agency. "Soda Ash." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp. 2-43--46.

U.S. Environmental Protection Agency. Multi-Media Assessment of the Inorganic Chemicals Industry. Vol. III. August 1980. Chapter 13.

SODIUM SULFATE

A. Commodity Summary

The domestic natural sodium sulfate industry consists of three producers in California, Texas, and Utah. In addition, the recovery of sodium sulfate as a byproduct from facilities that manufacture rayon and various chemicals accounts for nearly 50% of total domestic production. The total value of sodium sulfate sold was estimated at $50 million in 1994. End uses of sodium sulfate are soap and detergents (40%), pulp and paper (25%), textiles (19%), glass (5%), and other uses (11%).[1]

In its natural form, sodium sulfate is found in two minerals, mirabilite (Glauber's salt) and thenardite. Its occurrence is widespread and it is commonly found in mineral waters such as sea water, atmospheric precipitation, and saline lakes. Essentially all commercial deposits of sodium sulfate resulted from the accumulation and evaporation of surface and ground water in basins with interior drainage. These basins, or playas, are found in arid to semiarid regions.[2]

At the present time, sodium sulfate production is chiefly from brine deposits in Searles Lake, California; Great Salt Lake, Utah; and in Western Texas. North American Chemical Company processes sodium sulfate from Searles Lake at Trona, California. Great Salt Lake Minerals and Chemicals Corp., an affiliate of North America Chemical Co., operates a plant at the north end of the Great Salt Lake, which produces sodium sulfate as a byproduct. This facility has a sodium sulfate capacity of 22.7 to 32.9 kilotons per year. Ozark-Mahoning Company operates one plant in Western Texas near Seagraves. Exhibit 1 presents the names and locations of the facilities involved in the production of sodium sulfate.[3]

EXHIBIT 1

SUMMARY OF SODIUM SULFATE PROCESSING FACILITIES

Facility Name	Location
Great Salt Lake Minerals and Chemicals Corp.	Great Salt Lake, UT
North American Chemical, Inc.	Searles Lake, CA
Ozark-Mahoning Co.	Western Texas

B. Generalized Process Description

1. Discussion of Typical Production Processes

There are three principle methods used to produce sodium sulfate from brines: (1) the Ozark-Mahoning process used in Western Texas, (2) the North American Chemical Company process at Searles Lake, and (3) the process used by the Great Salt Lake Minerals and Chemical Corp. in Utah. Because these three processes are all slightly different, each is described in more detail below. Exhibits 2 and 3 present process flow diagrams for sodium sulfate production.

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[1] Dennis Kostick, "Sodium Sulfate," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 158-159.

[2] Sid McIlveen and Robert L. Cheek, Jr., "Sodium Sulfate Resources," from Industrial Minerals and Rocks, 6th edition, Society for Mining, Metallurgy, and Exploration, 1994, pp. 959-970.

[3] Ibid.

2. Generalized Process Flow Diagram

Ozark-Mahoning Co. Process

The Ozark-Mahoning Company, the nation's second largest natural producer, operates a facility in Western Texas. As shown in Exhibit 2, brines are refrigerated to selectively precipitate Glauber's salt which is subsequently filtered and washed. Washing produces a saturated solution of Glauber's salt which is converted to the anhydrous form in mechanical vapor recompression crystallizers. Hydroclones and centrifuges separate the anhydrous crystals from the saturated solution, which is returned to evaporators. Anhydrous sodium sulfate is then dried in a rotary kiln and the resultant material is a product of 99.7% purity.[4]

North American Chemicals, Inc. Process (Searles Lake)

North American Chemicals, Inc. operates two facilities near Searles Lake, CA--the West End plant and the Argus plant. The West End plant is North America's only source of sodium sulfate. Here, sodium sulfate is recovered along with soda ash and borax. As shown in Exhibit 3, mixed brines are carbonated with carbon dioxide to precipitate sodium bicarbonate, which is removed by filtration. The decarbonated brine is cooled three times to produce two successive batches of borax and one of Glauber's salt. By heating, the sodium bicarbonate is converted to soda ash and the borax is either crystallized as a hydrate or dehydrated to anhydrous form. The Glauber's salt is washed, melted, and recrystallized as anhydrous sodium sulfate; 99.3% purity can be obtained.[5]

Great Salt Lake Minerals and Chemical Corp. Process

Great Salt Lake Minerals and Chemicals Corp. operates a facility on the Great Salt Lake for the production of potassium sulfate and magnesium chloride, of which sodium sulfate is a byproduct. Brine is pumped from the Great Salt Lake into solar evaporation ponds where sodium chloride precipitates. Sodium sulfate crystals precipitate in a fairly pure state when winter weather cools the brine to -1 to 4ºC. The crystals are picked up by large earthmoving machinery and stored outdoors until further processing can take place. The harvested Glauber's salt is melted and anhydrous sodium sulfate precipitated by the addition of sodium chloride to reduce its solubility through the common ion effect. The final product is 99.5% pure.[6]

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

None identified.

4. Beneficiation/Processing Boundaries

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

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[4] Sid McIlveen and Robert L. Cheek, Jr., 1994, Op. Cit., pp. 959-970.

[5] Ibid.

[6] Ibid.

EXHIBIT 2

OZARK-MAHONING PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-47 - 2-51.)

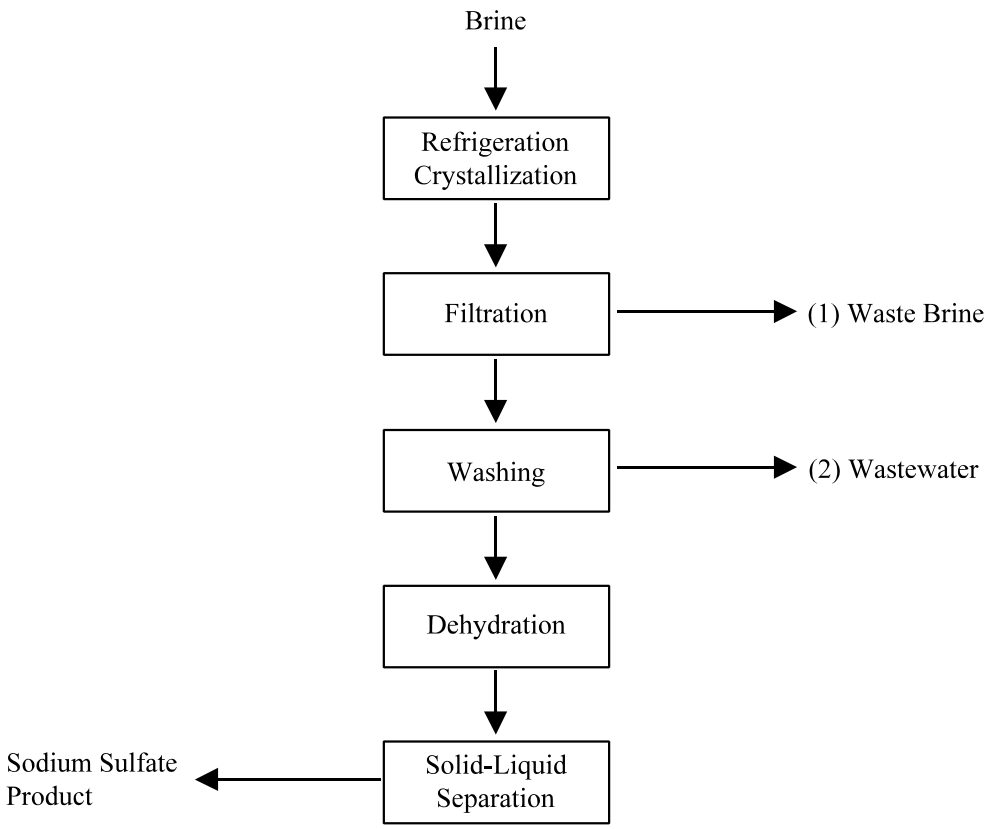
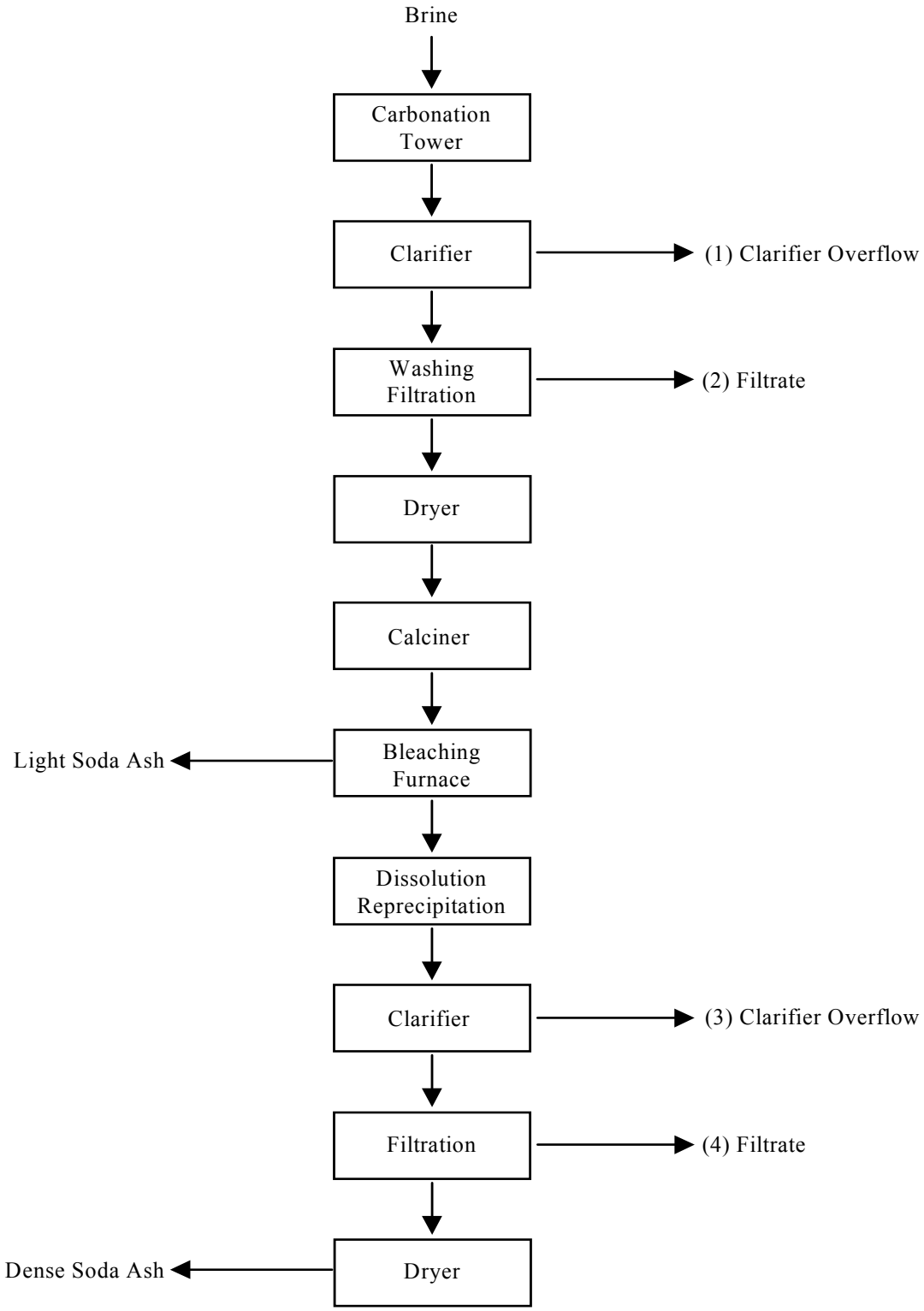


EXHIBIT 3

THE SEARLES LAKE PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-47 - 2-51.)



C. Process Waste Streams

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

1. Extraction/Beneficiation Wastes

Ozark-Mahoning Process

Waste brine and **wastewater** are wastes from filtrating and washing Glauber's salt. Literature reports that these wastes are reinjected into the salt formation.

Searles Lake Process

Clarifier overflow.

Filtrate.

2. Mineral Processing Wastes

None identified.

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

BIBLIOGRAPHY

Kostick, Dennis. "Sodium Sulfate." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 158-159.

Kostick, Dennis. "Sodium Sulfate." From Minerals Yearbook Volume 1. Metals and Minerals. 1992. pp. 1261-1268.

Kostick, Dennis. "Soda Ash and Sodium Sulfate." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 741-755.

McIlveen, Sid and Robert L. Cheek, Jr. "Sodium Sulfate Resources." From Industrial Minerals and Rocks. 6th ed. Society of Mining, Metallurgy, and Exploration. 1994. pp. 959-970.

"Sodium Compounds, Sodium Sulfates." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XXI. 1983. pp. 251.

U.S. Environmental Protection Agency. "Sodium Sulfate." From 1988 Final Draft Summary Report of Mineral Industry Processing Waste. 1988. pp. 2-47 - 2-51.

STRONTIUM

A. Commodity Summary

According to the U.S. Bureau of Mines, no strontium minerals have been produced in the United States since 1959. The United States is however, a major producer of strontium compounds. In 1994, primary strontium compounds were used in color television picture tube glass (66%), pyrotechnic materials (11%), ferrite ceramic magnets (13%), and other miscellaneous uses (10%)[1]. Although consumption demands fluctuate from year to year, the overall consumption of strontium compounds and metals appears to be increasing.[2]

In early 1984, Chemical Products Corporation (CPC) in Cartersville, Georgia expanded its capacity by 30% to meet shortfalls in supply that resulted from the 1984 closure of the FMC Corporation plant in Modesto, California. CPC is now the sole domestic producer of strontium carbonate and strontium nitrate; CPC sells these products as raw materials to other industries.[3] Strontium metal is produced by CALSTRON near Memphis, Tennessee using an aluminothermic reaction.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Celestite, the most common strontium mineral, consists primarily of strontium sulfate. The second most common strontium mineral, strontianite, consists primarily of strontium carbonate.

Reportedly, it is very difficult to concentrate strontium minerals to grades acceptable for producing chemical compounds. The two most common celestite-to-strontium carbonate conversion processes are the soda ash process and the calcining process. Strontium metal is produced by (1) the thermal reduction of strontium oxide with metallic aluminum and (2) the electrolysis of fused strontium chloride and ammonium or potassium chloride.

Of the two strontium production processes, the soda ash method is a simpler process; however, the resulting product is of a lower grade. The calcining method or black ash method, produces chemical-grade strontium carbonate ($SrCO_3$) which is at least 98% strontium carbonate; whereas, the soda ash method only produces technical-grade strontium carbonate $\geq$95% pure. Although the soda ash method is a simpler process, the lower grade product causes it to be the less preferred method of recovery. The black ash method is used by CPC.

2. Generalized Process Flow Diagram

<u>Strontium Carbonate Process</u>

Soda Ash Process

Finely powdered celestite is mixed with soda ash and treated with steam for one to three hours. The celestite and soda ash react to produce less soluble strontium carbonate and soluble sodium sulfate. The two are separated by centrifuging. Exhibit 1 presents a process flow diagram for the soda ash process.

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[1] Joyce Ober, "Strontium," from <u>Mineral Commodity Summaries</u>, U.S. Bureau of Mines, January 1995, pp. 164-165.

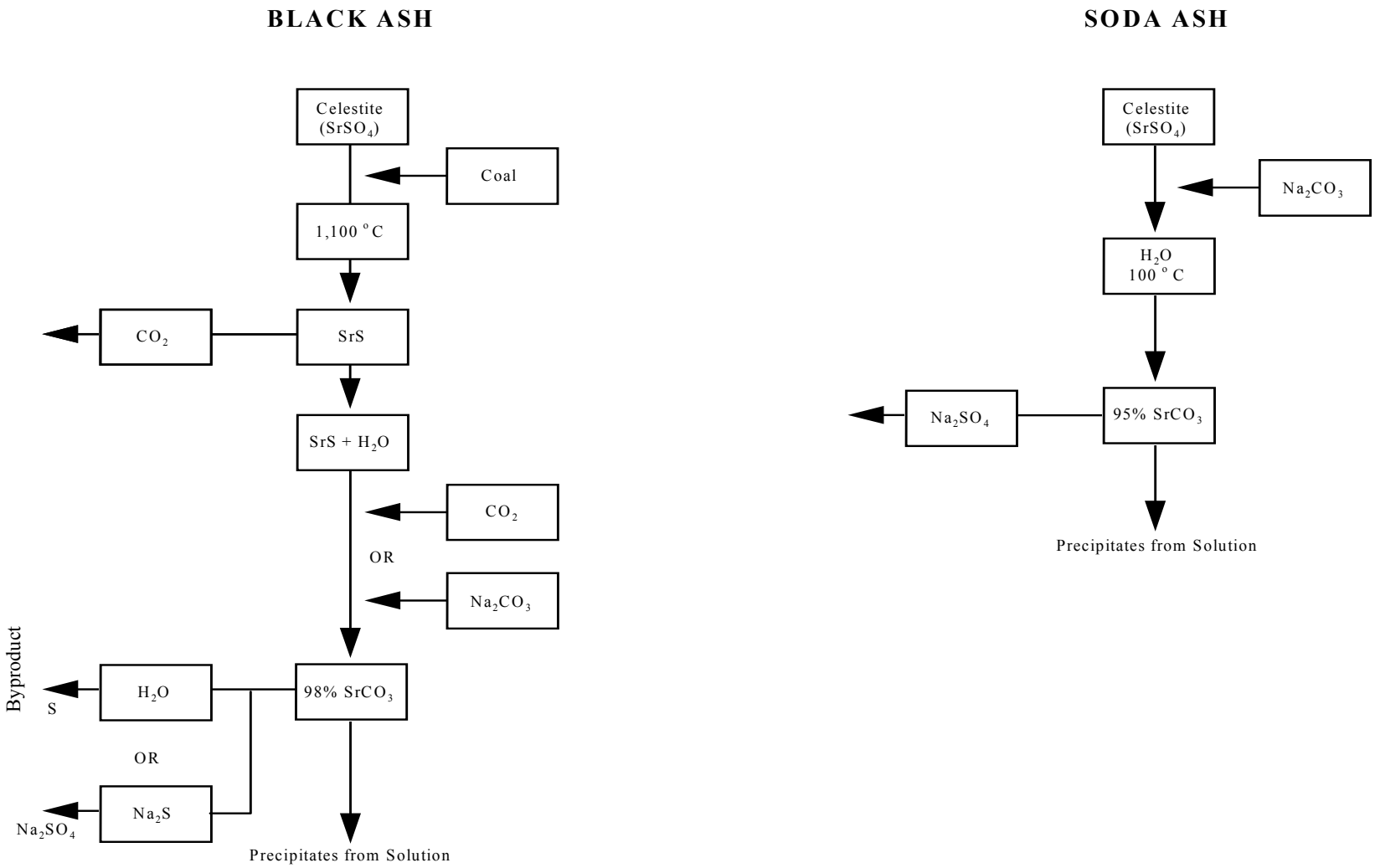
[2] Joyce A. Ober, "Strontium," <u>Minerals Yearbook Volume 1. Metals and Minerals</u>, U.S. Bureau of Mines, 1992, pp. 1323-1332.

[3] Personal communication between ICF Incorporated and Joyce Ober, Bureau of Mines, July 21, 1994.

EXHIBIT 1

SIMPLIFIED FLOWCHART OF TWO METHODS FOR STRONTIUM CARBONATE PRODUCTION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-198 - 3-199.)



Calcining Process (Black Ash Process)

Finely powdered coal is mixed with celestite which produces a "black ash." The mixture is heated to 1,100ºC in a rotary kiln, expelling oxygen in the form of carbon dioxide from the insoluble strontium sulfate to form water-soluble strontium sulfide. The strontium sulfide is dissolved in water and the solution is filtered, and then either treated with carbon dioxide or soda ash in an agitation tank. Strontium carbonate may then form and precipitate from the solution. The strontium carbonate precipitate is removed from solution by filtering in vacuum drum filters, dried, ground, and packaged. The sulfur released in the process is either recovered as elemental sulfur or as other by-product sulfur compounds. This process is used by the CPC plant in Georgia but is called the "white ash method" because the sodium sulfide is white in color.[4] A process flow diagram is shown in Exhibit 1.

Production of Strontium Chemicals

Strontium nitrate is produced by reacting strontium carbonate with nitric acid. Other strontium chemicals are produced similarly by reacting strontium carbonate with the acid appropriate for the desired result.

Production of Other Strontium Compounds

Chemical-grade strontium carbonate can be used without further purification to produce most other strontium compounds. Either chemical-grade or technical-grade (greater than 95% pure) can be used for transformation to other strontium compounds, and in the conversion processes further purification occurs. For some processes, higher grades of strontium carbonate are necessary and elimination of contamination by particular elements is emphasized.

Strontium Metal Production

Strontium metal can be produced in two ways. The more common method is through the thermal reduction of strontium oxide and aluminum metal, subsequent distillation and condensation of metallic strontium on a cooled plate. The other method is electrolysis of a fused bath of strontium chloride and ammonium chloride or potassium chloride.[5]

Other Processes

Strontium ferrite magnets are usually prepared by mixing strontium carbonate, iron oxide, and crystal growth inhibitors and presintering at 1,000ºC to 1,300ºC. Strontium titanate is formed by reacting a mixture of high purity strontium carbonate and titanium dioxide at 2,000º to 2,200ºC for several hours.[6]

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

Technologically, there is very little known about strontium. As technology becomes more sophisticated and the search for alternate materials is intensified, specific properties of strontium will become better known. Strontium appears to have applications in the metallurgy of aluminum, silicon, and other light metals, as well as potential use as a solid electrolyte in fuel cells.[7]

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[4] "Strontium--Uses, Supply, and Technology," U.S. Bureau of Mines Information Circular, 1989, p. 6.

[5] Ibid.

[6] Ibid.

[7] John E. Ferrell, "Strontium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp.777-782.

A new process for the extraction and recovery of strontium from acidic waste streams is being developed. In this process, SREX (Strontium Extraction), strontium is extracted from acidic solution and is stripped from the organic phase using either water or dilute HNO_3. Prolonged exposure of the process solvent to nitric acid at elevated temperatures or to radiation from a ^{60}CO source produces essentially no deterioration in its performance. Experiments show that 99.7% of the strontium initially present in a feed solution can be removed using only three extraction stages.[8]

4. Beneficiation/Processing Boundaries

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

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Black Ash Method

Calciner offgas. Calciner emissions may contain carbon dioxide which may or may not be recycled into the agitation tank. This offgas may also contain sulfur dioxide and ore particles.[9]

Dilute sodium sulfide solution
Filter muds
Spent ore
Vacuum drum filtrate
Waste solution

Soda Ash Method

Waste sodium sulfate solutions

2. Mineral Processing Wastes

None identified.

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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[8] Philip E. Horowitz, Mark L. Dietz, and Dan E. Fisher, "SREX: A New Process for the Extraction and Recovery of Strontium from Acidic Nuclear Waste Streams," Argonne National Laboratory, 1991, pg. 1.

[9] U.S. Environmental Protection Agency, "Strontium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-198 - 3-203.

BIBLIOGRAPHY

Ferrell, John E. "Strontium." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 777-782.

Horwitz, E. Philip, Mark L. Dietz, and Dan E. Fisher. "SREX: A New Process for the Extraction and Recovery of Strontium from Acidic Nuclear Waste Streams." Argonne National Laboratory. 1991. pg. 1.

Ober, Joyce A. "Strontium." From Mineral Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 1323-1332.

Ober, Joyce. "Strontium." From Mineral Commodity Summaries, U.S. Bureau of Mines. January 1995. p. 164-165.

Personal communication between ICF Incorporated and Joyce Ober, Bureau of Mines. July 21, 1994.

"Strontium--Uses, Supply, and Technology." U.S. Bureau of Mines Information Circular. 1989. p. 6.

U.S. Environmental Protection Agency. "Strontium." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp.3-198 - 3-199.

SULFUR

A. Commodity Summary

The United States is the world's foremost producer and consumer of sulfur and sulfuric acid, with production from Frasch, recovered, and byproduct sources. According to the U.S. Bureau of Mines, sulfur (in all forms) was produced at 169 operations in 30 states, Puerto Rico, and the U.S. Virgin Islands for a total shipment value of nearly $500 million in 1994. Texas and Louisiana accounted for nearly 50% of domestic production. Agricultural chemicals (fertilizers) accounted for 61% of sulfur demand; organic and inorganic chemicals accounted for 10%; metal mining accounted for 5%; and petroleum refining accounted for 7%. Other miscellaneous uses, accounting for 17% of demand, were widespread because many products produced by industry require sulfur in one form or another during some stage of their manufacture.[1]

Sulfur is a non-metallic element widely used in industry both as elemental sulfur (brimstone) and as sulfuric acid. Sulfur production is from three sources: combined sulfur, recovered sulfur, and formed sulfur. Combined sulfur occurs in natural compounds such as iron pyrite, copper sulfides, and gypsum. Recovered sulfur is produced as a byproduct of other processes such as oil refining or air pollution control. Formed sulfur is elemental sulfur cast or pressed into particular shapes to enhance handling and to suppress dust generation and moisture retention.[2]

In 1994, recovered elemental sulfur was produced by 59 companies at 150 plants in 26 states, one plant in Puerto Rico, and one plant in the U.S. Virgin Islands. Byproduct sulfuric acid was produced by 16 facilities in 1994.[3] The three companies listed in Exhibit 1 produce the bulk of mined sulfur in the United States. These three companies accounted for 32% of the U.S. production of sulfur in all forms in 1990. All three companies use the Frasch process for sulfur mining. Penzoil produces sulfur from its Culberson mine in western Texas and is currently engaged in exploration activities in western Texas, the Gulf Coast, and elsewhere. Texasgulf currently operates one mine in Texas (Boling dome), extracting about 40,000 tpy of sulfur. Freeport currently operates two mines in the Gulf Coast.[4] The names and locations of the smaller facilities are not available.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Sulfur is mined from both surface and underground deposits, and is recovered as a byproduct from a number of industrial processes. In sulfur mining, three techniques are applied: conventional underground methods, conventional open pit methods, and the Frasch mining method. About 90% of all sulfur mined is obtained through Frasch mining.[5] Frasch mining and sulfur production from recovered, combined, and formed sulfur are described below in addition to the production process for sulfuric acid.

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[1] Joyce Ober, "Sulfur," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 166-167.

[2] Gregory R. Wessel, "Sulfur Resources," from Industrial Minerals and Rocks, 6th edition, Society for Mining, Metallurgy, and Exploration, 1994, pp. 1011-1046.

[3] Joyce Ober, 1995, Op. Cite., pp. 166-167.

[4] Gregory R. Wessel, 1994, Op. Cit., pp. 1011-1046.

[5] Ibid.

EXHIBIT 1

SUMMARY OF MAJOR PRIMARY SULFUR PROCESSING FACILITIES

Facility Name	Location
Freeport Sulphur Co.	Caminada, offshore LA
Penzoil Sulphur Co.	Culberson, W. TX
Texasgulf Inc.	Boling, TX

2. Generalized Process Flow

Frasch Mining

The Frasch mining process uses hot water to melt sulfur trapped in salt domes. The sulfur is then pumped to the surface and is either sold as a liquid or cooled and solidified into a number of forms for market. Exhibit 2 presents a process flow diagram for the Frasch process.

Recovered Elemental Sulfur (Claus Process)

Recovered elemental sulfur is a non-discretionary byproduct of petroleum refining, natural gas processing, and coking plants. Recovered sulfur is produced primarily to comply with environmental regulations applicable directly to processing facilities or indirectly by restricting the sulfur content of fuels sold or used. The principal sources of recovered sulfur are hydrogen sulfide in sour natural gas and organic sulfur compounds in crude oil. Recovery is mainly in the elemental form, although some is converted directly to sulfuric acid. Sulfur in crude oil is recovered during the refining process. Organic sulfur compounds in crude oil are removed from the refinery feed and converted to hydrogen sulfide by a hydrogenation process. The sulfur in natural gas is already in the form of hydrogen sulfide. Hydrogen sulfide from both sources is converted to elemental sulfur by the Claus process. In this process, concentrated hydrogen sulfide is fired in a combustion chamber connected to a waste heat boiler. Air is regulated to the combustion chamber so that part of the hydrogen sulfide is burned to produce sulfur dioxide, water vapor, and sulfur vapor. The high temperature gases are cooled in a waste heat boiler and sulfur is removed in a condenser. The efficiency of the process is raised by adding as many as three further stages in which the gases leaving the sulfur condenser are reheated and passed through catalytic converters and additional condensers. Finally, the total gas stream is incinerated to convert all remaining sulfur-bearing gases to sulfur dioxide before release to the atmosphere. The sulfur is collected in liquid form. Exhibit 3 presents a process flow diagram for the Claus process.

Combined Sulfur

Combined sulfur can be recovered during the smelting of nonferrous sulfides. Sulfur dioxide in the smelter gases is converted to sulfuric acid, liquid sulfur dioxide, or oleum. In the United States, byproduct sulfuric acid from nonferrous metal smelters and roasters supplied about 11% of the total domestic production of sulfur in all forms in 1990. Sulfur may also be recovered from sulfur dioxide emissions. Regenerative or throwaway flue-gas desulfurization methods may be used either to recover sulfur in a useful form or to dispose of it as solid waste. Both recovery methods may employ wet or dry systems and use a variety of compounds such as limestone, sodium carbonate, and magnesium oxide to neutralize or collect the sulfur dioxide. End products include gypsum, sulfuric

EXHIBIT 2

FRASCH PROCESS

(Adapted from: Multi-Medial Assessment of the Inorganic Chemicals Industry, 1980, Chapter 14.)

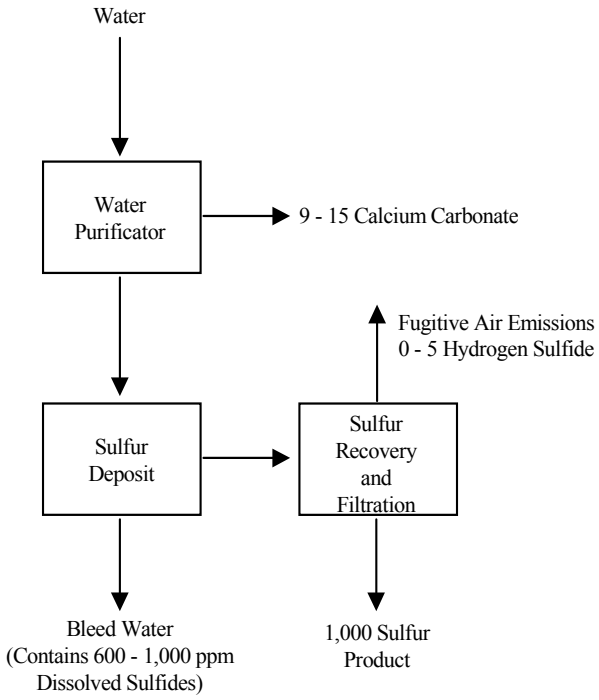
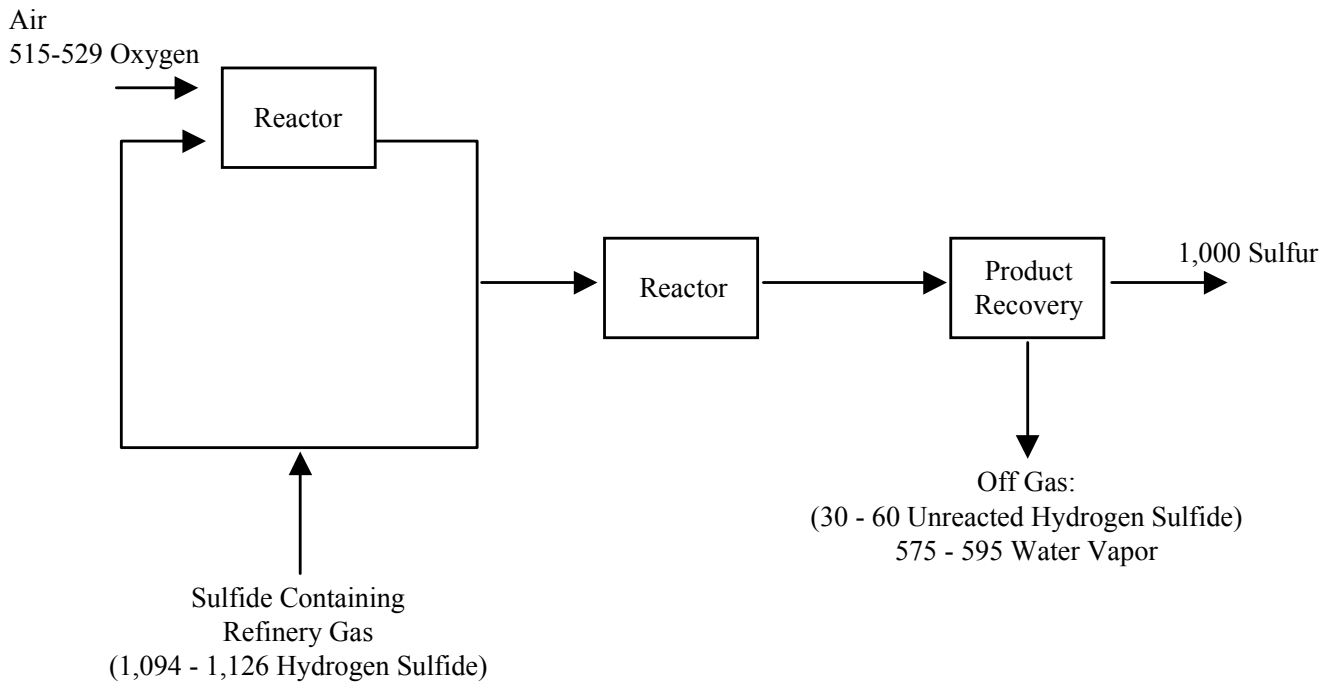


EXHIBIT 3

CLAUS PROCESS

(Adapted from: Multi-Medial Assessment of the Inorganic Chemicals Industry, 1980, Chapter 14.)



acid, liquid sulfur dioxide, and elemental sulfur, all of which can be used if a local market exists. If no local markets exist, large quantities of gypsum or sulfuric acid may have to be neutralized or otherwise disposed.[6]

Formed Sulfur

Formed sulfur may be made in one of several forms, including: flakes, slates, prills, nuggets, granules, pastilles, and briquettes. To produce flakes, the sulfur is cooled and solidified on the outside of large rotating drums, from which it peels off into small flakes. To produce slates, molten sulfur is cast onto a continuous conveyer belt and is cooled with air or water so that it solidifies into a thin sheet. As the slate reaches the end of the belt, the sheet breaks into smaller pieces. Sulfur prilling can be accomplished with air or water. In air prilling, molten sulfur is sprayed from the top of a tower against an upward flow of air. As it falls, the sulfur breaks into small droplets and cools into prills. In water prilling, the sulfur is sprayed into tanks containing water, from which the prills are collected and dried. Minor modifications to prilling techniques are used to produce nuggets. Granulation involves applying successive coats of sulfur to solid particles of sulfur in a granulator until the particle size reaches the required diameter. In the Procor GX granulation process, liquid sulfur is sprayed into a rotating drum in which small seed particles of sulfur are recycled from the end of the process. Pastilles are individual droplets of molten sulfur that have been dropped on a steel belt and cooled by conduction. The Sandvik Rotoform process uses a patented

[6] Ibid.

Rotoformer to distribute the sulfur on the belt. At the end of the belt, the pastilles are scraped off and fall onto a collecting conveyer.[7]

Sulfuric Acid

Sulfuric acid is usually produced near consumption sites. To produce sulfuric acid, elemental sulfur or any number of sulfur-bearing materials are burned. The resulting sulfur dioxide is mixed with additional air or oxygen and passed through a packed bed of supported vanadium pentoxide catalyst. The sulfur dioxide is converted to sulfur trioxide. The gases emerging from the catalytic reactor are cooled and absorbed in 98-99% sulfuric acid to generate 98-99% acid. Plants can be either single or double absorption units. In double absorption units, tail gases from the initial absorption step are mixed with additional sulfur dioxide, reheated and passed through another catalytic reactor to form additional sulfur trioxide. This material is cooled and absorbed in a second stream of sulfuric acid to generate additional 98-99% sulfuric acid. Exhibit 4 presents a process flow diagram for the production of sulfuric acid.[8]

The process is modified somewhat if feed materials other than pure sulfur are used. Materials such as spent sulfuric acid, hydrogen sulfide, and off-gases from smelters are also used for the manufacture of sulfuric acid.[9]

If spent acid is the feed material, it is thermally decomposed to yield a gas stream containing sulfur dioxide, small amounts of sulfur trioxide, water vapor, and small amounts of organic materials. The gas stream is cooled or the sulfuric acid is scrubbed to condense out water and organics, and is then demisted to remove residual water. The purified sulfur dioxide gas stream is reheated, mixed with additional air or oxygen, and sent to catalytic converters. The process proceeds from this point as it does with pure sulfur as the feed.[10]

When smelter or pyrite roasting off-gases containing sulfur dioxide are used as the feed material, the gas stream is passed through a series of dry filtration devices to remove entrained particulate matter. The gas is cooled to remove water vapor before it can be used in the process.[11]

Sulfur from pyrite is produced by roasting the iron sulfide to produce sulfur dioxide gas and iron oxide solid. The gas is treated to produce either elemental sulfur or sulfuric acid and the iron oxide is sold as feed for iron making. There are no wastes from this process.[12]

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

There has been sporadic production of elemental sulfur from volcanic deposits in the western United States, but the selective mining techniques used would eliminate the generation of wastes.[13]

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[7] Ibid.

[8] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Vol. III, 1980, Chapter 14.

[9] Ibid.

[10] Ibid.

[11] Ibid.

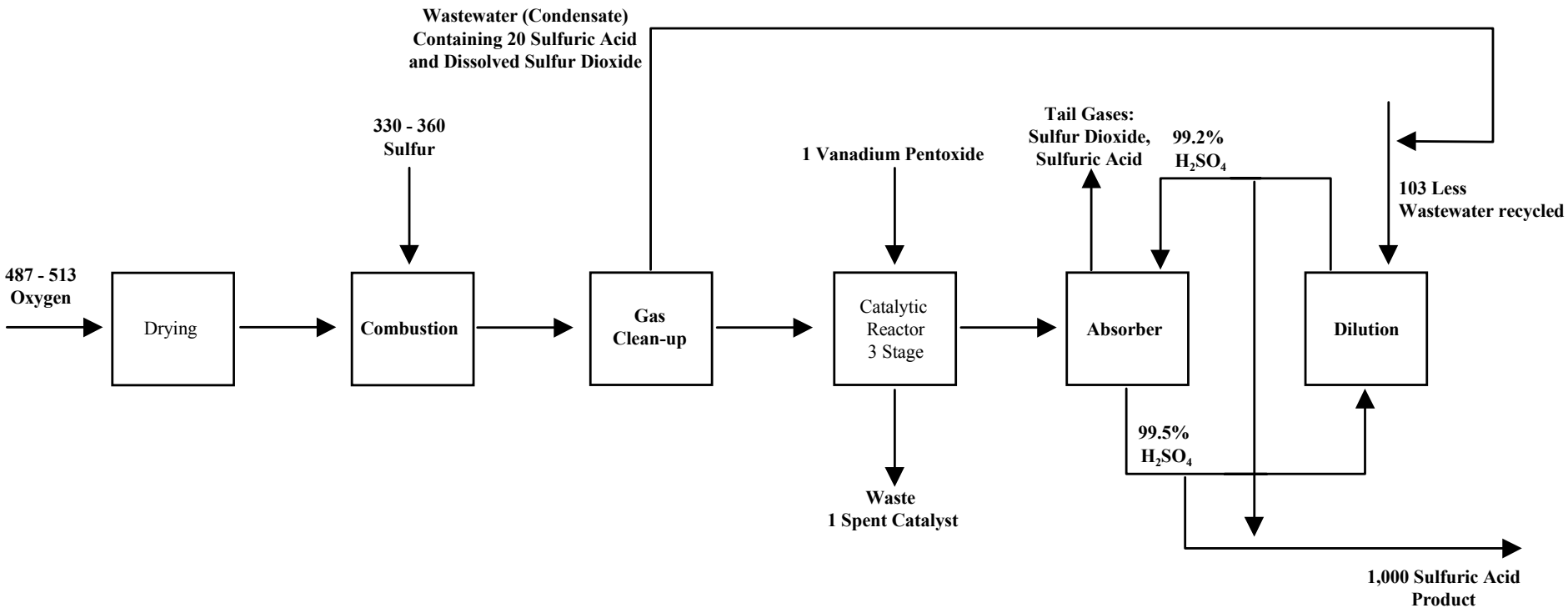
[12] Ibid.

[13] U.S. Environmental Protection Agency, "Sulfur," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-55 - 2-56.

EXHIBIT 4

SULFURIC ACID PRODUCTION

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, Chapter 14.)



4. Beneficiation/Processing Boundaries

Frasch Processing

Based on a review of this process, there are no mineral processing operations involved in the production of sulfur via the Frasch proces.

Claus Process and Combined Sulfur

Based on EPA's review of these processes, both were determined to start with sulfur recovered from other operations such as petroleum refining and other mineral smelting operations and as such, are completely outside the scope of the Mining Waste Exclusion.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Based on existing data and best engineering judgement, none of the wastes listed below from sulfur production are expected to exhibit characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

Frasch Process Wastestreams

Wastewater. Wastewater from Frasch mining may contain 600 to 1,000 ppm dissolved sulfides and 14,000 to 60,000 ppm of dissolved chlorides. Bleed water retrieved from the formation is produced in amounts ranging from 38,000,000 to 1.6 billion liters per day. Well seal water is generated in amounts ranging from 5,000 to 20,000 liters per day and contains up to 60 ppm dissolved sulfides. At anhydrite plants, seal water and water recovered from the formation are treated and reused. At off-shore salt dome plants, bleed water and seal water are combined and discharged without further treatment. At on-shore facilities, bleed water, area runoff, seal water, and other wastewater are combined and sent to aeration lagoons. There, sulfides are oxidized to sulfates and thiosulfates. The sulfide content of the raw effluent is reduced from the range of 600 to 1,000 ppm to the range of 10 to 40 ppm prior to discharge.[14]

Air emissions. Emissions from the mine, generated during sulfur recovery, may contain hydrogen sulfide. The hydrogen sulfide fugitive emissions may range from 0 to 5 kg per kkg of product.[15]

Sludge. Calcium carbonate sludge is generated by water pretreatment and ranges from 9 to 15 kg per kkg of product. The calcium carbonate water treatment sludge is recovered and reused. At anhydrite plants, it is used as drilling mud.

Filter cake. At salt dome plants, about 3.5 kg per kkg of product of waste filter cakes from sulfur filtration are generated. At salt dome facilities, filter cakes from sulfur purification are stored for future recovery of additional product.

Miscellaneous wastes such as **residues** and **spilled sulfur** are generated from the Frasch process. After processing, residues are landfilled.

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[14] U.S. Environmental Protection Agency, 1980, Op. Cit, Chapter 14.

[15] Ibid.

2. Mineral Processing Wastes

Based on existing data and best engineering judgement, the wastes listed below from sulfur production and sulfuric acid production are not primary mineral processing wastes. Therefore, the Agency did not evaluate these materials further.

Claus Process

Tail gases. An airborne waste from product recovery is generated and contains unconverted hydrogen sulfide gas ranging from 5,000 to 12,000 ppm, 300 to 500 ppm carbon disulfide, 300 to 5,000 ppm carbon oxysulfide, and up to 200 ppm sulfur vapor. (The carbon disulfide and carbon oxysulfide are produced by side reactions of organic compounds present in the feed stream and sulfur dioxide generated in the process.) From 950 to 4,400 cubic meters of tail gases are produced per kkg of sulfur product.[16] Tail gases are typically recovered and processed to recycle sulfur compounds. There are several methods used to recover sulfur compounds from these gases. The processes are described briefly below.

The SCOT process reconverts sulfur compounds in tail gases to hydrogen sulfide. This stream is scrubbed from the tail gases with amine solution, the regeneration of which releases a purified hydrogen sulfide which is recycled to the Claus process. This process recovers over 98% of the sulfur compounds in the tail gases.[17]

The Beavon and Stretford processes are also used to recover sulfur from tail gases. The Beavon process catalytically reduces sulfur oxides to hydrogen sulfide and the Stretford process removes the hydrogen sulfide by absorption in an amine solvent. Regeneration of the solvent releases a purified hydrogen sulfide which is converted to sulfur. About 98% removal of sulfur compounds from the tail gases is achieved.[18]

The Citrate process, developed by the Bureau of Mines, and the Wellman Lord process are used to recover most sulfur compounds from the tail gases as sulfur. These processes involve reduction of the sulfur dioxide present in the tail gases to sulfur.[19]

Spent catalysts. Spent catalysts are recycled or landfilled.[20]

Sulfuric Acid Production

Airborne emissions from double absorption plants range from 0.5 to 3 kg per kkg of sulfur dioxide and from 0.1 to 0.15 kg per kkg of sulfuric acid mists. The high end of the range represents plants using wet feed materials. Emissions from single absorption plants are controlled in one of five ways: (1) demisters and wet scrubbers, (2) scrubbing with aqueous ammonia solutions, (3) the Wellman Lord process, (4) molecular sieves to absorb sulfur dioxide, and (5) no control.[21]

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[16] Ibid.

[17] Ibid.

[18] Ibid.

[19] Ibid.

[20] Ibid.

[21] Ibid.

Wastewater. This wastewater includes wastewater from wet scrubbing, spilled product, and condensates. This waste contains dissolved sulfur dioxide and sulfuric acid values. This wastewater is usually neutralized and lagooned to settle suspended solids prior to discharge.[22]

Spent catalyst. Spent catalyst, generally vanadium pentoxide, are usually landfilled and sometimes reprocessed.[23]

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received by EPA

EPA received no comments that address this specific spector.

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[22] Ibid.

[23] Ibid.

BIBLIOGRAPHY

Ober, Joyce. "Sulfur." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 166-167.

U.S. Environmental Protection Agency. "Sulfur." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp. 2-55 -2-56.

U.S. Environmental Protection Agency. Multi-Media Assessment of the Inorganic Chemicals Industry. 1980. Vol. III. Chapter 14.

Wessel, Gregory R. "Sulfur Resources." From Industrial Minerals and Rocks, 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 1011-1046.