TANTALUM, COLUMBIUM, AND FERROCOLUMBIUM

A. Commodity Summary

Tantalum is used in the electronics industry, as well as in aerospace and transportation applications. Columbium (the commonly used synonym for the element niobium) is used as an alloying element in steels and in superalloys. Tantalum and columbium are often found together in pyrochlore and baripyrochlore, the main columbium containing minerals, as well as in columbite. These minerals contain relatively small amounts of tantalum, pyrochlore, and baripyrochlore, having a columbium pentoxide-to-tantalum pentoxide ratio of 200 to 1 or greater.[1] Columbite contains slightly larger amounts (up to eight percent) of tantalum.[2] Tantalite is the primary source of tantalum pentoxide, and contains small amounts of columbium pentoxide. Microlite is another source of tantalum pentoxide. Tantalum is also recovered from tin slags.[3] There has been no significant mining of tantalum or columbium ores in the United States since 1959. Producers of columbium metal and ferrocolumbium use imported concentrates, columbium pentoxide, and ferrocolumbium. Tantalum products are made from imported concentrates and metal, and foreign/domestic scrap.[4]

Ferrocolumbium is an alloy of iron and columbium. Ferrocolumbium is used principally as an additive to improve the strength and corrosion resistance of steel used in high strength linepipe, structural members, lightweight components in cars and trucks, and exhaust manifolds. High purity ferrocolumbium is used in superalloys for applications such as jet engine components, rocket assemblies, and heat-resisting and combustion equipment.[5] Exhibit 1 summarizes the principal producers of tantalum, columbium and ferrocolumbium in the United States in 1992. Only Cabot Corporation and Shieldalloy Metallurgical Corporation use ores as their starting material.[6]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Tantalum and columbium ores are processed by physically and chemically breaking down the ore to form columbium and tantalum salts or oxides, and separating the columbium and tantalum salts or oxides from each other. These salts or oxides may be sold, or further processed to reduce the salts to the respective metals. Ferrocolumbium is made by smelting the ore with iron, and can be sold as a product or further processed to produce tantalum and columbium products.[7] These processes are described in greater detail below.

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[1] L.D. Cunningham, "Columbium (Niobium) and Tantalum," Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 435-436.

[2] L.D. Cunningham, "Columbium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 187.

[3] L.D. Cunningham, 1992, Op. Cit., p. 438.

[4] L.D. Cunningham, "Columbium" and "Tantalum," Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 48 and 170.

[5] L.D. Cunningham, 1992, Op. Cit., pp. 435-436.

[6] Personal Communication between ICF Incorporated and Larry D. Cunningham, U.S. Bureau of Mines, November 1994.

[7] Ibid.

EXHIBIT 1

SUMMARY OF TANTALUM, COLUMBIUM, AND FERROCOLUMBIUM PRODUCERS (IN 1992)[a]

Facility Name	Location	Type of Products
Cabot Corp.	Boyertown, PA	Cb and Ta pentoxide/metal, FeCb, Ta capacitor powder
Kennametals, Inc.	Latrobe, PA	Cb and Ta carbide
Herman C. Stark Inc. (NRC, Inc.)	Newtown, MA	Cb and Ta metal, Ta capacitor powder
Reading Alloys, Inc.	Robesonia, PA	FeCb
Shieldalloy Metallurgical Corp.	Newfield, NJ	FeCb
Teledyne Wah Chang Albany	Albany, OR	Cb pentoxide/metal, FeCb
Thai Tantalum Inc.	Gernee, IL	Ta metal

[a] - Cunningham, L.D., "Columbium (niobium) and Tantalum," Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. p.453
[b] - Personal Communication between ICF Incorporated and Larry D. Cunningham, U.S. Bureau of Mines, November 1994.

2. Generalized Process Flow Diagram

Tantalum and Columbium Production

Exhibit 2 illustrates the processing of tantalum and columbium. There is no domestic mining of columbium or tantalum, and the ore is imported either directly or as a concentrate. Therefore, domestic processing of columbium and tantalum may begin after the milling step shown in Exhibit 2. Tantalum and columbium are extracted from the source materials, imported concentrates, and tin slags, by digestion and liquid-liquid extraction. (Teledyne Wah Chang Albany does not use this process. In previous years they had operated a chlorination/ hydrolysis process, but now operates an acid digestion process. However, their acid process does not use liquid-liquid extraction.)[8] When tin slags are used for the recovery of tantalum, they are sometimes upgraded in an electric furnace process (not shown), yielding a synthetic concentrate.[9] The slag is smelted with carbon to reduce the iron, tantalum, and columbium components, which are collected as a high carbon ferroalloy containing columbium- and tantalum carbides. This ferroalloy is treated with a metal oxide to selectively oxidize carbided components other than tantalum and columbium. The tantalum and columbium carbides are reoxidized and can be substituted for tantalum and columbium concentrates.[10]

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[8] Personal Communication between ICF incorporated and Chuck Knoll, Teledyne Wah Chang, Albany, OR, November 1994.

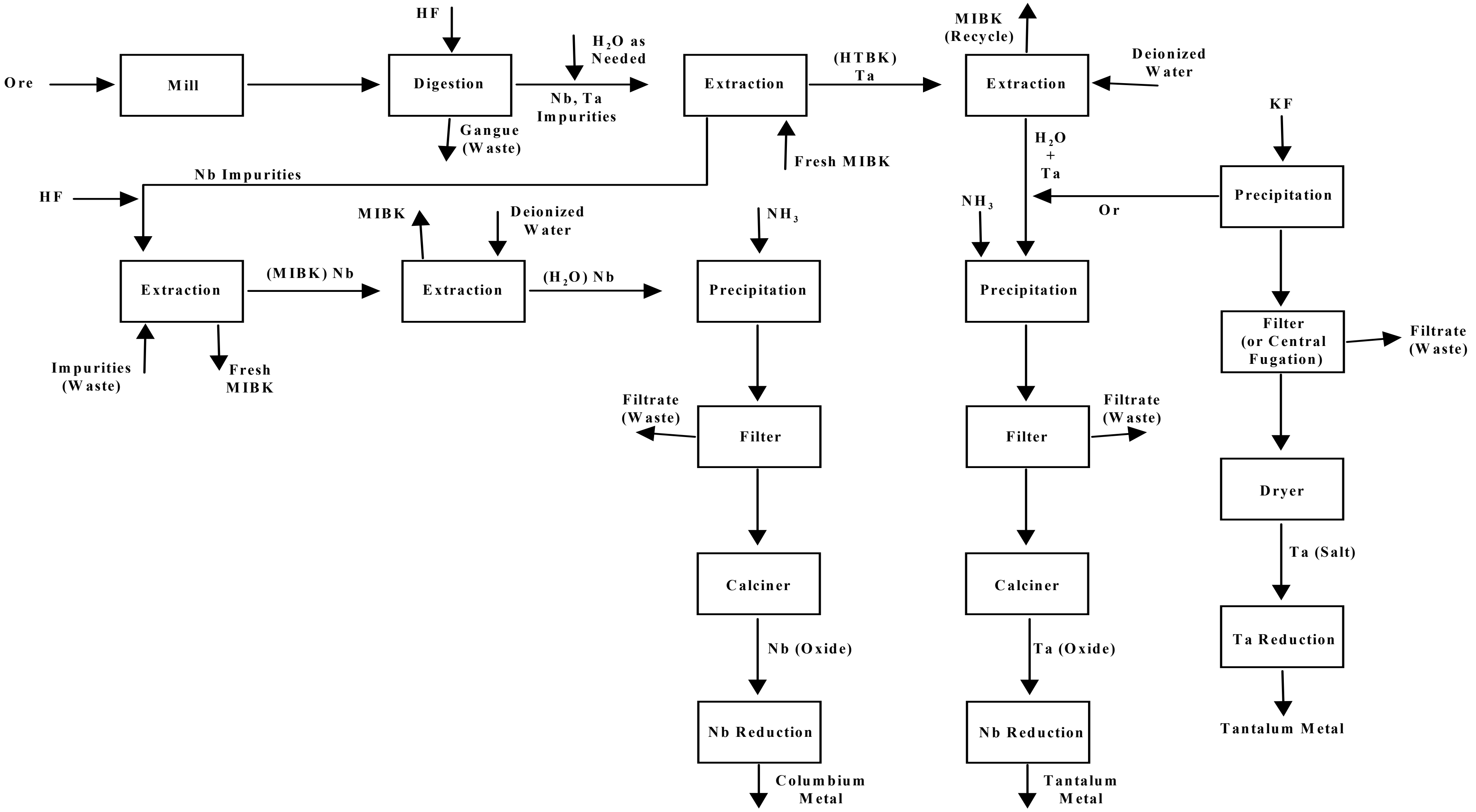
[9] L.D. Cunningham, 1992, Op. Cit., pp. 438-39.

[10] "Tantalum and Tantalum Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, p. 549.

EXHIBIT 2

PRIMARY COLUMBIUM-TANTALUM PROCESS

(Adapted from: U.S. Environmental Protection Agency, 1989, p. 4359.)



The concentrate or slag is digested with aqueous hydrofluoric acid (sometimes in conjunction with sulfuric acid) to form fluoride salts of the metals. Unreacted concentrate or slag (gangue) is removed by settling and decantation and is disposed of as a low level radioactive waste. This leaching process also generates an acid mist that may be controlled by wet scrubbers. The scrubber liquor is a source of wastewater.[11]

These metal-fluoride salts are then extracted with methyl isobutyl ketone (MIBK). The liquid-liquid extraction procedure first recovers the tantalum salt. Additional hydrofluoric acid is added to change the solubility of the columbium salt, which is then extracted by MIBK. The raffinate (containing the spent hydrofluoric acid solution) from this step is considered wastewater. The salts are then recovered from each of the MIBK solutions by liquid-liquid extraction with deionized water. The raffinate from this second set of extractions is the barren MIBK, which is recycled. Fugitive air fumes from the solvent extraction process are controlled by wet air pollution control devices, which generate wastewater.[12] The water and tantalum solution from the extractor contains a fluotantalic acid solution, from which potassium fluotantalate (K-salt, K_2TaF_7) or tantalum pentoxide (Ta_2O_5) can be precipitated through the addition of either potassium fluoride, or ammonia. Potassium chloride (not shown) is used sometimes in place of potassium fluoride.[13] Columbium pentoxide is precipitated from the columbium stream by the addition of ammonia. A wet scrubber may be used to control fluoride fumes generated during precipitation of either metals' oxide or salt. The aqueous liquor (filtrate) is discarded. The resulting crystals are washed with water and dried.[14] The columbium oxide precipitates are calcined in a kiln; wet scrubbers are used to control gaseous fumes. Tantalum salts are also dried, but wet scrubbers are not normally used. The water vapor, however, may be condensed, captured, and discharged.[15]

Columbium and tantalum salts are reduced to metal by a number of methods, including: sodium reduction, aluminothermic reduction, carbon reduction, and electrolysis. Sodium reduction (not shown) is a popular method for producing both columbium and tantalum from their salts. In this process, sodium reduces the columbium or tantalum to metal. Layers of the columbium or tantalum salt are alternated with layers of sodium in a reaction vessel, then capped with sodium chloride to prevent oxidation of the reduced metal. The reaction mixture is often ignited electrically, but once ignited, the exothermic reaction is self-sustaining. Wet scrubbers are often used to control the gaseous emissions from the reaction vessel. After cooling, the columbium or tantalum metal-containing material is crushed, and any iron picked up from the reaction vessel is removed magnetically. The remaining metal powder is further purified by leaching with water, followed by nitric or hydrofluoric acid.[16]

The aluminothermic reaction (not shown) also may be used on both columbium and tantalum salts. This method also may be used on certain ferrocolumbium ores that do not require digestion and separation of columbium and tantalum salts. The salt (or ore) is mixed with aluminum powder. Potassium chlorate is added to provide additional reaction heat, and magnesium is added to properly ignite the mixture. Columbium and tantalum are reduced to metal while aluminum is oxidized.[17]

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[11] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Volume VIII, Office of Water Regulations and Standards, May 1989, p. 4352.

[12] Ibid.

[13] L.D. Cunningham, 1992, Op. Cit., pp. 438-39.

[14] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 4352.

[15] Ibid., p. 4353.

[16] Ibid.

[17] Ibid.

Carbon reduction (not shown) takes place through a two-step route known as the Balke process and can be used on both columbium and tantalum salts. Its predominant use, however, is in the reduction of the metal oxides. The metal oxide is first mixed with fine carbon and heated under vacuum to 1800°C, where a metal carbide and carbon monoxide are formed. The carbide is then mixed with more oxide and reacts to form the pure metals and additional carbon monoxide. No known wastewater is generated during this process.[18]

Electrolytic reduction (not shown) of tantalum is sometimes practiced, using fused salt techniques. Potassium fluotantalate (K-salt), the crystal which was precipitated by potassium fluoride in the separation of salts step, is electrolyzed to yield pure tantalum metal. The pure tantalum metal is then separated from the cathode by pulverizing the cathode and subsequent acid leaching, resulting in a metal solution and the cathode material (usually carbon).[19]

Electron beam melting is currently the most common method of consolidation, as shown in Exhibit 3.[20] A beam of high voltage, low current electrons is focused onto the crude metal and the top of a retractable tantalum ingot contained in a water cooled copper cylinder. The beam melts the crude metal, and the falling molten globules from a pool on top of the ingot. The process is continuous, with the ingot being lowered as the molten metal solidifies. Most impurities boil out of the pool into the high vacuum environment (required by the electron beam) and are removed.[21] Arc melting, as shown in Exhibit 4, occurs in much the same way as electron beam melting, except that a low voltage, high current arc of electricity melts the crude metal.[22]

Simultaneous compaction and direct resistance heating (not shown) is the oldest process and is somewhat undesirable, as the metal must be processed two or three times to reach sufficient purity. The metal is typically compacted at about 6,900 atmospheres and heated to 1,400-1,500°C for several hours. It is then rolled and sintered at 2,300°C. Several rolling and sintering steps may be required.[23]

Ferrocolumbium Production

Ferrocolumbium is made from pyrochlore concentrates, usually by an aluminothermic process with an iron-iron oxide mixture. Exhibit 5 illustrates this process. Pyrochlore, aluminum powder, and iron scrap, and/or iron oxide are mixed together, frequently with small amounts of lime or fluorspar as fluxing agents, in a batch reactor. Sometimes sodium chlorate or some other powerful oxidizer is added to provide additional reaction heat. A typical reactor consists of a refractory lined steel shell, and occasionally a floor consisting of slag from previous reduction reactions is used. After the reaction has come to completion, the molten ferrocolumbium lies at the bottom of the reactor and the slag floats on it. Most of the impurities go into the slag and some easily reduced metals go into the ferrocolumbium. After a period of cooling, the metal is separated from the slag, and is crushed and sized. At some facilities, an electric furnace is used to provide the heat necessary for the reaction, in place of the aluminothermic.

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[18] Ibid.

[19] Ibid.

[20] "Tantalum and Tantalum Compounds," 1983, Op. Cit., p. 552.

[21] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 4354.

[22] "Tantalum and Tantalum Compounds," 1983, Op. Cit., p. 551.

[23] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 4354.

EXHIBIT 3

ELECTRON BEAM MELTING

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 552.)

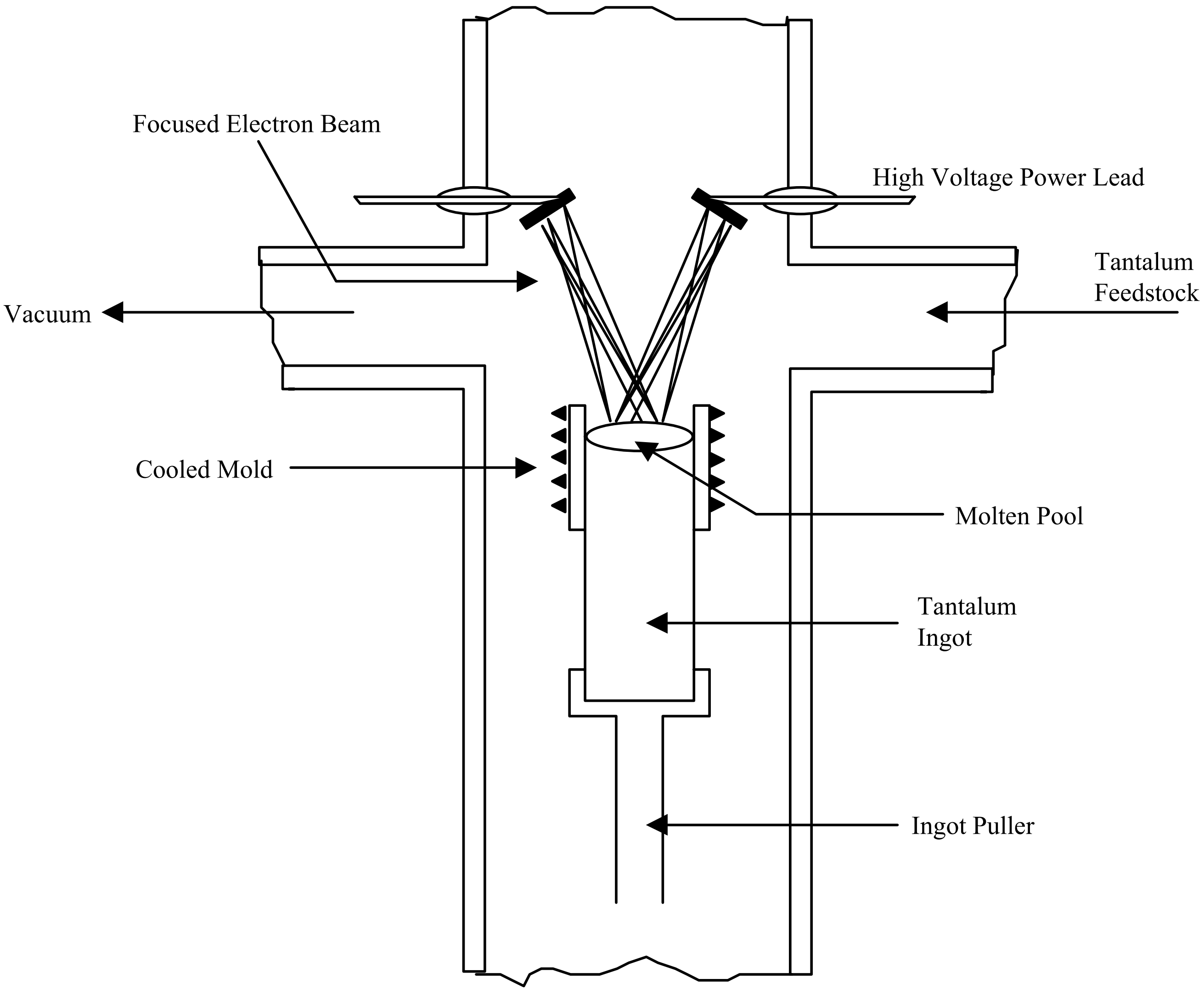


EXHIBIT 4

VACUUM ARC MELTING

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 551.)

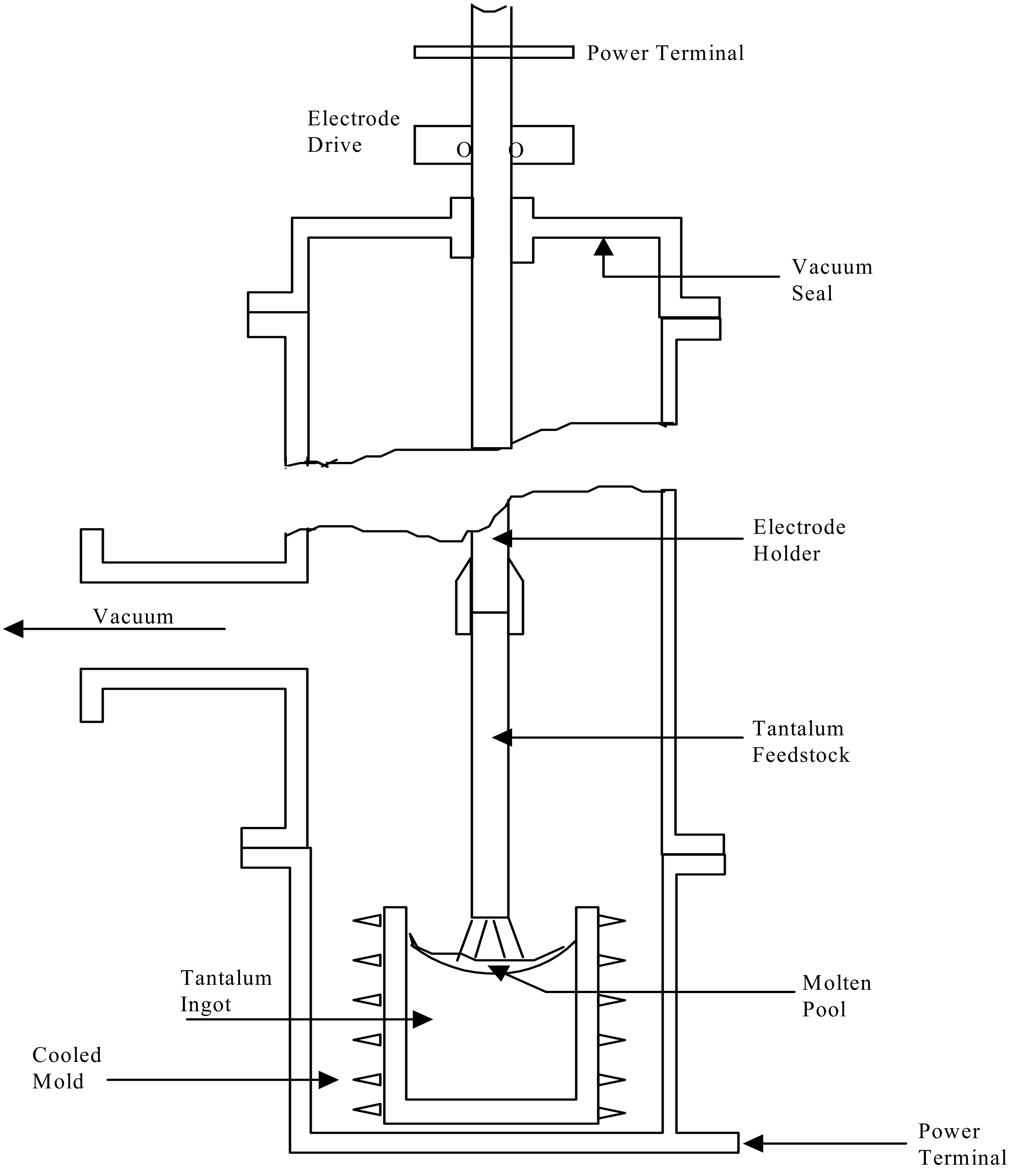
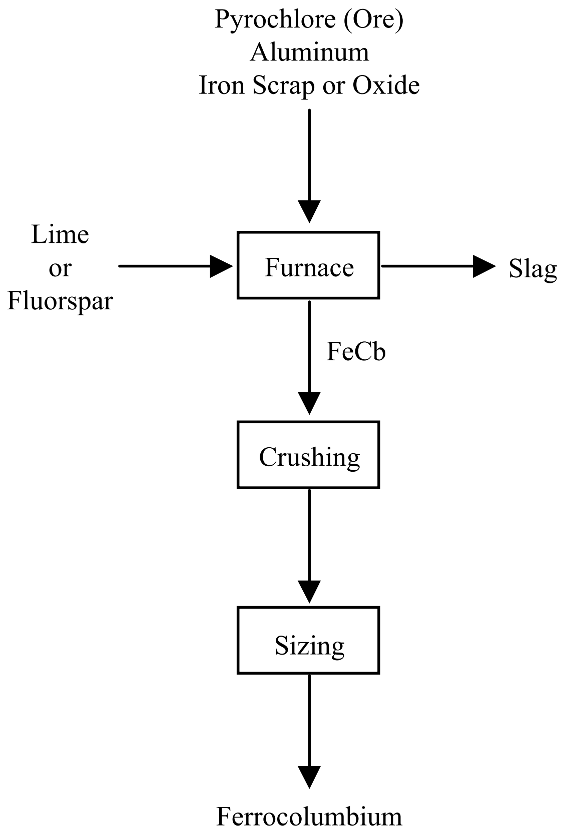


EXHIBIT 5

FERROCOLUMBIUM PRODUCTION



method. In this process, the quantity of aluminum can be substantially reduced and other reducing agents such as ferrosilicon can be used.[24] High purity ferrocolumbium cannot be made directly from pyrochlore because of the high alkali content. It can, however, be manufactured from columbium pentoxide produced by treating the lower purity ferrocolumbium made from pyrochlore concentrates.[25]

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

Direct chlorination of tin slag is being investigated as an alternative to digestion and leaching, as a way to reduce the amount of toxic waste generated.[26]

4. Extraction/Beneficiation Boundaries

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

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

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.

Tantalum/Columbium

EPA determined that for the production of tantalum/columbium, the beneficiation/processing line occurs between milling and digestion because the physical structure of the ore is destroyed. 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

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[24] "Niobium and Niobium Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XV, 1982, pp. 823-824.

[25] Cunningham, L.D., 1992, Op. Cit., p. 436.

[26] I. Gaballah, E. Allain, and M. Djona, "Chlorination and Carbochlorination of a Tantalum and Niobium Pentoxides Bearing Concentrates," Mineral Processing and Environmental Engineering, Vandoeuvre, France, 1993, p. 760.

generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

Ferrocolumbium

EPA determined that for ferrochromium, processing begins with the reaction of iron and the ore in the furnace because the ore is changed into a more useful form by significant physical and chemical changes 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

The following waste streams have been associated with the processing of tantalum and columbium concentrates and slags.

1. Extraction and Beneficiation Wastes

Currently, there is no domestic extraction of columbium or tantalum ores.

2. Mineral Processing Wastes

Digestion

Scrubber Overflow. Approximately 19,000 metric tons of scrubber overflow are produced annually in the United States. Available data do not indicate the waste exhibits hazardous characteristics.[27] Therefore, the Agency did not evaluate this material further.

WWTP Liquid Effluent. Approximately 206,000 metric tons of WWTP Liquid Effluent are produced annually in the United States.[28] Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Potassium Titanium Chloride. Available data do not indicate the waste exhibits hazardous characteristics.[29] Therefore, the Agency did not evaluate this material further.

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[27] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Volume 1, Office of Solid Waste, August 1992, p. I-7.

[28] Ibid.

[29] Ibid.

Spent Raffinate Solids. Approximately 2,000 metric tons of raffinate solids, from the liquid-liquid extraction procedure are produced annually in the United States.[30] This waste may exhibit the hazardous characteristic of corrosivity.[31] The waste is not recycled.

Digester Sludge. Approximately 1,000 metric tons of digester sludge are produced annually in the United States.[32] This waste may exhibit the hazardous characteristic of corrosivity.[33] The waste is not recycled.

WWTP Sludge. 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.

Process Wastewater. There are several operations which produce wastewater (see Exhibit 3). Process wastewater may contain fluoride, copper, lead, zinc, cadmium, 1,2-dichloroethane, chloroform, chromium, selenium, arsenic, nickel, and ammonia. The pH of the individual waste streams may be high or low depending on the operations that generated each waste stream. For instance, the pH of the wastewater generated through digestion is likely to be low, while wastewater resulting from ammonia precipitation is likely to be high.[34] Therefore, the pH of the mixture of these streams will depend on the quantity and pH of each contributing stream. We used best engineering judgement to determine that this waste stream may be recycled. The waste was formerly classified as a spent material. Approximately 146,000 metric tons of process wastewater are produced annually in the United States.[35] Attachment 1 contains data on process wastewater.

APC Dust Sludge. Available data do not indicate that APC dust sludge generated by the production of ferrocolumbium exhibits hazardous characteristics.[36] Therefore, the Agency did not evaluate this material further.

Slag. This material is generated by the aluminothermic production of ferrocolumbium. During the processing sequence, most of the impurities contained in the raw materials report to the slag. However, some of the easily reduced metals will go into the ferrocolumbium layer.[37] 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.

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[30] Ibid.

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

[32] Ibid.

[33] U.S. Environmental Protection Agency, Op. Cit., August 1989, p. 3-6.

[34] U.S. Environmental Protection Agency, "Columbium and Tantalum," 1988 Final Summary Report of Mineral Industrial Processing Wastes, 1988, pp. 3-84 - 3-85.

[35] U.S. EPA, 1992, Op. Cit., p. I-7.

[36] Ibid., p. I-4.

[37] "Niobium and Niobium Compounds," 1982, Op. Cit., pp. 823-824.

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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ATTACHMENT 1

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

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Min.	Avg.	Max.	# Detects	Level	In Excess
Aluminum	50000	50000	50000	1/1	-	-	-	0/0	-	-
Antimony	0.010	6.461	30.00	10/10	-	-	-	0/0	-	-
Arsenic	0.003	6.256	45.00	13/13	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.001	0.126	0.500	13/13	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.008	6.392	40.00	13/13	-	-	-	0/0	1.0	0
Chromium	0.006	232.846	1000	13/13	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.200	56.553	300	13/13	-	-	-	0/0	-	-
Iron	25000	25000	25000	1/1	-	-	-	0/0	-	-
Lead	0.020	255.869	1000	13/13	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.000	0.013	0.063	13/13	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.500	2.460	10	10/10	-	-	-	0/0	-	-
Selenium	0.002	13.507	70	10/10	-	-	-	0/0	1.0	0
Silver	0.000	0.040	0.070	4/4	-	-	-	0/0	5.0	0
Thallium	0.000	0.365	1.180	9/9	-	-	-	0/0	-	-
Vanadium	7800	7800	7800	1/1	-	-	-	0/0	-	-
Zinc	0.600	331.960	1000	10/10	-	-	-	0/0	-	-
Cyanide	0.001	0.006	0.033	17/17	-	-	-	0/0	-	-
Sulfide	2650	14037.50	45000	4/4	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	10000	45750	130000	4/4	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	40000	40000	40000	1/1	-	-	-	0/0	-	-
Chloride	900	9450	18000	2/2	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	3.0	8.4	12.0	5/5					2<pH>12	2
Organics (TOC)	-	-	-	0/0					-	-

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

TELLURIUM

A. Commodity Summary

According to the U.S. Bureau of Mines, commercial grade tellurium and tellurium dioxide are recovered from anode slimes at one electrolytic copper refinery in the United States (ASARCO - Amarillo, TX). Selenium is also recovered from the copper anode slimes during this process (see Selenium sector report). High purity tellurium, tellurium master alloys, and tellurium compounds are produced by primary and intermediate processors from commercial-grade metal and tellurium dioxide. Tellurium is used mainly in the production of free-machining steels. It is also used as a minor additive in copper and lead alloys and malleable cast iron, as an accelerator in rubber compounding, in thermoelectric applications, and as a semiconductor in thermal-imaging and photoelectric applications. Tellurium is added to selenium-base photoreceptor alloys to increase the photo speed. In 1994, iron and steel products remained the largest end use, followed by nonferrous metals, chemicals, and other uses.[1] Some common commercial tellurium products include tellurium dioxide, sodium tellurate, ferrotellurium, and tellurium diethyldithiocarbamate.[2]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Nearly all tellurium is obtained as a material formerly labeled as byproduct of the electrolytic refining of copper. Although copper slimes are valued primarily for gold, silver, and occasionally platinum-group metals, tellurium is available to the refiner for the added cost of recovery and refining.[3] Tellurium is present in copper refinery slimes in concentrations ranging from a trace to 8 percent and is recovered as precipitated tellurous acid. Tellurium metal can be produced from the crude tellurous acid by one of three purification methods described below. Metal tellurides for semiconductors are made by direct melting, after which, the excess tellurium is volatilized under reduced pressure. The resultant tellurium vapor is then passed over a heated metal in an inert gas carrier and undergoes a high temperature reduction of oxy compounds with hydrogen or ammonia.[4]

2. Generalized Process Flow Diagram

The process flow for the production of tellurium can be separated into two stages. The first stage involves the removal of copper from the copper slimes (an intermediary product is tellurous acid). The second stage involves the recovery of tellurium metal and purification of the recovered tellurium. The process flow diagrams for a typical recovery process are presented in Exhibits 1 through 3. Exhibit 1 shows the steps involved in producing tellurous acid from copper anode slimes. The process flow diagrams for two methods of recovering tellurium metal from tellurous acid, acid precipitation and electrolytic purification, are presented in Exhibits 2 and 3, respectively.

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[1] Stephen M. Jasinski, "Tellurium," from Mineral Commodities Summary, U.S. Bureau of Mines, 1995, pp. 172-173.

[2] "Tellurium," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXII, 1983, p. 663.

[3] Neldon L. Jensen, "Tellurium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 825.

[4] "Tellurium," 1983, Op. Cit., p. 663.

EXHIBIT 1

TELLURIUM RECOVERY FROM COPPER SLIMES

(Adapted from: 1988 Final Draft Summary Report of Mineral Processing Wastes, 1988, pp. 204 - 210.)

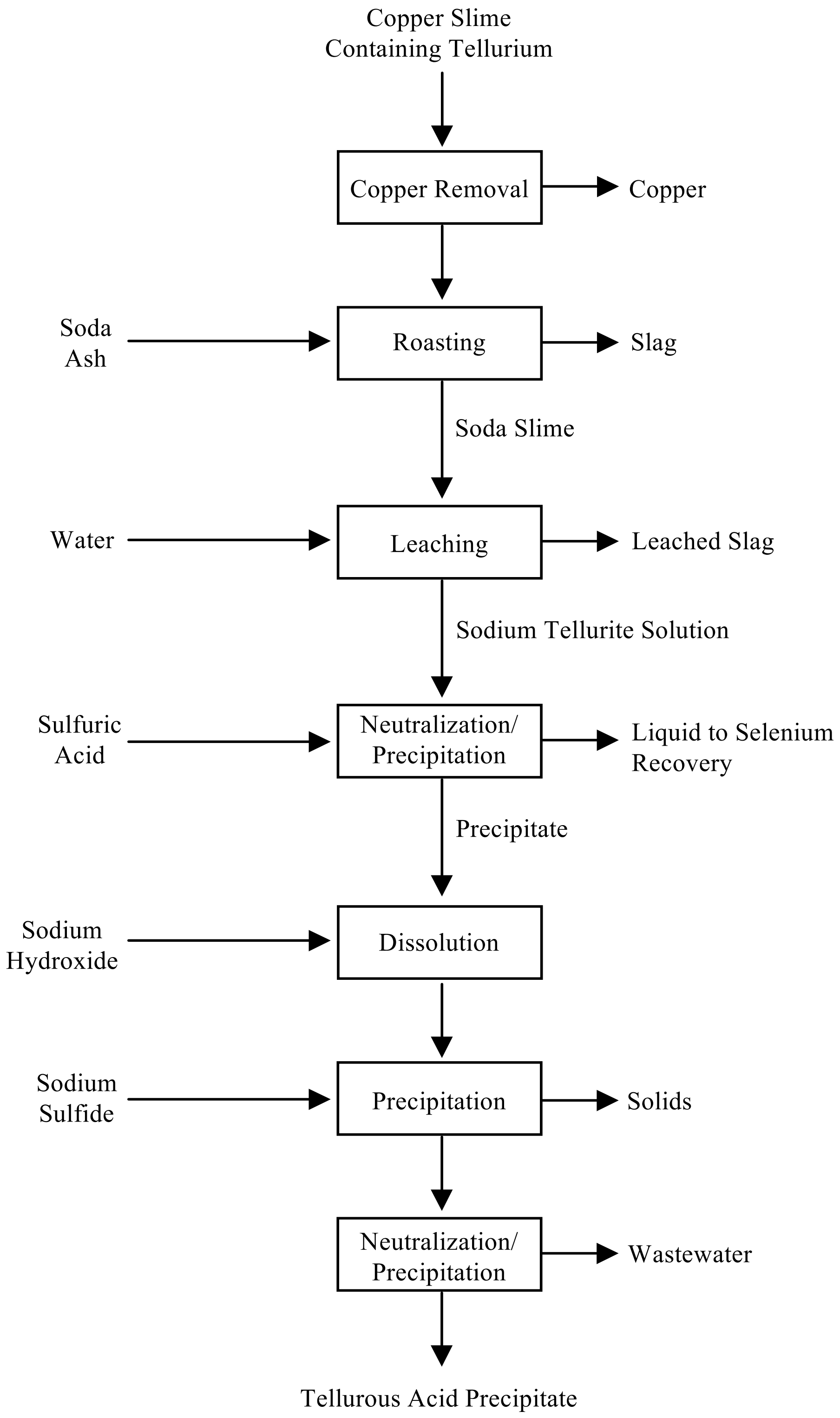


EXHIBIT 2

PURIFICATION OF TELLURIUM BY ACID PRECIPITATION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 204 - 210.)

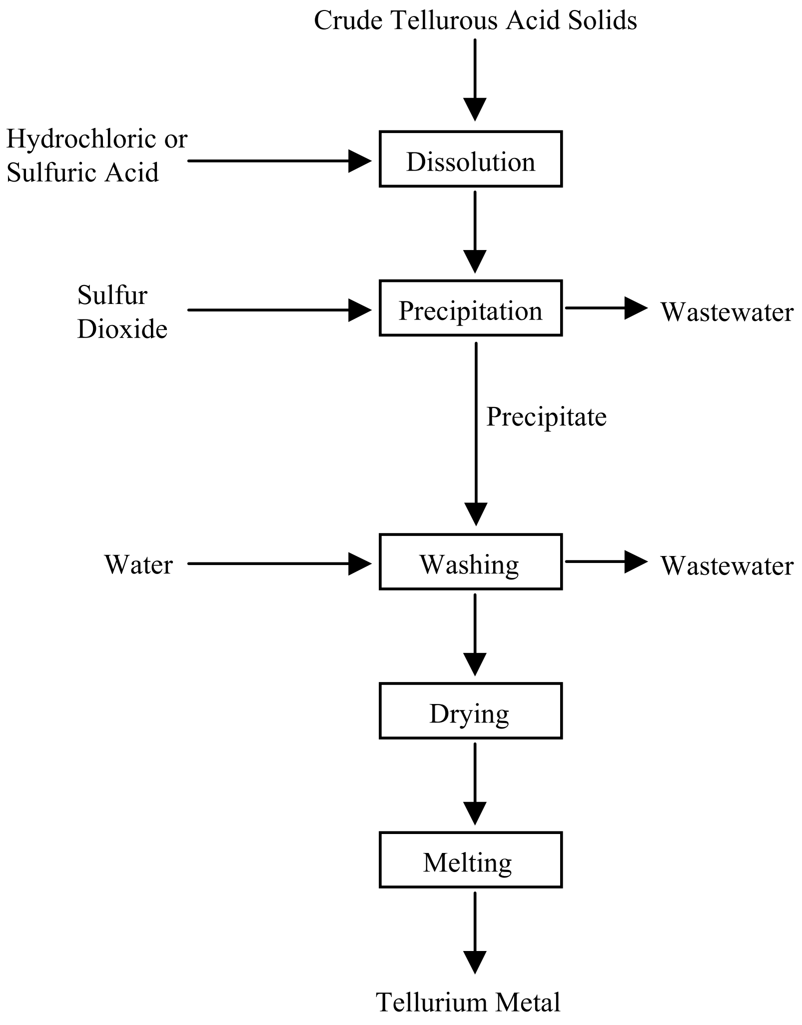
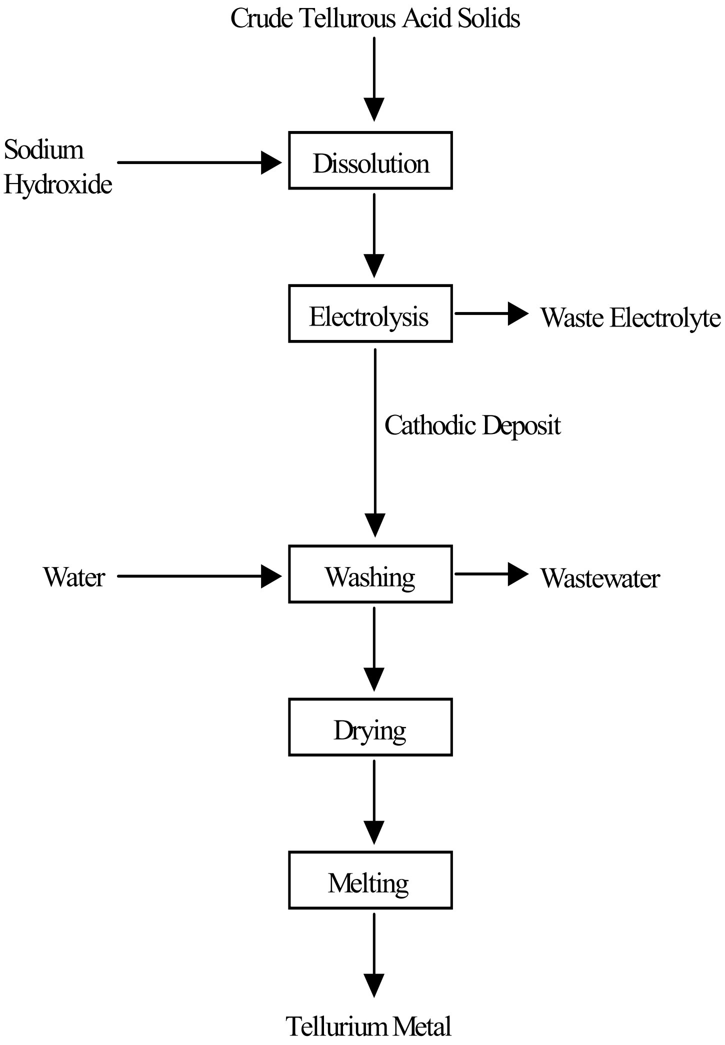


EXHIBIT 3

ELECTROLYTIC PURIFICATION OF TELLURIUM

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 204 - 210.)



Removal of copper and production of tellurous acid

Since tellurium is recovered from copper refinery slimes, the first step in the recovery process shown in Exhibit 1 is the removal of copper from the slimes. Copper is generally removed by aeration in dilute sulfuric acid, oxidative pressure-leaching with dilute sulfuric acid, or digestion with strong acid followed by water-leaching. During the copper removal, much of the tellurium is dissolved. This tellurium is recovered by cementing (precipitation of metallic copper), leaching the cement mud with dilute caustic soda, and neutralizing with sulfuric acid. The precipitate from the neutralization contains tellurium as tellurous acid suitable for recovery.[5] Some of the liquid wastes from this neutralization/precipitation step are sent to selenium recovery.

Copper-free slimes are treated by one of the four following methods: (1) refining with soda ash in a doré or cupeling furnace; (2) combined oxidation and alkalinization by roasting or baking a slime-soda ash mix; (3) removal of selenium by roasting and caustic soda leaching; or (4) boiling the slime with caustic soda. The soda slag from the soda refinement or the roasted product of the oxidation is leached with water to extract sodium tellurite. The insoluble sodium tellurate in the leached slag is returned to the copper-anode furnace. The liquor obtained from the selenium removal and the boiling with caustic soda contains lead. In all cases, the solution contains selenium and impurities. Whatever the method, the liquor is neutralized to pH 6-6.2 with sulfuric acid to precipitate impure tellurous acid as tellurium mud, which contains lead sulfate, silica, and other impurities. The mud is purified by redissolving in caustic soda and reprecipitating. Impurities, such as lead are, removed by careful precipitation from the caustic solution with sodium sulfide. Fractional neutralization of the initial impure caustic solution yields tellurous acid of a purity acceptable for reduction to the metal.[6]

Recovery and purification of tellurium

Tellurium is recovered from the precipitated tellurous acid by three methods: (1) direct reduction; (2) acid precipitation; and (3) electrolytic purification. The electrolytic purification method is the preferred method.[7] The high boiling temperature of tellurium precludes purification by atmospheric distillation, but low pressure distillation is feasible. Heavy metal impurities (iron, copper, tin, lead, antimony, bismuth) remain in the still residue. Volatile selenium is a persistent contaminant, and may be as high as 500 ppm in the distilled tellurium.[8]

Direct Reduction. Some of the drawbacks associated with direct reduction include heavy fuming of telluride dioxide and the formation of organic decomposition products. The reduction with sulfur is rapid and leaves a clean melt, but the heavy fumes are problematic.[9]

Acid Precipitation. As presented in Exhibit 2, purification by acid precipitation first involves dissolving the crude tellurous acid solids in hydrochloric acid or sulfuric acid. Crude common salt is added to the acidified solution, and tellurium is precipitated by adding sulfur dioxide. The resultant precipitate undergoes filtration, washing, drying, and melting. In an alternative method, tellurium is dissolved in a strong nitric acid, hydrolyzed to white $2TeO_2NO_3$ and precipitated by diluting and boiling, and separating. The resultant precipitate is washed (redissolving and rehydrolyzing, if desired), dissolved in hydrochloric acid, and reduced with sulfur dioxide. Ultra high-purity tellurium is prepared by zone refining in a hydrogen or inert-gas atmosphere.[10]

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[5] Ibid., p. 662.

[6] Ibid.

[7] Ibid.

[8] Ibid.

[9] Ibid.

[10] Ibid.

Electrolytic Purification. As shown in Exhibit 3, electrolytic purification involves dissolving crude tellurous acid solids in caustic soda to yield a solution containing sodium tellurite and free caustic soda. The solution then undergoes electrolysis in a cell equipped with stainless-steel electrodes. The cathodes are then removed, washed, dried, and melted.[11]

As a result of a modernization, KUCC also recovers tellurium. Following decopperization, the autoclave liquid is processed through a column containing copper to extract copper telluride. The tellurium cementate is then packaged in drums for sale.[12]

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

None Identified.

4. Beneficiation/Processing Boundary

Since tellurium is recovered from anode slimes from a copper refinery, all wastes generated by this mineral commodity sector are mineral processing wastes. For a description of the beneficiation/processing boundary for this sector, please see the report on copper presented elsewhere in this background document.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Not Applicable

2. Mineral Processing Wastes

Recovery from Copper Anode Slimes

Slag. As shown in Exhibit 1, slag is generated from roasting and leaching. Slag from leaching may be wasted or returned to a copper anode for further processing while the slag from roasting is wasted.[13] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 1,000 metric tons/yr, and 4,500 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity for selenium. This waste formerly was classified as a by-product.

Solid waste residues. Solids, likely containing sulfur, are generated from precipitation as impurities and are discarded as waste.[14] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 1,000 metric tons/yr, and 4,500 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for selenium.

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[11] Ibid.

[12] 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.

[13] U.S. Environmental Protection Agency, "Tellurium", from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, Office of Solid Waste, 1988, pp. 204 - 210.

[14] U.S. Environmental Protection Agency, 1988, Op. Cit, pp. 204 - 210.

Wastewater. There is wastewater associated with the neutralization steps that follow both the addition of sulfuric acid and the addition of sodium sulfide in Exhibit 1. The liquid resulting from the addition of sulfuric acid is sent to selenium recovery. Generation rate estimates for this waste stream are included in the estimates for the wastewater stream from purification of tellurous acid as discussed below.

Purification of Tellurous Acid

The following wastes have been identified as generated during the purification step.

Fumes of Telluride dioxide. Telluride dioxide fumes are generated during the direct reduction step.

Wastewater. One of the waste streams associated with the acid precipitation step of tellurium recovery is wastewater from washing, with an acidic pH. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 10,000 metric tons/yr, and 20,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristics of toxicity (selenium) and corrosivity. This waste formerly was classified as a spent material.

Waste Electrolyte. Waste electrolytes are generated during electrolytic purification. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 1,000 metric tons/yr, and 10,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (lead and 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 naphtha), and acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors.

E. Summary of Comments Received by EPA

New Factual Information

One commenter indicated that its facility now recovers tellurium (COMM 40). This new information has been incorporated in the "Recovery and puification of tellurium" section.

Sector-specific Issues

None.

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"Tellurium." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XXII. 1983. pp. 658-663.

U.S. Environmental Protection Agency. "Tellurium." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste. 1988. pp. 204-210.

TIN

A. Commodity Summary

The primary source of tin is the mineral cassiterite, SnO_2, which occurs in vein and lode deposits. More than 80% of the tin ore in the world is found in placer deposits with tin content as low as 0.015%.[1] Final uses of tin include cans and containers, electrical components, construction, transportation, and other uses.[2]

China and Brazil are the world's largest producers of tin, followed by Indonesia and Bolivia. These countries account for 77% of U.S. tin imports. Tin production in the United States is negligible, with small amounts of tin concentrates mined from a placer deposit at Cache Creek Gold Mine near Fairbanks, Alaska in 1993.[3] The sole U.S. tin smelter in Texas City, Texas ceased production in 1989.[4]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Tin concentrate is processed by smelting and refining. Prior to smelting, any impurities in the concentrate are removed by roasting, leaching with water, and acid leaching. Cassiterite, a carbon reducing agent, and limestone and silica are smelted to create molten tin, which is cast in slabs. These slabs are then refined either pyrometallurgically or electrolytically.

2. Generalized Process Flow Diagram

Tin smelting is most commonly conducted in reverberatory furnaces because they offer better process control and yield cleaner slags. Electric furnaces are sometimes used by smaller smelters for their energy efficiency.[5] Blast furnaces, kilns, and horizontal furnaces are used to smelt low-grade tin concentrate.[6]

As shown in Exhibit 1, smelting is conducted as a batch operation in which a charge of cassiterite (tin oxide) concentrate, a carbon reducing agent (coke), and fluxes consisting of limestone and silica is smelted for 10 to 12 hours in a two-stage process. In the first stage, carbon monoxide is formed in the furnace and reacts with cassiterite (tin oxide concentrate) to produce tin and carbon dioxide. The silica flux reacts with cassiterite under reducing conditions to yield stannous silicate. Iron, which is also present in the concentrate, reacts with silica to yield ferrous silicate. In the second stage, the silicates fuse with fluxes to create a liquid slag. Unreacted carbon in the fuel reduces the stannous silicate to tin and the ferrous silicate to iron.[7,8] In addition to molten tin and slag, an off-gas is

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[1] "Tin and Tin Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, pp. 18, 23.

[2] J. Carlin, "Tin," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 182-178.

[3] Randol Mining Directory 1994/95, p. 189.

[4] J. Carlin, 1994, Op. Cit., pp. 182-183.

[5] U.S. Bureau of Mines, Mineral Facts and Problems, Bulletin 675, 1985, p. 850.

[6] Carr, D., ed., Industrial Minerals and Rocks, Society for Mining, Metallurgy, and Exploration, Inc., 1994, p. 672.

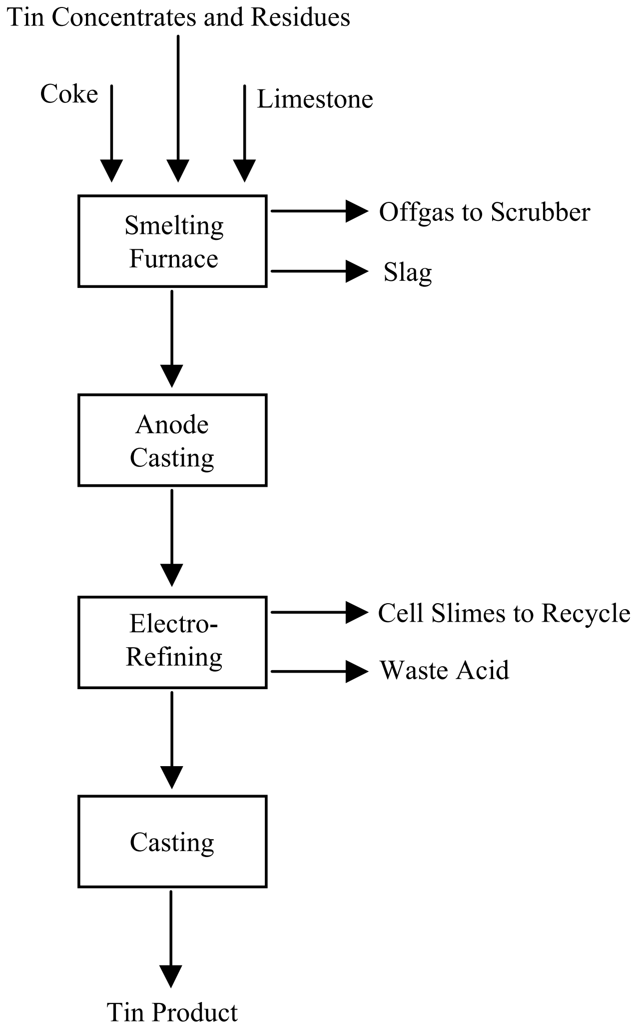
[7] U.S. Environmental Protection Agency, “Tin,” from 1988 Final Draft Summary Report to Mineral Industry Processing Wastes, 1988, pp. 3-214.

[8] Carr, D., ed., 1994, Op. Cit., p. 672.

EXHIBIT 1

TIN SMELTING PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3 - 214.)



also generated and is sent to a caustic scrubber to control sulfur dioxide emissions. Additional wastes include brick linings from the furnace and spent fabric filters, both of which are recycled.

After smelting, the batch is tapped into a settler; slag overflows the settler and is collected and resmelted, while the remaining molten tin is cast into slabs (tin anodes) to be refined.[9] Crude tin is most commonly refined by heat treatment (pyrometallurgical) but can also be refined by electrolytic methods.

Heat treatment consists of heating the tin slab slightly above its melting point but below the melting points of impurities, such as iron and copper. The molten tin is poured into kettles and agitated in a process called boiling. Remaining impurities collect in a surface layer of dross, which is skimmed and resmelted. The remaining tin, with a purity greater than 99.8%, is cast in molds.

Electrolytic refining (see Exhibit 1) requires greater capital expenditures for equipment but yields a purer product. Electrorefining may be conducted in either an acid or alkaline bath.[10] The acid bath consists of stannous sulfate, creosulfonic or phenolsulfonic acids, and free sulfuric acid with beta naphthol and glue to prevent deposits from forming on the cathodes. Slimes can form on the tin anodes if the anodes have high lead levels; the slimes are scrubbed off. The alkaline bath consists of potassium or sodium stannite and free alkali. Lead is precipitated as lead plumbite in slimes that form on the anodes. Pure tin generated in either bath is recast into ingots for sale.[11] Waste slimes and waste acid or alkaline baths are shipped off-site for reprocessing and recycle.

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

A research program is being conducted at the Colorado School of Mines for developing a pyrochemical process using molten salts for recovering reactive metals, including tin, from beneficiated ore. The process takes place in a hybrid reactor combining electrolytic production of a calcium reductant and *in situ* utilization of the reductant to reduce metal compounds, specifically tin oxide. The reactor operates at a temperature less than 1,000°C. The technology is reported to generate little waste.[12]

4. Beneficiation/Processing Boundary

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

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

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[9] U.S. Bureau of Mines, 1985, Op. Cit., p. 850.

[10] "Tin and Tin Alloys," 1983, Op. Cit., p. 23.

[11] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-214.

[12] Mishra, B., D. Olson, and W. Averill, "Applications of Molten Salts in Reactive Metals Processing," presented at the Conference for Emerging Separation Technologies for Metals and Fuels, Palm Coast, FL, March 13-18, 1993, sponsored by the Minerals, Metals, & Materials Society, Warrendale, PA.

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between acid leaching and smelting. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the cassiterite occurs. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Waste streams include tailings slurry and process wastewater from mining placer deposits, which are held in a tailings pond for settling of solids. The remaining water is either discharged to receiving waters through an NPDES outfall or reused in the mining process.[13] Most likely contaminants are arsenic, lead, and zinc. Other beneficiation wastes generated during roasting and acid leaching include spent waste acids, sludges, and waste liquids.

2. Mineral Processing Wastes

Smelting operations generate solid, liquid, and gaseous wastes. However, since tin is no longer produced domestically, these waste streams were not included in our analysis.

Slag

Slag is generated during smelting of tin concentrates through the fusion of ferrous silicate with limestone flux. Slag is collected when molten tin is tapped into a settler. Slag is believed to be resmelted and is therefore most likely not disposed as a solid waste. The Newly Identified Mineral Processing Waste Characterization Data Set (NIMPW Characterization Data Set) indicates that, when operating, the sole U.S. tin smelter generated approximately 15,000 metric tons of slag annually.[14] 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.

Process Wastewater and Treatment Impoundment Sludge

Process wastewater is generated as blowdown from the scrubbing of off-gases generated during smelting. Approximately 83,000 metric tons are generated annually by two plants when they are operating;[15] in 1984, the

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[13] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-211.

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

[15] Ibid.

Texas City smelter generated 22,000 liters of wastewater per metric ton of tin produced.[16] Process wastewater is disposed in impoundments and treated by chemical precipitation and sedimentation; solids settle to create treatment impoundment sludge.

EP toxicity tests conducted in 1984 on samples of scrubber solids and pond water revealed the wastes to exhibit the characteristic of EP toxicity for arsenic (15.5 ppm for scrubber solids, 22.9 ppm for scrubber pond water).[17] Sampling results are shown in Attachment 1.

Brick Lining and Fabric Filters

Furnaces used in smelting tin concentrates are lined with brick, which periodically must be replaced. Spent brick is resmelted for its tin value.

Fabric filters used in baghouses for filtering off-gases are recycled when spent.

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.

Refining, both through heat treatment (pyrometallurgically) and electrolytically, generate solid and liquid wastes, as described below.

Dross

Dross forms during pyrometallurgical refining when tin slab is heated above its melting point; impurities such as lead and copper are captured in a layer of dross at the surface of the molten tin. Dross is skimmed and resmelted. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

Waste Acid and Alkaline Baths

A waste electrolyte stream (waste baths), generated in electrolytic refining, most likely contains high metals concentrations and may exhibit the corrosivity and EP toxicity characteristics.[18] Waste baths are shipped off-site for reprocessing.[19] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (arsenic, cadmium, chromium, lead, and mercury) and corrosivity.

Slimes

Slimes, which form on tin anodes during electrolytic refining, may be corrosive and contain high levels of lead. Slimes are shipped off-site for reprocessing.[20] 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,

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[16] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-214.

[17] U.S. Environmental Protection Agency, 1992, Op. Cit., pp. 34-2.

[18] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-212.

[19] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-215.

[20] Ibid.

medium, and high annual waste generation rate of 0 metric tons/yr, 100 metric tons/yr, and 200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (lead) and corrosivity.

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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U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992.

TITANIUM

A. Commodity Summary

Titanium (Ti) metal is known for its high strength-to-weight ratio and corrosion resistance. Titanium metal is alloyed with aluminum and vanadium, among other metals, for use in aircraft and spacecraft; in 1994, about 70 percent of titanium metal produced was used in jet engines, airframes, and space and missile applications.[1] Titanium metal is also employed in the chemical, power generation, marine, ordnance, and medical industries. Titanium is also used in ceramics, coatings for welding rods, heavy aggregate, and steel furnace flux. The major use of titanium, however, is as a white pigment for paints, rubber, paper, and plastics.[2] Titanium tetrachloride, an intermediate in TiO_2 production, is also sold for use in the production of titanium metal.

Ilmenite ($FeTiO_3$) is the most abundant titanium-bearing mineral and is comprised of about 43 percent to 65 percent titanium dioxide (TiO_2). A second major mineral form of titanium is rutile, a crystalline, high-temperature polymorph of TiO_2, containing about 95 percent TiO_2. Another crystalline form of TiO_2, anatase, is not commercially available at present, but deposits of anatase-bearing ore are being developed in Brazil.[3] Titanium minerals are found in hard rock deposits in New York, Virginia, North Carolina, Arkansas, Wyoming, and California, and in beach and alluvial sands ("black sands") in the Atlantic and Gulf Coastal Plain geologic provinces in the southeast and southern U.S.[4] Other sources of titanium include titaniferous slags (70-85 percent TiO_2) made by electric furnace smelting of ilmenite with carbon.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Titanium dioxide pigment is manufactured through either the sulfate, chloride, sulfate-chloride, or chloride-ilmenite process. The sulfate process, used at two U.S. plants, employs digestion of ilmenite ore or TiO_2-rich slag with sulfuric acid to produce a cake, which is purified and calcined to produce TiO_2 pigment. The sulfate process generates sulfuric acid wastes in as much as two times the product weight, requiring treatment by neutralization before disposal of the wastes. In the more common chloride process, rutile, synthetic rutile, or high-purity ilmenite is chlorinated to form titanium tetrachloride, which is then purified to form TiO_2 pigment. The sulfate-chloride process, used by one facility, employs both the sulfate and chloride processes to manufacture TiO_2 pigment. In the sulfate phase of the sulfate-chloride process, TiO_2 rich slag is digested with sulfuric acid to produce a porous cake, which is purified and calcined to produce TiO_2 pigment. In the chloride phase, rutile ore is chlorinated to form titanium tetrachloride, which is then purified to form TiO_2 pigment. A fourth process, the chloride-ilmenite process, is similar to the chloride process, but a low-purity ilmenite is converted to titanium tetrachloride in a two-stage chlorination process. This proprietary process is conducted exclusively by Du Pont at its Edgemoor, DE and New Johnsonville, TN plants and at its DeLisle plant in Pass Christian, MS. Exhibit 1 presents active U.S. titanium dioxide production facilities and the processes and ores utilized at each.

Titanium sponge, which is cast into ingots for further processing into titanium metal, is produced by purifying titanium tetrachloride generated by the chloride process. Exhibit 2 presents the active U.S. titanium sponge and ingot production facilities.

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[1] J. Gambogi, "Titanium and Titanium Dioxide," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 180.

[2] J. Gambogi, Annual Report: Titanium-1992, U.S. Bureau of Mines, December 1993, p. 1.

[3] J. Gambogi, 1993, Op. Cit., p. 1.

[4] U.S. Environmental Protection Agency, "Titanium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. p. 3-217.

EXHIBIT 1
U.S. TITANIUM DIOXIDE PRODUCTION FACILITIES[a]

Facility Name	Location	Process	Ore Type
E.I. Du Pont de Nemours & Co., Inc. (Du Pont)	Antioch, CA	Chloride	Rutile
Du Pont	Edgemoor, DE	Chloride-Ilmenite	Ilmenite
Du Pont	New Johnsonville, TN	Chloride-Ilmenite	Ilmenite
Du Pont	Pass Christian, MS	Chloride-Ilmenite	Ilmenite
Kemira, Inc.	Savannah, GA	Sulfate-Chloride	Slag/Rutile
Kerr-McGee Chemical Corp.	Hamilton, MS	Chloride	Synthetic Rutile
Kronos, Inc.	Lake Charles, LA	Chloride	Unknown
SCM Chemicals, Inc.	Ashtabula, OH	Chloride	Rutile S. African Slag
SCM Chemicals, Inc.	Baltimore, MD	Chloride	Rutile
		Sulfate	S. African Slag

[a] J. Gambogi, 1993, Op. Cit., p. 13.

2. Generalized Process Flow Diagram

Sulfate Process

In the sulfate process, which is presented in Exhibit 3, ilmenite ore or slag with high TiO_2 content is digested with sulfuric acid, forming a porous cake; this cake is further dissolved by dilute acid to form titanyl sulfate ($TiOSO_4$). Scrap iron is added to the digestion process to ensure that iron impurities remain in the ferrous (Fe^{2+}) state so that the eventual TiO_2 product can be easily washed. The titanyl sulfate solution is then clarified, yielding what was formerly characterized as a waste sludge, and then concentrated through vacuum evaporation, which promotes crystallization of copperas (ferrous sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$) to remove iron. (If low-iron, high-TiO_2 slag is used as feed, it is not necessary to crystallize copperas.) Copperas by-product is separated by filtration, which also removes a second material formerly characterized as a waste sludge. The filtered titanyl sulfate solution is vacuum-evaporated a second time and hydrolyzed at 90° C to precipitate hydrated titania ($TiO(OH)_2$). The titania hydrate is then filtered and washed, yielding filtrate waste and wastewater, respectively, before being calcined at 1,000° C to produce TiO_2 product.[5]

Chloride Process

In the chloride process, presented in Exhibit 4, rutile or high-grade ilmenite is converted to titanium tetrachloride ($TiCl_4$). The conversion takes place in a chlorinator (e.g., fluidized bed reactor) in the presence of

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[5] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-221 - 3-222.

EXHIBIT 2
U.S. TITANIUM SPONGE AND INGOT PRODUCTION FACILITIES[b]

Facility Name	Location	Product
Howmet Corp., Titanium Ingot Div.	Whitehall, MI	Ingot
A. Johnson Metals Corp.	Lionville, PA	Ingot
Lawrence Aviation Industries, Inc.	Port Jefferson, NY	Ingot
Oregon Metallurgical Corp. (Oremet)	Albany, OR	Sponge & Ingot
RMI Co.	Niles, OH	Ingot
Teledyne Allvac	Monroe, NC	Ingot
Teledyne Wah Chang Albany	Albany, OR	Ingot
Titanium Hearth Technologies of America	Lionville, PA	Ingot
Titanium Metals Corp. of America (Timet)	Henderson, NV	Sponge & Ingot
Viking Metallurgical Corp.	Verdi, NV	Ingot
Wyman-Gordon Co.	Worcester, MA	Ingot

[b] J. Gambogi, 1993, Op. Cit., p. 11.

chlorine gas at 850° C to 950° C, with petroleum coke added as a reductant. All U.S. producers of $TiCl_4$ use fluid-bed chlorinators; static-bed systems also can be used.[6] The volatile metal chlorides, including $TiCl_4$, are collected, and the non-volatile chlorides and the unreacted solids that remain in the chlorinator are wasted, forming the special waste stream "chloride process waste solids."[7] The gaseous product stream is purified to separate the titanium tetrachloride from other chlorides. Separation is by fractional condensation, double distillation, and chemical treatment. Ferric chloride ($FeCl_3$) is removed as an acidic liquid waste stream through fractional condensation. Additional trace metal chlorides are removed through double distillation. Finally, vanadium oxychloride ($VOCl_3$), which has a boiling point close to that of $TiCl_4$ (136° C), is removed as a low-volume non-special waste by complexing with mineral oil and reducing with hydrogen sulfide to $VOCl_2$, or by complexing with copper (not shown in Exhibit 4). The purified $TiCl_4$ is then oxidized to TiO_2 at 985° C, driving off chlorine gas, which is recycled to the chlorinator. Aluminum chloride is added in the oxidation step to promote formation of the rutile crystal, which is the TiO_2 product.[8]

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[6] J. Gambogi, 1993, Op. Cit., p. 3.

[7] U.S. Environmental Protection Agency, "Titanium Tetrachloride Production," from Report to Congress on Special Wastes from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, p. 13-3.

[8] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-222.

EXHIBIT 3

SULFATE PROCESS FOR TITANIUM DIOXIDE PRODUCTION

(Adapted from: U.S. Environmental Protection Agency, 1988, p. 3-221.)

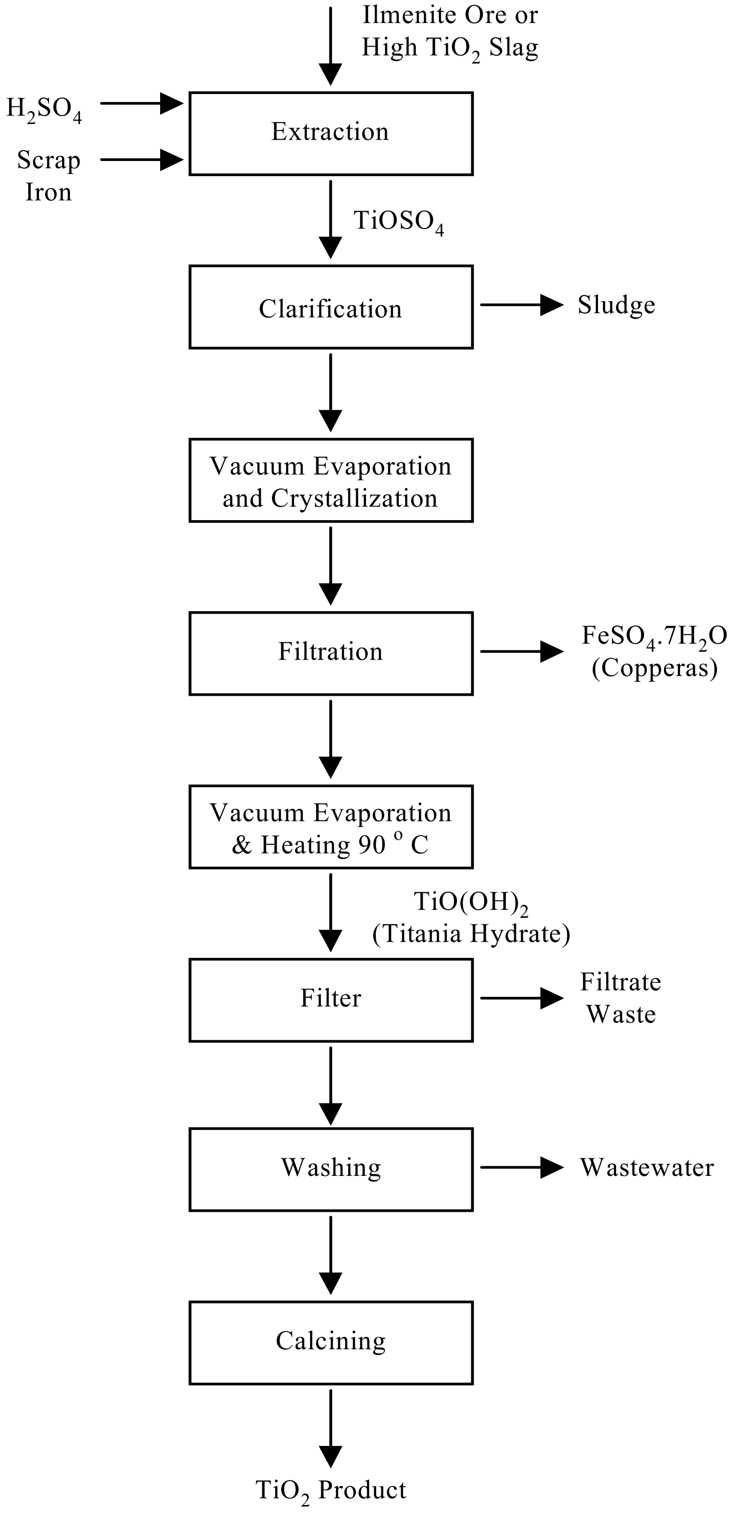
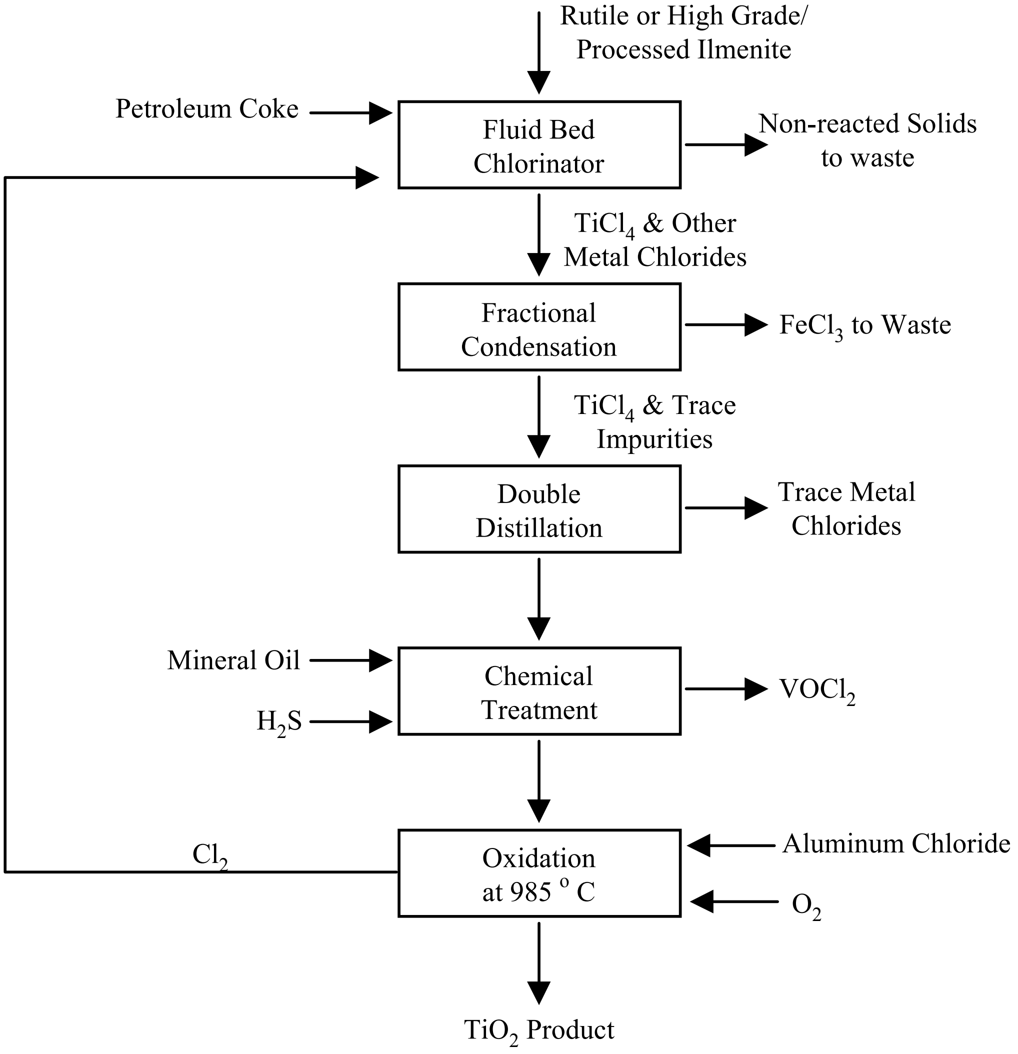


EXHIBIT 4

CHLORIDE PROCESS FOR TITANIUM DIOXIDE PRODUCTION

(Adapted from: U.S. Environmental Protection Agency, 1988, p. 3-223.)



Sulfate-Chloride Process

The sulfate-chloride processes uses both the sulfate and chloride processes. Kemira, located in Savannah, Georgia, is the only facility known to use this combined process to manufacture TiO_2 pigment. In the sulfate process, TiO_2 rich slag is digested with sulfuric acid to produce a porous cake, which is purified and calcined to produce TiO_2 pigment. In the facility's chloride process, rutile ore is chlorinated to form titanium tetrachloride, which is then purified to form TiO_2 pigment. As part of the sulfate process, the facility transports the weak acid wastewater from the manufacturing process in above ground pipes to an on-site elementary neutralization unit for neutralization. The wastewater is discharged via an NPDES-permitted outfall to the Savannah River; the remaining non-hazardous solids are then sold as a product. Other wastewater generated by Kemira is treated in an in-plant neutralization system, and pumped through a series of ponds and then discharged to an NPDES-permitted outfall.

Chloride-Ilmenite Process

In the chloride-ilmenite process, presented in Exhibit 5, low-grade ilmenite (approximately 65 percent TiO_2) is converted to $TiCl_4$. The ilmenite ore used in the process contains a much larger amount of iron than the other ores (i.e., rutile or high-grade ilmenite) used to produce $TiCl_4$. As in the chloride process, the chloride-ilmenite process takes place in a chlorinator in which the ore is chlorinated in the presence of coke as a reducing agent. According to Du Pont, however, the process differs from the chloride process in that it is a two-step reaction sequence referred to as "selective chlorination." Both of these steps occur in the chlorinator. In the first step, ilmenite ore is reacted with the chlorine gas and coke. Within seconds, the chlorine reacts with the iron oxide in the ilmenite ore, producing gaseous iron chlorides that are subsequently condensed in a spray condenser to form iron chloride waste acids, which are either sold as product or disposed as part of the waste stream "titanium tetrachloride waste acids." This step reportedly yields enriched ilmenite ore consisting of more than 95 percent TiO_2 and having the same basic particle structure as the original ilmenite ore feed.[9] In the second (or processing) step of the simultaneous beneficiation-chlorination process, the beneficiated ore, which remains in the chlorinator, is converted to gaseous $TiCl_4$ over a period of several hours. The $TiCl_4$ is further refined to remove contaminants, which are combined with the iron chloride waste stream.[10] The process for converting $TiCl_4$ to TiO_2 is similar to that used in the chloride process, as described above.

Titanium Sponge (Kroll Process)

The production of titanium sponge by the Kroll process, as shown in Exhibit 6, requires the same feed materials as does the chloride process for pigment production, because both require $TiCl_4$. $TiCl_4$ used for sponge production is made in the same manner as that for pigment production; however, because $TiCl_4$ needed for metal production must have high purity, more effort is expended to remove impurities, particularly oxygen and carbon compounds.[11] Rutile and rutile substitutes are the only titanium feed materials used for sponge production,[12] presumably because they offer a more pure source of titanium than ilmenite.

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[9] Memorandum from D. Derkics, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, "Notes of the October 24, 1989 Meeting with Representatives of E.I. DuPont de Nemours & Company," submitted to Mining Waste Docket No. F-89-MW2P-FFFFF, 1989, p. 2.

[10] Letter from C. Goldstein, Covington & Burling, Washington, D.C., to Randolph L. Hill, U.S. Environmental Protection Agency, Office of General Counsel, November 16, 1990, p. 2.

[11] "Titanium and Titanium Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1981, p. 114.

[12] J. Gambogi, 1993, Op. Cit., p. 4.

EXHIBIT 5

CHLORIDE-ILMENITE PROCESS SCHEMATIC - DELISLE PLANT

(Adapted from: U.S. EPA National Survey of Solid Wastes from mineral Processing Facilities: Questionnaire # 102013, 1989.)

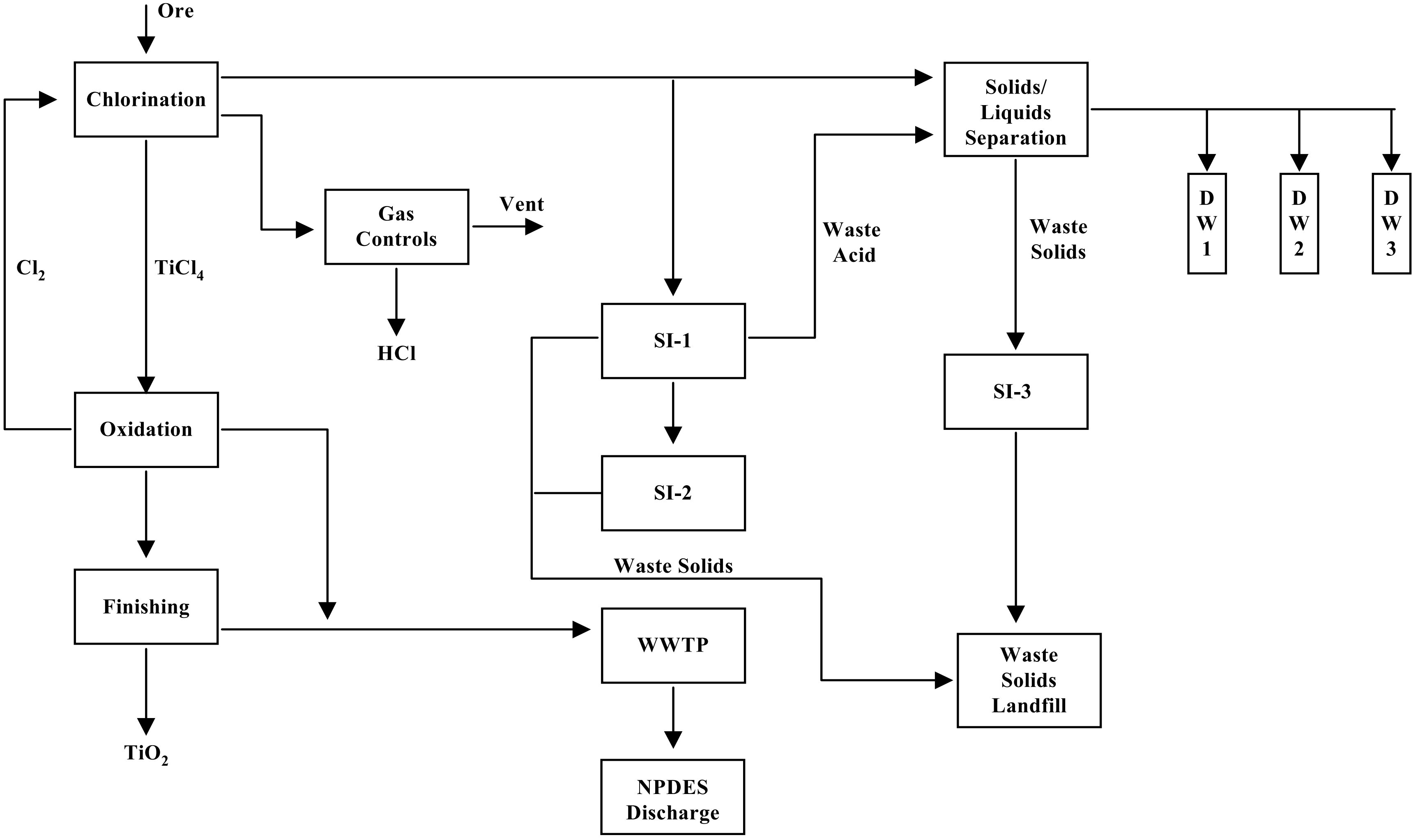
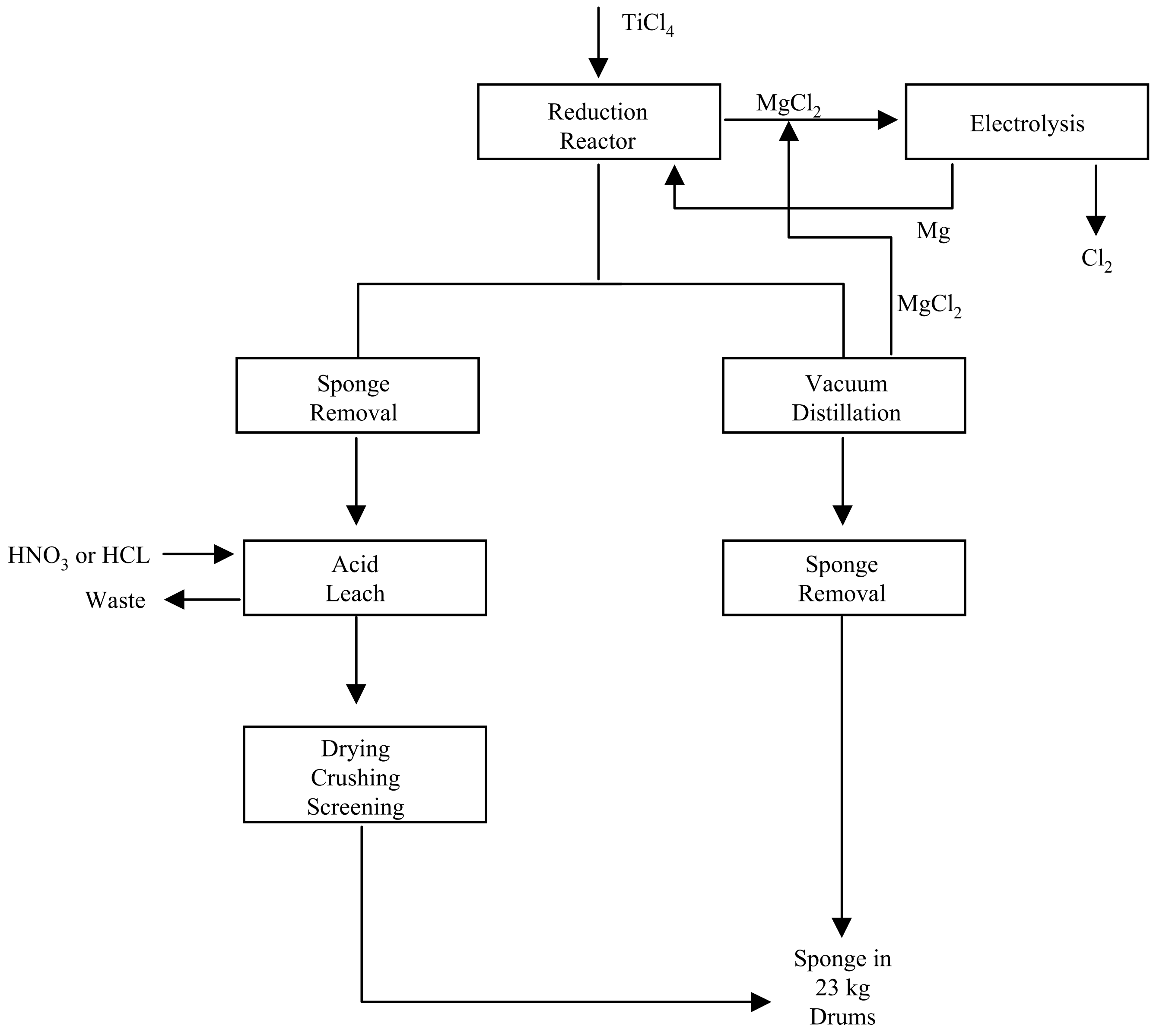


EXHIBIT 6

KROLL PROCESS FOR TITANIUM SPONGE PRODUCTION

(Adapted from: U.S. Environmental Protection Agency, 1988, p. 3-223.)



The Kroll process, based on the use of liquid magnesium as a reductant in an argon or helium atmosphere, is the major commercial process for producing titanium sponge. (The Hunter process, which relies on sodium as the reductant, is another sponge production process.) $TiCl_4$ and liquid magnesium are combined in a reduction reactor at 900° C to form molten magnesium chloride ($MgCl_2$), which is tapped from the bottom of the reactor. The $MgCl_2$ is reduced by electrolysis to form magnesium metal (which is recycled to the reactor) and chlorine gas. The product, called sponge because of its appearance and high porosity, is processed further to remove residual magnesium, $MgCl_2$, and unreacted $TiCl_4$, which can comprise as much as 30% by weight.[13] (Prior to purification, the sponge is crushed to improve purification.) Two methods are commonly used. Nitric acid (HNO_3) or hydrochloric acid (HCl) is used to acid leach the sponge, creating an acidic liquid waste, known as leach liquor, containing the impurities (primarily $MgCl_2$), while vacuum distillation at 960-1,020° C separates the sponge from a $MgCl_2$ stream that can be recycled to the electrolysis step and used in the reduction reactor.[14] Sponge can also be purified using an inert (argon) gas sweep at 1,000° C.[15,16] After drying, crushing, and screening, the sponge is packaged in air-tight 23-kg drums before further processing into ingots. Sponge also can be crushed to create titanium powder.

Titanium Ingot

Titanium ingots are formed from sponge using two or more successive vacuum-arc melting operations.[17] Scrap titanium metal or alloys can be added. Ingots can be milled by conventional methods of forging, hot- and cold-rolling, and extrusion.

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

The U.S. Bureau of Mines has studied new processes to produce titanium alloys, with a focus on developing a continuous process to produce titanium powder for metallurgical applications. The Bureau also has researched methods to improve present methods of batch-type reduction, arc melting, and fabrication of titanium alloys.[18]

4. Beneficiation/Processing Boundary

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

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

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[13] "Titanium and Titanium Alloys," 1981, Op. Cit., p. 116.

[14] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-224 - 3-225.

[15] J. Gambogi, 1993, Op. Cit., p. 4.

[16] "Titanium and Titanium Alloys," 1981, Op. Cit., p. 116.

[17] J. Gambogi, 1993, Op. Cit., p. 4.

[18] J. Gambogi, 1993, Op. Cit., p. 8.

operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs just before the acid digestion step in the sulfate process (identified as the "extraction" step in Exhibit 3). EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because this is where TiO_2 in the ore undergoes a significant chemical change through conversion by H_2SO_4 to $TiOSO_4$. In both the chloride and chloride-ilmenite processes, the beneficiation/processing line occurs just before the chlorination step. Similarly, beneficiation ends and mineral processing begins at this point because TiO_2 is chemically converted to $TiCl_4$ through reaction with chlorine. 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/Beneficiation Wastes

Hard rock deposits of ilmenite and rutile are mined in open pits; mined ore is crushed, ground, classified, magnetically separated, and floated to recover ore values. The major wastes from these operations are tailings from separators and flotation cells and, based on EPA data, these wastes are not expected to exhibit hazardous characteristics. Beach/alluvial sands containing ilmenite and rutile are excavated by dragline, front-end loader, or suction dredging; the sands are spiral concentrated to remove low density tailings. The sands are then dried and separated electrostatically to remove quartz and other nonconducting minerals, which are processed to produce zircon and monazite product and wastes consisting of quartz and epidote minerals. Conducting materials are magnetically separated to sort ilmenite from rutile, followed by screening and cleaning. No wastes from beach sand processing are expected to exhibit hazardous characteristics.[19]

2. Mineral Processing Wastes

The **sulfate process** for producing titanium dioxide yields two mineral processing wastes, waste solids and waste acids. These wastes are described below.

Sulfate Process Waste Solids

Waste solids are generated at two points in the sulfate process. The first point occurs when titanyl sulfate ($TiOSO_4$), which is generated by digesting ilmenite or slag with sulfuric acid, is clarified. This material (formerly characterized as a waste sludge) also is generated when copperas by-product ($FeSO_4 \cdot 7H_2O$) is separated from the solution containing titanyl sulfate after the solution is concentrated through vacuum evaporation. This waste stream was removed from the Mining Waste Exclusion because it is generated in volumes less than the high volume criterion of 45,000 metric tons per facility annually. (Volume data are unavailable for this waste stream due to

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[19] U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-219.

confidential business information [CBI] designation.) The waste did pass the low hazard criterion for special waste status.[20]

Sulfate Process Waste Acids

Waste acids are generated when titania hydrate, generated by vacuum-evaporation and hydrolysis of titania sulfate, is filtered prior to washing. The operator of the Kemira, Inc. facility in Savannah, GA, treats this waste acid filtrate (which has a field pH of 0.5) with lime in its waste acid neutralization plant and discharges the treated effluent through an NPDES outfall to the Savannah River.[21] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 200 metric tons/yr, 39,000 metric tons/yr, and 77,000 metric tons/yr, respectively. This waste stream was removed from the Mining Waste Exclusion because it failed the low hazard criterion for chromium and pH (i.e., it exhibits the characteristics of toxicity and corrosivity).[22] Additional data (Attachment 1) also suggest that this waste stream exhibits the toxicity characteristic for arsenic, chromium, selenium, and silver.

The **chloride process** and **chloride-ilmenite process** for manufacturing $TiCl_4$ each generate two primary mineral processing wastes, waste acids and waste solids. Waste acids and solids are recovered from the fluid-bed chlorinator as a slurry and separated; descriptions of the separated acids and solids are provided below. Several other waste streams are generated in the treatment and disposal of these wastes, including wastewater treatment effluent and solids, which are commonly discharged to on-site surface impoundments prior to the effluent being discharged through an NPDES outfall and the solids being disposed in a landfill. In addition, the chloride and chloride-ilmenite processes generate several other waste streams, including ferric chloride and ferric chloride sludge, scrubber water and solids, and vanadium oxychloride.

Chloride and Chloride-ilmenite Process Waste Acid and Solids

Waste acids and solids from the chloride and the chloride-ilmenite processes are generated in the chlorination step as a combined acids/solids slurry. The combined waste acids and solids are treated by a solids/liquids separation process, and the resulting chloride process waste solids (a mineral processing special waste) are landfilled, while the chloride process waste acids are deep-well injected at some plants. Approximately 49,000 metric tons of waste acids and 414,000 metric tons of waste solids are generated annually.[23] We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristics of toxicity (chromium, selenium, and lead) and corrosivity. This waste was formerly characterized as a spent material. Data for this waste stream are presented in Attachment 1.

Waste Ferric Chloride and Ferric Chloride Treatment Sludge

Waste ferric chloride is generated in both the chloride and the chloride-ilmenite processes when gaseous titanium tetrachloride is separated from other chlorides. Ferric chloride is removed as an acidic, liquid waste stream through fractional condensation and treated with lime and either landfilled or sold as a by-product. Although EPA found no published information regarding waste generation rate or characteristics, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for waste ferric chloride of 22,000 metric tons/yr, 29,000 metric tons/yr, and 35,000 metric tons/yr, respectively. We used best engineering judgment to determine that waste ferric chloride may exhibit the characteristic of corrosivity and the characteristic of toxicity for cadmium, chromium, lead, and silver. This waste is fully recycled and was formerly

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[20] 55 FR 2341-2342.

[21] ICF Incorporated, Kemira, Inc.: Mineral Processing Waste Sampling Visit — Trip Report, September 1989, p. 3.

[22] 55 FR 2342.

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

classified as a by-product. Data for this waste stream are presented in Attachment 1. For ferric chloride treatment sludge, we estimated that the medium annual waste generation rate would be 75 percent of that for waste ferric chloride, with the high and low rates ±20 percent of the medium rate. Therefore, we estimated a low, medium, and high annual waste generation rate for ferric chloride treatment sludge of 18,000 metric tons/yr, 22,000 metric tons/yr, and 26,000 metric tons/yr, respectively. 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.

Two scrubber water waste streams are generated in the chloride process, as described below. Data describing these waste stream are presented in Attachment 1.

Chlorination Off-gas Scrubber Water

Chlorination off-gas scrubber water is generated by the scrubbing of off-gases created in the condensation of the reaction gas produced in the chlorination step. Off-gases are cleaned in water wash towers and then passed through a caustic tower and a Venturi scrubber. After leaving the scrubber, the gas stream is either released to the atmosphere, or passed through three additional scrubbers for further cleansing.[24] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for chlorination off-gas scrubber water of 1.2 million metric tons/yr, 1.5 million metric tons/yr, and 1.8 million metric tons/yr, respectively. (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous individual waste streams.) We used best engineering judgment to determine that chlorination off-gas scrubber water may exhibit the characteristics of corrosivity and toxicity for chromium.

Chlorination Area-Vent Scrubber Water

Chlorination area-vent scrubber water is generated by the scrubbing of cleaned gas from the chlorination off-gas scrubbers (described above) and ventilation vapors from $TiCl_4$ purification operations. This scrubber system, like that for chlorination off-gases, consists of a wash water tower and a Venturi scrubber operated in series. After leaving this scrubber system, the cleaned gases are vented to the atmosphere.[25] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for chlorination area-vent scrubber water of 150,000 metric tons/yr, 180,000 metric tons/yr, and 220,000 metric tons/yr, respectively. We used best engineering judgment to determine that chlorination area-vent scrubber water may exhibit the characteristics of corrosivity and toxicity for chromium.

Spent Vanadium Oxychloride

Vanadium chloride is removed from the gaseous product stream containing $TiCl_4$ by complexing with mineral oil and reducing to vanadium oxychloride ($VOCl_2$), a low-volume non-special mineral processing waste, with hydrogen sulfide, or by complexing with copper. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 22,000 metric tons/yr, and 45,000 metric tons/yr, respectively. 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.

Wastewater Treatment Plant Liquid Effluent

Wastewater treatment plant liquid effluent, a post-mineral processing waste, consists of treated wastewaters such as contact cooling water and/or liquid wastes from the chlorination step (i.e., waste acids) and the $TiCl_4$

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[24] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Volume IX: Primary and Secondary Titanium, Primary Zirconium and Hafnium, EPA 440/1-89-019.9, Office of Water Regulations and Standards, May 1989, p. 4861.

[25] Ibid.

purification, oxidation, or finishing steps. Effluent is sent to a surface impoundment for settling of solids before discharge through an NPDES outfall. 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 900 metric tons/yr, 140 million metric tons/yr, and 270 million metric tons/yr, respectively. (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous waste streams.) Existing data (Attachment 1) and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater Treatment Plant Sludge/Solids

Wastewater treatment plant sludge/solids, also a post-mineral processing waste, consists of what was formerly characterized as sludges and solids resulting from the treatment of the wastewaters described above. These materials are disposed in on- or off-site landfills. Approximately 420,000 metric tons are generated annually.[26] We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (chromium). Data describing this waste stream are presented in Attachment 1.

Spent Surface Impoundment Liquids

Surface impoundment liquids consist of various waste streams, such as chloride process waste acids and solids in slurry form and wastewater treatment plant effluent. Waste acids managed in surface impoundments are generally routed to a solids/liquids separation process and then disposed by deep-well injection. Treated effluent is discharged through NPDES outfalls after solids have settled. This waste stream is considered post-mineral processing. 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 630 metric tons/yr, 3,400 metric tons/yr, and 6,700 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristics of toxicity (chromium and lead). This waste was formerly characterized as a spent material. Data describing this waste stream are presented in Attachment 1.

Spent Surface Impoundment Solids

Surface impoundment solids settle out of liquid and slurry waste streams, such as chloride process waste acids and solids in slurry form and wastewater treatment plant effluent, that are managed in surface impoundments. Surface impoundment solids may be dredged from the impoundment and moved to on- or off-site solids landfills. This waste stream is considered post-mineral processing; approximately 36,000 metric tons are generated annually.[27] We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (chromium and lead). Data describing this waste stream are presented in Attachment 1.

The **Kroll process for manufacturing titanium sponge** from $TiCl_4$ generates seven waste streams, one of which is a mineral processing waste and the others, post-mineral processing wastes.

$TiCl_4$ Purification Effluent

$TiCl_4$ purification effluent, classified as a mineral processing waste, is generated in preparing $TiCl_4$ for the Kroll process. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 26,000 metric tons/yr, 33,000 metric tons/yr, and 39,000 metric tons/yr, respectively. 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.

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[26] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-7.

[27] Ibid.

Reduction Area Scrubber Water

Reduction area scrubber water is generated by the scrubbing of vapors released during magnesium reduction of $TiCl_4$ in the reduction vessel. The vapors are cleansed in the reduction area scrubber and released to the atmosphere, while the resulting scrubber water is treated in the facility wastewater treatment plant.[28] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for reduction area scrubber water of 870,000 metric tons/yr, 1.1 million metric tons/yr, and 1.3 million metric tons/yr, respectively. (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous waste streams.) 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.

Melt Cell Scrubber Water

If the reduction process is conducted rapidly, excess $MgCl_2$ can be generated and is collected in a melt cell before it is recovered through electrolysis. The molten $MgCl_2$ generates vapors that are cleaned by wet scrubbers, which generates melt cell scrubber water containing low concentrations of toxic metals and acidity.[29] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for melt cell scrubber water of 230,000 metric tons/yr, 280,000 metric tons/yr, and 340,000 metric tons/yr, respectively. 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.

Chlorine Liquefaction Scrubber Water

Chlorine liquefaction scrubber water is created by the scrubbing of chlorine gas generated in the electrolytic reduction of $MgCl_2$. The chlorine gas is passed first to bag filters and is then either returned to the reduction process or liquefied and sold. During liquefaction, air saturated with chlorine escapes and is treated by burning to convert the chlorine to hydrochloric acid vapor. This vapor is scrubbed with water, creating the scrubber wastewater.[30] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for chlorine liquefaction scrubber water of 1.6 million metric tons/yr, 2 million metric tons/yr, and 2.4 million metric tons/yr, respectively. (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous waste streams.) 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.

Sodium Reduction Container Reconditioning Wash Water

Sodium reduction container reconditioning wash water is generated in the cleaning the container (retort vessel) in which $TiCl_4$ is converted to titanium metal through sodium reduction.[31] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for sodium reduction container reconditioning wash water of 6,800 metric tons/yr, 8,600 metric tons/yr, and 10,000 metric tons/yr, respectively. 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.

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[28] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 4862.

[29] Ibid.

[30] Ibid.

[31] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 4863.

Chip Crushing Scrubber Water

Chip crushing scrubber water is generated in the cleaning of dust-laden air released during the crushing of titanium chips after they are removed from the reduction container.[32] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for chip crushing scrubber water of 260,000 metric tons/yr, 320,000 metric tons/yr, and 390,000 metric tons/yr, respectively. 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.

Leach Liquor and Sponge Wash Water

Leach liquor, a post-mineral processing waste, is generated in the acid leaching of titanium sponge to remove impurities consisting of $MgCl_2$ and unreacted $TiCl_4$. At Timet in Henderson, NV, leach liquor is held in a polyvinyl chloride-lined pond, neutralized with lime in a concrete mixing tank, and concentrated in a series of solar evaporation ponds. The resulting solution, close to saturation with magnesium chloride, is sold for use as a dust suppressant on unpaved roads.[33] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for leach liquor and sponge wash water of 380,000 metric tons/yr, 480,000 metric tons/yr, and 580,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristics of corrosivity and toxicity (chromium and lead). This waste is classified as what was formerly characterized as a spent material. After the sponge is acid-leached, it is rinsed with water, generating sponge wash water, which may also exhibit the corrosivity characteristic. Data describing these waste streams are presented in Attachment 1.

Waste Non-Contact Cooling Water

Non-contact cooling water generated in the Kroll process is a post-mineral processing waste. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for waste non-contact cooling water of 100 metric tons/yr, 500,000 metric tons/yr, and 1 million metric tons/yr, respectively. (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous waste streams.) 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.

Additional Waste Streams

Two additional waste streams are generated in the Kroll process: smut from magnesium recovery, and spent brine treatment filter cake. Smut is generated in the recovery of magnesium from the magnesium chloride solution generated in the reduction process. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for smut from magnesium recovery of 100 metric tons/yr, 22,000 metric tons/yr, and 45,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of reactivity with water. This waste was formerly classified as a by-product. Brine treatment filter cake is created in the solar evaporation of leach liquor. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for spent brine treatment filter cake of 100 metric tons/yr, 22,000 metric tons/yr, and 45,000 metric tons/yr, respectively. Existing data (Attachment 1) and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

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[32] Ibid.

[33] ICF Incorporated, Timet Corporation: Mineral Processing Waste Sampling Visit — Trip Report, August 1989, p. 3.

Ingot production generates the following post-mineral processing waste streams:

Pickling Liquor and Wash Water

Three ingot plants use acid pickling to remove surface oxides from massive titanium scrap (plate and sheet metal) before the scrap is blended with titanium sponge and alloying metals. The pickling liquor is comprised of hydrochloric, hydrofluoric, and nitric acids; spent pickling liquor and wash water form an acidic wastewater stream.[34] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for pickling liquor and wash water of 2,200 metric tons/yr, 2,700 metric tons/yr, and 3,200 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristics of corrosivity and toxicity for cadmium, chromium, and lead. This waste was formerly characterized as a spent material. Data describing this waste stream are presented in Attachment 1.

Scrap Detergent Wash Water

Titanium scrap chips and millings are washed with a detergent solution before alloying to remove oil and dirt, creating an oily, caustic wastewater stream.[35] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for scrap detergent wash water of 360,000 metric tons/yr, 450,000 metric tons/yr, and 540,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity for cadmium, chromium, selenium, and lead; and the characteristic of corrosivity.

Scrap Milling Scrubber Water

Before alloying, titanium scrap chips and millings are also crushed. A dust scrubber cleans dust-laden air from this operation, generating scrubber water containing oil and grease, suspended solids, and metals.[36] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for scrap milling scrubber water of 4,000 metric tons/yr, 5,000 metric tons/yr, and 6,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity for cadmium, chromium, selenium, and lead.

Casting Crucible Contact Cooling Water and Wash Water

At one ingot plant, water is used to cool the casting equipment, generating a wastewater containing oil and grease, metals, and solids. This cooling water is treated through lime precipitation and sedimentation. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for casting crucible contact cooling water of 190,000 metric tons/yr, 240,000 metric tons/yr, and 290,000 metric tons/yr, respectively. 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. Casting crucibles are washed following casting, generating oily wastewater, which is treated by oil skimming, lime precipitation, and sedimentation.[37] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for casting crucible wash water of 4,000 metric tons/yr, 5,000 metric tons/yr, and 6,000 metric tons/yr, respectively. 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.

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[34] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 4843, 4864, 4945.

[35] Ibid.

[36] Ibid.

[37] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 4946.

Finishing Scrap

Finishing scrap is generated in the melting or milling operations used to convert titanium sponge into ingots. Scrap is generally recycled back into the melting or milling operation and is not regarded as a solid waste.[38] We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate for finishing scrap of 100 metric tons/yr, 22,000 metric tons/yr, and 45,000 metric tons/yr, respectively. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

D. Non-uniquely Associated Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples (e.g., hydrofluoric acid at titanium sponge facilities). 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, and waste oil and other lubricants.

E. Summary of Comments Received by EPA

Three commenters submitted comments on the titanium sector report.

New Factual Information

One commenter provided new factual information about its titanium dioxide pigment manufacturing facility in Savannah, GA that uses the sulfate-chloride process (COMM 49). This information has been included in the sector report.

Sector-specific Issues

Two commenters addressed the extraction/beneficiation boundary. One commenter agreed with the Agency's conclusion that iron chloride waste acid from the production of titanium tetrachloride by the chloride ilmenite process is a mineral processing waste not eligible for the Bevill Exemption (COMM 22). Another commenter disagreed with the Agency's position that chlorination constitutes beneficiation only when it is used in preparation for a leaching operation that does not produce a final or intermediate product that does not undergo further beneficiation or processing (COMM 18). This issue is more fully discussed in the Agency's technical background document on titanium thresholds.

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[38] Ibid.

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ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PICKLE LIQUOR AND WASH WATER FROM INGOT PRODUCTION - TITANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.027	0.579	0.88	3/3	-	-	-	0/0	-	-
Arsenic	0.06	0.3167	0.62	3/3	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.0002	0.0011	0.002	3/3	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.19	0.227	0.28	3/3	-	-	-	0/0	1.0	0
Chromium	0.21	0.26	0.3	3/3	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.54	0.94	1.7	3/3	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	2.6	3.17	4	3/3	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0011	0.002	3/3	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	1.3	1.83	2.6	3/3	-	-	-	0/0	-	-
Selenium	0.009	0.14	0.22	3/3	-	-	-	0/0	1.0	0
Silver	0.0014	0.50	1.2	3/3	-	-	-	0/0	5.0	0
Thallium	1.7	2.83	3.8	3/3	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.43	0.53	0.67	3/3	-	-	-	0/0	-	-
Cyanide	0.01	3333.67	10000	3/3	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT BRINE TREATMENT FILTER CAKE - TITANIUM

Constituents	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	-	-	-	0/0	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	-	-	-	0/0	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	-	-	-	0/0	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	40000	40,000	40,000	1/1	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	10.1	10.1	10.1	1/1					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

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

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	0.01	0.01	0.01	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	1.10	1.10	1.10	1/1	-	-	-	0/0	-	-
Lead	0.01	0.01	0.01	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.02	0.02	0.02	1/1	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	-	-	-	0/0	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	160,000	160,000	160,000	1/1	-	-	-	0/0	-	-
TSS	70,000	70,000	70,000	1/1	-	-	-	0/0	-	-
pH *	7	7.15	7.3	2/2					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

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

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	3900	12,543	16,000	7/7	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	60	60.00	60.00	2/2	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	203	338	524	9/9	-	-	-	0/0	5.0	0
Cobalt	20	20.00	20.00	2/2	-	-	-	0/0	-	-
Copper	9	9.00	9.00	2/2	-	-	-	0/0	-	-
Iron	0.2	67,194	97,000	10/10	-	-	-	0/0	-	-
Lead	0.005	74.60	139	10/10	-	-	-	0/0	5.0	0
Magnesium	100000	100,000	100,000	1/1	-	-	-	0/0	-	-
Manganese	200	1,629	5,200	7/7	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	13.00	13.00	13.00	2/2	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	553	553	553	2/2	-	-	-	0/0	-	-
Zinc	-	-	-	0/0	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	0.2	0	0	1/1	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	6,100	108,773	200,000	13/13	-	-	-	0/0	-	-
TSS	0.60	592	2,000	11/11	-	-	-	0/0	-	-
pH *	4.00	6.25	7.00	4/4					2<pH>12	0
Organics (TOC)	#VALUE!	#VALUE!	#VALUE!	2/2					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT SOLIDS - TITANIUM DIOXIDE

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	2,822	11,502	14,395	4/4	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	43.00	138	169	4/4	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	10.00	497	887	6/6	-	-	-	0/0	5.0	0
Cobalt	20.00	20.00	20.00	1/1	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	17,000	51,509	70,000	5/5	-	-	-	0/0	-	-
Lead	8.00	113	167	5/5	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	730	2,200	3,700	5/5	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	6.00	60.75	79.00	4/4	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	10.00	628	893	5/5	-	-	-	0/0	-	-
Zinc	62.00	62.00	62.00	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	290	290	290	1/1	-	-	-	0/0	-	-
Silica	57,369	57,369	57,369	3/3	-	-	-	0/0	-	-
Chloride	1,500	26,175	100,000	4/4	-	-	-	0/0	-	-
TSS	98,000	512,000	800,000	4/4	-	-	-	0/0	-	-
pH *	3.9	5.9	7.0	7/7					2<pH>12	0
Organics (TOC)	19.00	318,755	425,000	4/4					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - LEACH LIQUOR AND SPONGE WASH WATER - TITANIUM AND TITANIUM DIOXIDE

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	2.50	2.50	2.50	1/1	0.05	0.28	0.50	2/2	-	-
Antimony	0.07	1.29	2.50	2/2	0.50	0.50	0.50	2/2	-	-
Arsenic	0.10	1.30	2.50	2/2	0.01	0.26	0.50	2/2	5.0	0
Barium	2.50	2.50	2.50	1/1	0.50	0.72	0.93	2/2	100.0	0
Beryllium	0.00	0.13	0.25	2/2	0.025	0.038	0.050	2/2	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.16	0.21	0.25	2/2	0.025	0.038	0.050	2/2	1.0	0
Chromium	1.20	1.85	2.50	2/2	0.080	0.29	0.50	2/2	5.0	0
Cobalt	2.50	2.50	2.50	1/1	0.050	0.28	0.50	2/2	-	-
Copper	2.50	2.70	2.90	2/2	0.50	1.05	1.60	2/2	-	-
Iron	9.42	9.42	9.42	1/1	0.020	3.29	6.55	2/2	-	-
Lead	1.25	2.03	2.80	2/2	0.010	0.13	0.25	2/2	5.0	0
Magnesium	5,000	25,667	40,000	3/3	25,700	43,800	61,900	2/2	-	-
Manganese	2.50	2.50	2.50	1/1	0.50	3.24	5.98	2/2	-	-
Mercury	0.0002	0.0009	0.0016	2/2	0.00010	0.00055	0.0010	2/2	0.2	0
Molybdenum	2.50	2.50	2.50	1/1	0.50	0.50	0.50	1/1	-	-
Nickel	2.50	4.75	7.00	2/2	0.17	0.34	0.50	2/2	-	-
Selenium	0.01	1.26	2.50	2/2	0.010	0.26	0.50	2/2	1.0	0
Silver	0.03	1.27	2.50	2/2	0.03	0.26	0.50	2/2	5.0	0
Thallium	2.40	7.45	12.50	1/2	0.55	1.53	2.50	2/2	-	-
Vanadium	2.50	2.50	2.50	1/1	0.50	1.10	1.70	2/2	-	-
Zinc	0.54	1.52	2.50	2/2	0.50	0.52	0.54	2/2	-	-
Cyanide	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	198	198	198	1/1	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	115	43,023	80,000	5/5	-	-	-	0/0	-	-
TSS	50,000	50,000	50,000	1/1	-	-	-	0/0	-	-
pH *	0	0.50	1	2/2					2<pH>12	2
Organics (TOC)	1,670	1,670	1,670	1/1					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SRUBBER WATER - TITANIUM (CHLORIDE PROCESS)

	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	0.50	0.50	0.50	0/1	-	-
Antimony	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Arsenic	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	5.0	0
Barium	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	100.0	0
Beryllium	0.15	0.15	0.15	1/1	0.10	0.10	0.10	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.050	0.050	0.050	0/1	0.050	0.050	0.050	0/1	1.0	0
Chromium	0.50	0.50	0.50	0/1	6.45	6.45	6.45	1/1	5.0	1
Cobalt	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Copper	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Iron	0.50	0.50	0.50	0/1	25.70	25.70	25.70	1/1	-	-
Lead	0.25	0.25	0.25	0/1	0.25	0.25	0.25	0/1	5.0	0
Magnesium	5.87	5.87	5.87	1/1	6.56	6.56	6.56	1/1	-	-
Manganese	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Mercury	0.00010	0.00010	0.00010	0/1	0.00028	0.00028	0.00028	1/1	0.2	0
Molybdenum	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Nickel	0.50	0.50	0.50	0/1	2.79	2.79	2.79	1/1	-	-
Selenium	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	1.0	0
Silver	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	5.0	0
Thallium	2.50	2.50	2.50	0/1	2.50	2.50	2.50	0/1	-	-
Vanadium	1.51	1.51	1.51	1/1	1.82	1.82	1.82	1/1	-	-
Zinc	0.50	0.50	0.50	0/1	0.50	0.50	0.50	0/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	15.40	15.40	15.40	1/1	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	235,000	235,000	235,000	1/1	-	-	-	0/0	-	-
TSS	3,740	3,740	3,740	1/1	-	-	-	0/0	-	-
pH *	0.5	1.2	1.9	2/2					2<pH>12	2
Organics (TOC)	-	-	-	0/0					-	-

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

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

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	-	-	-	0/0	-	-	-	0/0	-	-
Arsenic	-	-	-	0/0	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	58	679	1,300	2/2	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	17000	27,000	37,000	2/2	-	-	-	0/0	-	-
Lead	8	8.00	8.00	1/1	-	-	-	0/0	5.0	0
Magnesium	9000	9,000	9,000	1/1	-	-	-	0/0	-	-
Manganese	730	1,865	3,000	2/2	-	-	-	0/0	-	-
Mercury	-	-	-	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	6	6.00	6.00	1/1	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	600	600	600	1/1	-	-	-	0/0	-	-
Zinc	-	-	-	0/0	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	11000	11,000	11,000	1/1	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	40000	40,000	40,000	1/1	-	-	-	0/0	-	-
Chloride	1500	40,750	80,000	2/2	-	-	-	0/0	-	-
TSS	98000	98,000	98,000	1/1	-	-	-	0/0	-	-
pH *	7.8	9.4	11	2/2					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - FERRIC CHLORIDE - TITANIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	930	930	930	1/1	-	-
Antimony	-	-	-	0/0	25	25	25	1/1	-	-
Arsenic	-	-	-	0/0	0.083	0.083	0.083	1/1	5.0	0
Barium	-	-	-	0/0	23	23	23	1/1	100.0	0
Beryllium	-	-	-	0/0	1.8	1.8	1.8	1/1	-	-
Boron	-	-	-	0/0	18	18	18	1/1	-	-
Cadmium	-	-	-	0/0	1.5	1.5	1.5	1/1	1.0	1
Chromium	-	-	-	0/0	310	310	310	1/1	5.0	1
Cobalt	-	-	-	0/0	9.9	9.9	9.9	1/1	-	-
Copper	-	-	-	0/0	18	18	18	1/1	-	-
Iron	-	-	-	0/0	48000	48000	48000	1/1	-	-
Lead	-	-	-	0/0	58	58	58	1/1	5.0	1
Magnesium	-	-	-	0/0	970	970	970	1/1	-	-
Manganese	-	-	-	0/0	2200	2200	2200	1/1	-	-
Mercury	-	-	-	0/0	0.02	0.02	0.02	1/1	0.2	0
Molybdenum	-	-	-	0/0	8.8	8.8	8.8	1/1	-	-
Nickel	-	-	-	0/0	30	30	30	1/1	-	-
Selenium	-	-	-	0/0	0.02	0.02	0.02	1/1	1.0	0
Silver	-	-	-	0/0	6.2	6.2	6.2	1/1	5.0	1
Thallium	-	-	-	0/0	0.004	0.004	0.004	1/1	-	-
Vanadium	-	-	-	0/0	320	320	320	1/1	-	-
Zinc	-	-	-	0/0	52	52	52	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	326	326	326	1/1	-	-
Fluoride	-	-	-	0/0	2	2	2	1/1	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	104160	104160	104160	1/1	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTE ACIDS - TITANIUM (CHLORIDE PROCESS)

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	447	10,612	16,000	4/4	-	-	-	0/0	-	-
Antimony	1.73	1.73	1.73	1/1	-	-	-	0/0	-	-
Arsenic	0.0050	0.0050	0.0050	0/1	-	-	-	0/0	5.0	0
Barium	0.50	0.50	0.50	0/1	-	-	-	0/0	100.0	0
Beryllium	0.05	0.05	0.05	0/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.11	0.11	0.11	1/1	-	-	-	0/0	1.0	0
Chromium	35.80	637	3,300	6/6	-	-	-	0/0	5.0	0
Cobalt	0.78	0.78	0.78	1/1	-	-	-	0/0	-	-
Copper	0.050	0.050	0.050	0/1	-	-	-	0/0	-	-
Iron	12.00	27,552	72,000	8/8	-	-	-	0/0	-	-
Lead	0.0025	38.67	58.00	2/3	-	-	-	0/0	5.0	0
Magnesium	7.60	1,916	4,800	3/3	-	-	-	0/0	-	-
Manganese	46.00	2,087	7,900	4/4	-	-	-	0/0	-	-
Mercury	0.00020	0.00020	0.00020	1/1	-	-	-	0/0	0.2	0
Molybdenum	0.25	0.25	0.25	0/1	-	-	-	0/0	-	-
Nickel	0.61	0.61	0.61	1/1	-	-	-	0/0	-	-
Selenium	0.0050	0.0050	0.0050	0/1	-	-	-	0/0	1.0	0
Silver	0.0050	0.0050	0.0050	0/1	-	-	-	0/0	5.0	0
Thallium	0.0050	0.0050	0.0050	0/1	-	-	-	0/0	-	-
Vanadium	13.00	331	1,500	5/5	-	-	-	0/0	-	-
Zinc	27.00	27.00	27.00	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	44.00	1,022	2,000	2/2	-	-	-	0/0	-	-
Chloride	76,000	124,500	210,000	4/4	-	-	-	0/0	-	-
TSS	10,000	47,000	200,000	6/6	-	-	-	0/0	-	-
pH *	2.00	2.00	2.00	1/1					2<pH>12	1
Organics (TOC)	40.00	40.00	40.00	1/1					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTE ACIDS - TITANIUM (SULFATE PROCESS)

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	2.50	253	480	3/4	0.05	363	1,030	2/4	-	-
Antimony	0.50	1.15	2.50	1/4	0.50	2.25	5.00	1/4	-	-
Arsenic	0.0050	0.88	2.50	0/4	0.01	1.33	5.00	1/5	5.0	1
Barium	0.50	1.00	2.50	0/4	0.05	1.31	5.00	2/5	100.0	0
Beryllium	0.050	0.10	0.25	0/4	0.0050	0.15	0.50	0/4	-	-
Boron	0.025	0.025	0.025	0/1	-	-	-	0/0	-	-
Cadmium	0.050	0.12	0.25	1/4	0.0050	0.12	0.50	1/5	1.0	0
Chromium	2.50	21.63	40.00	3/4	0.080	31.12	83.00	4/5	5.0	3
Cobalt	0.50	1.28	2.50	1/4	0.050	1.64	5.00	1/4	-	-
Copper	0.05	0.89	2.50	0/4	0.050	1.79	5.00	1/4	-	-
Iron	9.42	1544	3000	4/4	0.020	2,174	5,910	4/4	-	-
Lead	0.0025	0.44	1.25	0/4	0.010	0.77	2.50	1/5	5.0	0
Magnesium	223	13,195	40,000	6/6	941	22,685	61,900	4/4	-	-
Manganese	2.50	28.13	51.00	3/4	0.50	39.12	111	3/4	-	-
Mercury	0.00010	0.00048	0.0016	1/4	0.00010	0.00028	0.0010	0/5	0.2	0
Molybdenum	0.25	0.94	2.50	0/4	0.50	2.75	5.00	0/2	-	-
Nickel	0.50	1.03	2.50	1/4	0.17	1.89	5.00	1/3	-	-
Selenium	0.0050	0.88	2.50	0/4	0.010	1.21	5.00	0/5	1.0	1
Silver	0.0050	0.88	2.50	0/4	0.005	1.12	5.00	0/5	5.0	1
Thallium	0.0050	5.00	12.50	1/4	0.55	9.76	25.00	2/4	-	-
Vanadium	2.50	54.63	100	3/4	0.50	77.55	225	3/4	-	-
Zinc	0.50	13.75	27.00	2/4	0.50	7.51	24.00	2/4	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	0	99	198	2/2	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	2.50	30,735	80,000	6/7	-	-	-	0/0	-	-
TSS	50000	65,450	80,900	2/2	-	-	-	0/0	-	-
pH *	0	0.33	1	3/3					2<pH>12	3
Organics (TOC)	20.00	845	1,670	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.

TUNGSTEN

A. Commodity Summary

More than 20 tungsten-bearing minerals are known, but the principle domestic ores used to produce ammonium paratungstate (APT) powder and tungsten metal powder are wolframite, ferberite, and scheelite. Tungsten occurs in association with minerals of copper, tin, bismuth, or molybdenum and can be recovered either as the primary product or as a coproduct or byproduct.[1]

Tungsten ores and concentrates are converted into the following intermediate products: APT, tungstic acid, sodium tungstate, tungsten metal powder, ferrotungsten, and tungsten carbide powder. Most of the APT is reduced to tungsten metal powder, which then may be processed into tungsten carbide powder or ferrotungsten.[2] End uses of tungsten include metalworking, mining, and construction machinery and equipment, 74%; electrical and electronic machinery and equipment and transportation, 10%; lamps and lighting, 9%; chemicals, 4%; and other, 3%. The total estimated value of primary tungsten material consumed in 1994 was $180 million.[3]

Eleven facilities in the United States produce either APT or tungsten metal. Three of the eleven facilities produce APT, a precursor to tungsten, as an end product. Four additional facilities are captive plants that produce APT, then tungsten. All seven of these plants appear to engage in beneficiation operations in the production of APT. They conduct a variety of operations, including milling (e.g., crushing, grinding, washing), physical separation (e.g., gravity concentration, magnetic or electrostatic separation, froth flotation), roasting as a pretreatment for leaching operations, concentration using liquid separation (e.g., soda autoclaving, solvent extraction, ion exchange), and calcining (i.e., heating to drive off water or carbon dioxide).

In addition, two plants produce tungsten powder and cemented tungsten carbide using proprietary processes. A Kennametal plant, located in Fallon, Nevada employs a unique process that produces tungsten carbide directly from ore. A Curtis Tungsten plant located in Upland, California was recently reopened and produces tungsten concentrate from ore. Little is known about the operations of these two facilities.

The two remaining facilities obtain APT (a "saleable" mineral product) and produce tungsten carbide or powder. Tungsten is produced from APT by reduction using hydrogen, followed by a second reduction step using aluminum, potassium, and silicon. The metal is then washed with hydrochloric acid, and cast into ingots. These two facilities do not perform beneficiation activities, and there is some question as to whether their operations could even be considered "mineral processing" operations, because they start with a saleable mineral product (see 54 FR 36592).

For the nine plants that conduct beneficiation and processing operations, names, locations, products, operations, and waste streams generated are presented in Exhibit 1. Two tungsten mines are in operation, Curtis Tungsten in Upland, California and U.S. Tungsten in Bishop, California. These are also listed in Exhibit 1.

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[1] Phillip T. Stafford, "Tungsten," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 881-891.

[2] Ibid.

[3] Gerald Smith, "Tungsten," from Mineral Commodity Summaries, January 1995, pp. 182-183.

EXHIBIT 1

SUMMARY OF TUNGSTEN FACILITIES

Facility Name	Location	Products
Buffalo Tungsten	Depew, NY	APT, Tungsten (carbide)
Curtis Tungsten, Incorporated	Upland, CA	Tungsten (concentrate)
General Electric	Euclid, OH	APT, Tungsten (carbide)
OSRAM Sylvania, Inc.	Towanda, PA	APT, Tungsten (carbide)
Kennametal	Fallon, NV LaTrobe, PA	Tungsten (carbide)
Teledyne Firth Sterling	La Vergne, TN	APT
Teledyne Advance Materials	Huntsville, AL	APT, Tungsten (carbide)
U.S. Tungsten	Bishop, CA	APT

B. Generalized Process Description

1. Discussion of Typical Production Processes

Tungsten is found primarily in quartz veins and contact-metamorphic scheelite deposits. Both underground and open pit methods are used in mining operations. Tungsten concentration operations, primarily gravity and flotation methods, usually are conducted at or near the mine. The concentrate is processed chemically to produce ammonium paratungstate (APT) from which tungsten metal powder is made. The metal is processed further into products such as tungsten carbide and ferrotungsten.[4]

2. Generalized Process Flow Diagram

The production of tungsten metal can be divided into four distinct stages - preparation of ores, leaching of ore concentrates, purification to APT, and reduction of APT to metal. The actual processes used in each stage vary with the type and purity of raw material used. The production steps are described in greater detail below. Exhibit 2 presents a process flow diagram of tungsten production.

Preparation of Ore Concentrates

Scheelite and wolframite are the major tungsten containing minerals. Ores containing these minerals are generally very friable and over grinding can cause sliming problems. Therefore, the ores are generally crushed and ground in stages and waste fines are kept to a minimum. Concentration of tungsten is usually accomplished by froth flotation, supplemented by leaching, roasting, or magnetic or high tension separation. The tailings from froth

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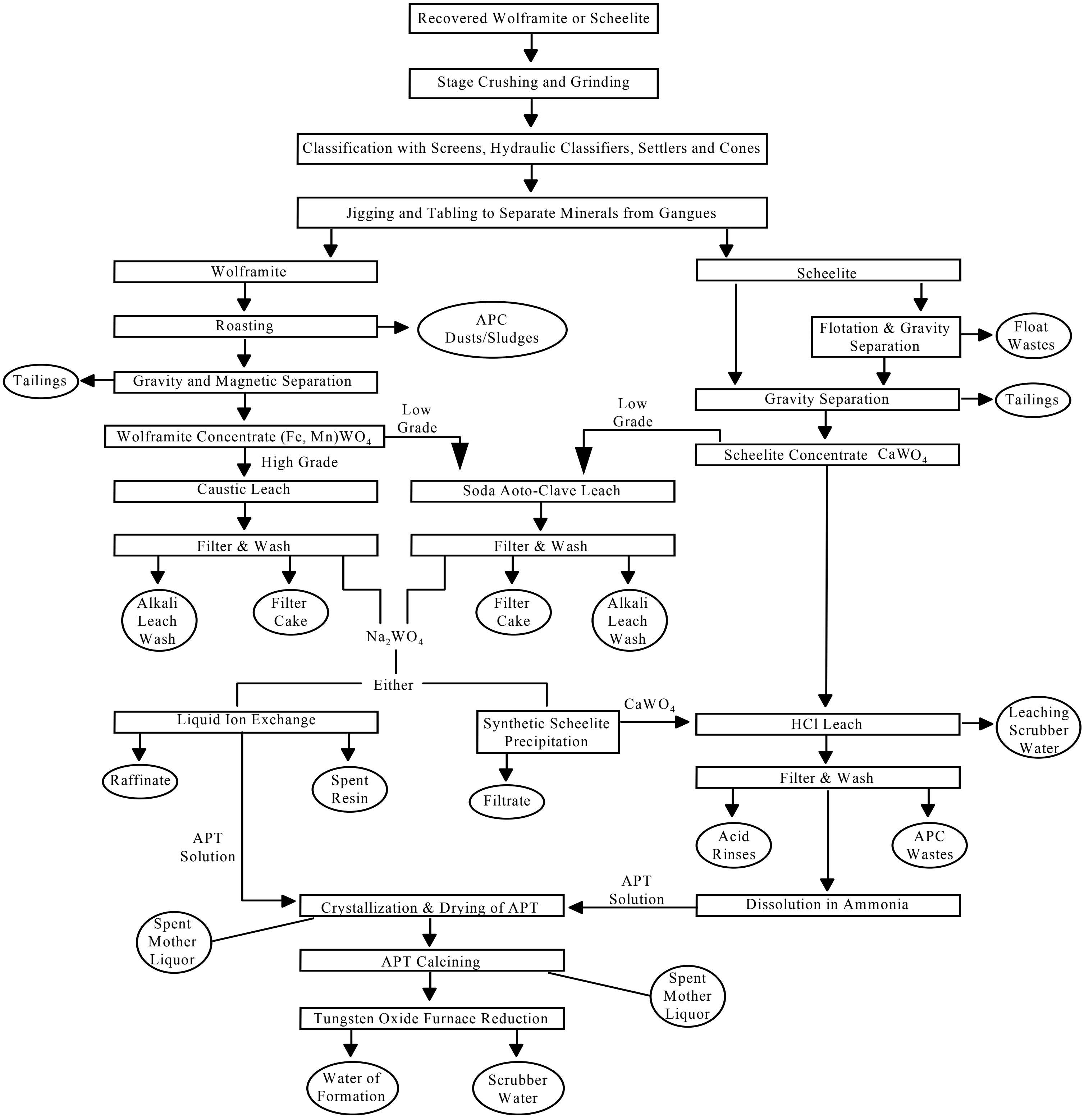
[4] Phillip T. Stafford, 1985, Op. Cit., pp. 881-891.

EXHIBIT 2

TUNGSTEN PRODUCTION

(Adapted from: Development Document for Effluent Limitations Guidelines, 1989, pp. 2963 - 3037.)



flotation usually are sent through a reprocessing and scavenger froth flotation circuit to maximize tungsten recovery. The beneficiation processes vary with the type of ore being mined.[5]

The concentrate may be retreated by roasting to remove impurities such as sulfur, arsenic, and organic residues from flotation. These compounds are oxidized and volatilized. After preparation of the concentrate, the concentrate is processed to APT via either sodium tungstate or tungstic acid.[6]

Leaching of Ore Concentrates

Scheelite ores of high quality are usually leached with hot hydrochloric acid to remove phosphorus, arsenic, and sulfur. An insoluble tungstic acid intermediate is formed which is filtered and washed with dilute hydrochloric acid.[7]

Lower grade scheelites are sometimes processed by the high pressure soda process. In this process, the concentrate is ground and digested in an autoclave with sodium carbonate. This produces a sodium tungstate solution that is filtered to remove calcium carbonate and silica solids and then further processed to APT or $CaWO_4$. If molybdenum impurities are present, the sodium tungstate solution is reacted with sodium hydrosulfide to precipitate molybdenum trisulfide. The molybdenum trisulfide solids are removed with a filter and the sodium tungstate solution is further processed.[8]

Scheelite or wolframite can be converted to sodium tungstate solution by the alkali roasting process. In this process, sodium carbonate is mixed with the concentrate and heated. The roasted concentrate is then leached with hot water. The leachate, which contains sodium tungstate, is separated from the solids by filtration and sent to other processes for conversion to APT.[9]

Purification to APT (Precipitation, Crystallization, and Drying)

Tungstic Acid Purification

Purification of tungstic acid is accomplished by a simple process involving digestion and crystallization. Insoluble tungstic acid is digested with aqueous ammonia to solubilize the tungsten as ammonia tungstate. The solution is separated from any remaining solids and magnesium oxide is added. Magnesium ammonium phosphates and arsenate are precipitated. Activated carbon is added to purify the solution. The activated carbon and precipitates are removed from the solution by filtration. APT is formed by crystallizing it from solution. The APT crystals are filtered, washed, and dried. Ammonia evolved during the process is usually recovered and recycled.[10]

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[5] U.S. Environmental Protection Agency, "Tungsten," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 3-228 - 3-244.

[6] Ibid.

[7] Ibid.

[8] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Office of Water Regulations Standards, Vol. VI, 1989, pp. 2963-3037.

[9] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 3-228 - 3-224.

[10] Ibid.

Sodium Tungstate Purification

Sodium tungstate from the high pressure soda process and from the alkali roasting process is converted to APT by two processes. The first approach is to precipitate calcium tungstate (synthetic scheelite) from the sodium tungstate solution by adding calcium chloride. The solution is filtered to yield sodium chloride, and is discharged. The calcium tungstate can then be digested with hydrochloric acid. From this point, the purification is the same as described above for the purification of the tungstic acid intermediate.[11]

Synthetic scheelite is also prepared from recycled process solutions and cleanup water, such as spent crystallization liquor and floor wash, that may contain tungsten values. The calcium tungstate is precipitated with calcium chloride and can be processed as described above. Alternatively, the calcium tungstate may be sent through solvent extraction instead of digestion with hydrochloric acid.[12]

The second approach for purifying the sodium tungstate intermediate is a newer solvent extraction method, the liquid ion exchange system, where the sodium tungstate solution is converted to ammonia tungstate solution. The sodium tungstate solution is contacted countercurrently with an organic solvent, which removes the tungstate ions from solution. The organic solvent is washed with water to remove impurities and then recycled. The ammonium tungstate solution is fed to a crystallizer where APT crystals are formed. The APT crystals are filtered and dried.[13]

APT Conversion to Oxide (Calcining)

Dried APT is calcined in a rotary furnace heated indirectly to drive off ammonia and produce tungsten oxides. The type of oxide produced is a function of furnace atmosphere (i.e. N_2, H_2, etc.) and temperature. Blue, brown, or yellow tungsten oxides are possible products.[14]

Tungsten Oxide Reduction to Metal

Tungsten oxides are reduced to metal powder in high temperature furnaces. The reducing agent is typically hydrogen. Powders of various particle sizes are produced by varying furnace reaction time, temperature gradient, hydrogen flow, and layer thickness. Tungsten powder to be used in high-purity applications is leached with acids such as hydrochloric and hydrofluoric acids, rinsed with water, and dried.[15]

Tungsten Carbide Production

Tungsten carbide is formed by reducing APT or tungsten oxides in the presence of carbon. Tungsten ores may also be reduced and carburized in a single reaction. In this latter process, impurities are leached with hydrochloric, sulfuric, or hydrofluoric acid from the furnace product to yield tungsten carbide crystals.[16]

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[11] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 2963-3037.

[12] Ibid.

[13] Ibid.

[14] Ibid.

[15] Ibid.

[16] Ibid.

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

A recently developed technique processes tungsten carbide from concentrate eliminating the conventional method of producing APT. The technique involves the formation of tungsten monocarbide from a molten tungstate halide phase using gas sparging. The process involves treating concentrates with chloride and silicate salts, with the resulting product being treated with methane gas to produce high purity tungsten carbide powder.[17]

4. Beneficiation/Processing Boundaries

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

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

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between APT calcining and tungsten furnace reduction because it is here, in the furnace, where tungsten oxide is thermally reduced in the presence of hydrogen to form tungsten powder. 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/Beneficiation Wastes

Mining and Concentrating Ore

Waste fines are generated from handling tungsten ore. The tailings are sent to tailings ponds.[18]

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[17] Phillip T. Stafford, 1985, Op. Cit., pp. 881-891.

[18] U.S. Environmental Protection Agency, 1988, Op. Cit., pp. 2963-3037.

Wastewater is generated from processing tungsten ore. Wastewater from thickeners and separators are sent to tailings ponds. Waters from tailings ponds are discharged to surface water.[19]

Wet scrubber wastewater is a waste stream generated from roasting.

Waste rock and tailings from mining and concentrating, respectively, are generated from extraction and beneficiation operations associated with tungsten production. Waste management practices for mine waste rock and mill tailings appear to be fairly typical of those used throughout the mining industry to manage similar wastes. Waste rock is generally disposed of in piles or dumps, and tailings are usually piped in slurry form to a tailings (disposal) impoundment.

Leaching or Ore Concentrates

Tungstic acid rinse water is a waste stream from ore concentrate leaching. This wastewater can be characterized by acidic pH, concentrations of metals including lead and zinc, and suspended solids. Two plants appear to leach scheelite ores or synthetic calcium tungstate with hydrochloric acid. Treatment at these plants involves lime and settling to precipitate metals before discharging the rinse water effluent. Treatment sludges presumably report to RCRA Subtitle D landfills or disposal impoundments (i.e., as non-hazardous solid wastes).[20] Attachment 1 presents additional waste characterization data for this waste stream.

Scrubber wastewater is a waste stream generated from wet air pollution control. This wastewater may have an acidic pH. The scrubber water is usually treated and discharged or recycled.[21] One of the two plants that leaches scheelite ores or synthetic calcium tungstate with hydrochloric acid neutralizes the scrubber water with lime and precipitates metals from the waste stream prior to discharge. The other plant recycles the entire waste stream for use as a tungsten acid rinse water. Sludges from the waste treatment are sent to Subtitle D landfills or disposal impoundments.

Alkali leach wash is generated from digesting wolframite type ores in caustic solutions to produce sodium tungstate. Four plants use an alkali leach wash. Sodium tungstate is filtered from the digestion-wash liquor, and the resulting filtrate is evaporated in surface impoundments, recycled, or discharged. From EPA's Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Point Source Category, Volume 3, (1989), two plants reduced waste flow to zero by filtering the insoluble impurities and using a combination of evaporation and recycling steps. A third plant discharges this and all liquid wastes to a settling pond for evaporation, and one plant discharged its wastewater after neutralization and chemical oxidation. This waste stream is characterized by concentrations of metals and suspended solids.[22]

Leach filter cake residues and impurities may be generated from the leaching step. This waste contains gangue, with small amounts of tungsten and other trace elements. Other impurities may include molybdenum and heavy metals--many in hydrous forms. These wastes may be disposed of in a RCRA Subtitle D landfill or disposed of in surface impoundments.

Molybdenum sulfide precipitation wet air pollution control waste is generated from the leaching of ore concentrates. This waste stream is expected to be acidic and contain captured particulates.[23]

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[19] Ibid.

[20] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 2963-3037.

[21] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 3-228 - 3-244.

[22] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 2963-3037.

[23] Ibid.

Purification to APT

Spent mother liquor evolved during crystallization is a possible waste stream from purification of intermediate products to APT. This wastewater is either recycled or discarded.[24] This waste stream may contain high levels of ammonia.

Wastewater from drying APT crystals is usually evaporated.[25] This waste stream may contain high levels of ammonia.

Ion exchange raffinate from the liquid ion exchange process is a source of wastewater. This waste stream is characterized by a low pH and concentrations of toxic metals, suspended solids, and ammonia. This waste stream also has concentrations of organics such as acenaphthene, napthalene, phenol, and fluorene.[26] Of the two plants using this method, one plant pumps all of its wastes to a settling pond for evaporation, and the second plant treats this wastewater with a lime and settle process. Treatment sludge disposal may involve disposal into a RCRA Subtitle D landfill or impoundment.

Ion Exchange Resins may be generated by the two plants using the ion exchange process. These plants would need to replace ion exchange resins at regular intervals. These resins may contain constituents and exhibit characteristics similar to those of raffinate, but with higher concentrations of contained metals.

Calcium tungstate precipitate wash is generated from calcium tungstate precipitation. Four plants are believed to generate this waste from calcium tungstate precipitation. None of the plants are believed to recycle the wastewater. This waste stream is characterized by a basic pH, concentrations of ammonia, oil, and grease. Reportedly, in 1983, one plant achieved zero discharge by sending wastewater to an evaporation pond. Other facilities used lime treatment and settling techniques, coagulated with polymers and lime, or discharged the waste without treatment.[27]

APT Conversion to Oxide

Wet scrubber wastewater from calciners is generated during the conversion of APT to tungsten oxides. In 1989, six plants reported this activity. Of the six plants, one plant recycled and reused the wastewater, another evaporated the water, recovered ammonia, and reused the ammonia and water. Other treatments included direct discharge, lime and settle scrubber water, ammonia recovery, direct discharge, primary and secondary settling, and indirect discharge. Treatment sludges may be landfilled or disposed of in surface impoundments. This wastewater is characterized by concentrations of ammonia and suspended solids and an alkaline pH.[28]

2. Mineral Processing Wastes

Reduction to Metal

Scrubber wastewater is generated by reducing tungsten oxides to metal powder. This waste stream is characterized by concentrations of particulates and soluble salts from fluxes used in the reduction furnaces. In addition, concentrations of ammonia and an alkaline pH may also be characteristic of this wastewater. This waste

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[24] Ibid.

[25] Ibid.

[26] Ibid.

[27] Ibid.

[28] Ibid.

may be recycled. Attachment 1 presents additional waste characterization data for this waste stream.[29] This waste is not expected to be hazardous.

Rinse water and spent acid. This wastewater is discharged to wastewater treatment.[30] Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 0 metric tons/yr, 0 metric tons/yr, and 21,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity prior to treatment. This waste may be recycled and is classified as a spent material.

Tungsten Carbide Production

Process Wastewater is generated from tungsten carbide production. This wastewater is likely to be very acidic and contain suspended solids.[31] This wastewater may be combined with rinse water, spent acid, and spent scrubber liquor for treatment. Attachment 1 presents waste characterization data for process wastewater treatment plant effluent. 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 1,800 metric tons/yr, 3,700 metric tons/yr, and 7,300 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity. This waste may be recycled and is classified as a spent material.

Water of formation is produced from reducing tungsten oxides to metal in a hydrogen atmosphere. In some plants, this water may be recondensed in the reduction furnace scrubber system. This wastewater is characterized by a basic pH and concentrations of ammonia and suspended solids.[32] Attachment 1 presents additional waste characterization data for this waste stream. This waste is not expected to be hazardous.

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.

[31] Ibid.

[32] Ibid.

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U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. Vol. III. August, 1992. pp. 39-1 - 39-2.

U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and

ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SCRUBBER WASTEWATER - TUNGSTEN

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.1	0.1	0.1	2/2	-	-	-	0/0	-	-
Arsenic	0.1	0.1	0.1	2/2	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	-	-	-	0/0	-	-	-	0/0	1.0	0
Chromium	0.04	0.04	0.04	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	-	-	-	0/0	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.02	0.02	0.02	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0003	0.0004	2/2	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.005	0.005	0.005	1/1	-	-	-	0/0	-	-
Selenium	0.01	0.01	0.01	2/2	-	-	-	0/0	1.0	0
Silver	0.02	0.02	0.02	2/2	-	-	-	0/0	5.0	0
Thallium	0.1	0.1	0.1	2/2	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.06	0.06	0.06	2/2	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - TUNGSTIC ACID RINSE WATER - TUNGSTEN

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.1	0.1	0.1	1/1	-	-	-	0/0	-	-
Arsenic	0.13	3.665	7.2	2/2	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.03	0.03	0.03	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.03	0.115	0.2	2/2	-	-	-	0/0	1.0	0
Chromium	0.1	1.05	2	2/2	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.2	2.6	5	2/2	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.2	10.1	20	2/2	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0005	0.0008	0.0011	2/2	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.05	0.525	1	2/2	-	-	-	0/0	-	-
Selenium	0.01	0.01	0.01	1/1	-	-	-	0/0	1.0	0
Silver	0.02	0.155	0.29	2/2	-	-	-	0/0	5.0	0
Thallium	0.1	0.4	0.7	2/2	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.6	1.3	2	2/2	-	-	-	0/0	-	-
Cyanide	0.001	0.00975	0.02	4/4	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - TREATMENT PLANT EFFLUENT - TUNGSTEN

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.002	0.116	0.8	7/7	-	-	-	0/0	-	-
Arsenic	0.018	0.118	0.446	9/9	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.002	0.009	0.01	7/7	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.02	0.044	0.08	10/10	-	-	-	0/0	1.0	0
Chromium	0.024	0.087	0.22	7/7	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.01	0.047	0.148	10/10	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.1	0.140	0.242	10/10	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.001	0.003	9/9	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.05	0.110	0.202	10/10	-	-	-	0/0	-	-
Selenium	0.016	0.234	1	8/8	-	-	-	0/0	1.0	0
Silver	0.03	0.030	0.03	1/1	-	-	-	0/0	5.0	0
Thallium	0.005	0.150	0.9	9/9	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.05	0.191	0.6	10/10	-	-	-	0/0	-	-
Cyanide	0.001	0.157	0.6	14/14	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WATER OF FORMATION - TUNGSTEN

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Arsenic	0.02	0.02	0.02	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.005	0.005	0.005	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.02	0.02	0.02	1/1	-	-	-	0/0	1.0	0
Chromium	0.02	0.02	0.02	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.25	0.25	0.25	1/1	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.05	0.05	0.05	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0002	0.0002	1/1	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.05	0.05	0.05	1/1	-	-	-	0/0	-	-
Selenium	0.01	0.01	0.01	1/1	-	-	-	0/0	1.0	0
Silver	0.01	0.01	0.01	1/1	-	-	-	0/0	5.0	0
Thallium	0.01	0.01	0.01	1/1	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.14	0.14	0.14	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

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

URANIUM

A. Commodity Summary

Uranium is present in the earth's crust at approximately 2 ppm. Acidic rocks with a high silicate content, such as granite, have a uranium content that is above average, whereas the uranium contents of basic rocks such as basalts are lower than the average. However, 90 percent of the world's known uranium resources are contained in conglomerates and in sandstone.[1]

From 1980 to 1993, the domestic production of uranium declined from almost 44 million pounds U_3O_8 to about 3 million pounds (1,361 metric tons/yr).[2] A total of 17 uranium mines were operational in 1992; five conventional mines (both underground and open pit), four *in situ*, and eight reported as "other" (heap leach, mine water, mill tailings, or low-grade stock piles). Extraction/beneficiation operations produce yellowcake (precipitate containing uraniferous compounds), which is typically shipped to a uranium hexafluoride convertor for processing.[3,4] The number of mineral processing facilities is currently unknown. Uranium was also produced to a limited extent as a byproduct of phosphoric acid production at four sites. The primary demand for uranium is by commercial power generating facilities for use in fuel rods.[5]

Regulatory Status

Uranium mill tailings are by-product materials from uranium mining (i.e., waste acids from solvent extraction, barren lixiviants, slimes from solvent extraction and waste solvents generated in the beneficiation process during the extraction of uranium ore) and therefore, are excluded from the treatment standards being promulgated today for TC metal wastes. 40 CFR 261.4(a)(4) states that source, special nuclear or by-product material as defined by the Atomic Energy Act of 1954 as amended, 42 U.S.C. 2100 *et seq*, are not solid wastes and thus, subject to this rule. However, all other wastes not excluded under 40 CFR 261.4, including radioactive mixed wastes, which satisfy the definition of radioactive waste at 10 CFR Part 61, and also contain waste that is either a listed hazardous waste, or that exhibits any of the hazardous characteristics identified in Subpart C of 40 CFR Part 261, are subject to this rulemaking (assuming the waste is otherwise subject to this rule).

B. Generalized Process Description

1. Discussion of Typical Production Processes

Uranium ore is recovered using either conventional milling or solution mining (*in situ leaching*). Beneficiation of conventionally mined ores involves crushing and grinding the extracted ores followed by placement in a leaching circuit. *In situ* operations use a leach solution to dissolve desirable uraniferous minerals from in-place deposits. Uranium in either case is removed from pregnant leach liquor and concentrated using solvent extraction or ion exchange and precipitated to form yellowcake. Yellowcake is then processed to produce uranium hexafluoride

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[1] "Uranium and Uranium Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, p. 504.

[2] Department of Energy, Decommissioning of U.S. Uranium Production Facilities, February 1995, p. vii.

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

[4] Rio Algom Mining Corp. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[5] U.S. Environmental Protection Agency, "Uranium," from Technical Resource Document, Extraction and Beneficiation of Ores and Minerals, Vol. 5, January 1995, pp. 3-5.

(UF_6), which is enriched and further refined to produce the fuel rods used in nuclear reactors.[6] Stockpiles of low grade ore removed from mines may be processed by heap leaching. It can also be economically feasible to separate the uranium as a by-product from the crude black acid (30 percent phosphoric acid) obtained from the leaching of phosphate for fertilizers.

2. Generalized Process Flow Diagram

Conventional Milling

Uranium ore is recovered by either open pit (for ore deposits close to the surface of the earth) or underground mining. The ore is blended, crushed, and ground. Ore high in vanadium is sometimes roasted with sodium chloride or soda ash prior to grinding in order to convert insoluble heavy metal vanadates (complex vanadium) into more soluble vanadate, which is then extracted with water. Two basic methods are employed to extract uranium from ore: acid leaching with sulfuric acid or alkaline leaching with a hot solution of sodium carbonate and sodium bicarbonate.[7] Exhibits 1 and 2 show process flow diagrams for two different leaching processes.[8,9] A process flow diagram for an alkaline leach mill is shown in Exhibit 3. Most mills use acid leaching, which provides a higher uranium-removal efficiency. Alkaline leaching is used in the treatment of uranium ores when the lime content results in excessive acid consumption (alkaline leaching is preferred if acid consumption exceeds 68 kg/ton of ore treated).[10,11] Leaching involves bringing a solvent (lixiviant) in contact with the crushed ore slurry. Uranyl ions are then dissolved by the lixiviant. The pregnant lixiviant is separated from the residual solids (tails); typically the solids are washed with fresh lixiviant until the desired level of recovery is attained. The pregnant leach solution then enters a solvent extraction or ion exchange circuit.[12]

Solution Mining (*In Situ* Leaching)

In situ leaching, the most commonly employed solution mining technique, involves injecting a barren solution and lixiviant into the permeable ore zone. The solution penetrates the pores in the ore, leaching out the uranium and other metals.[13] The pregnant solution is then pumped up through production wells, passed through sand filters to remove any large particles, and transferred to ion exchange units. Ultimately, the uraniferous compounds are stripped from the ion exchange resins and precipitated to form yellowcake.[14] After the uranium is removed, the barren solutions are reconditioned and recycled. A typical *in situ* leach process is shown in Exhibit 4.

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[6] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 13-16.

[7] Werthman, P., and K. Bainbridge, "An Investigation of Uranium Mill Wastewater Treatability," Proceedings of the 35th Purdue Industrial Waste Conference, 1980, p. 248.

[8] Kennecott Corporation. Op. Cit.

[9] Rio Algom Mining Corp. Op. Cit.

[10] "Uranium and Uranium Compounds," 1983, Op. Cit., pp. 516-517.

[11] "Uranium," in SME Mineral Processing Handbook, Vol. 2, 1985, p. 24-3.

[12] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 18, 21.

[13] Department of Energy, February 1995, Op Cit., p. 30.

[14] U.S. Environmental Protection Agency, January 1995, Op. Cit., p. 27.

EXHIBIT 1

PROCESS FLOW CHART FOR ACID-LEACH PROCESS 1

(Adapted from: Assessment of Environmental Aspects of Uranium Mining and Milling, U.S. EPA, 1976, p. 36.)

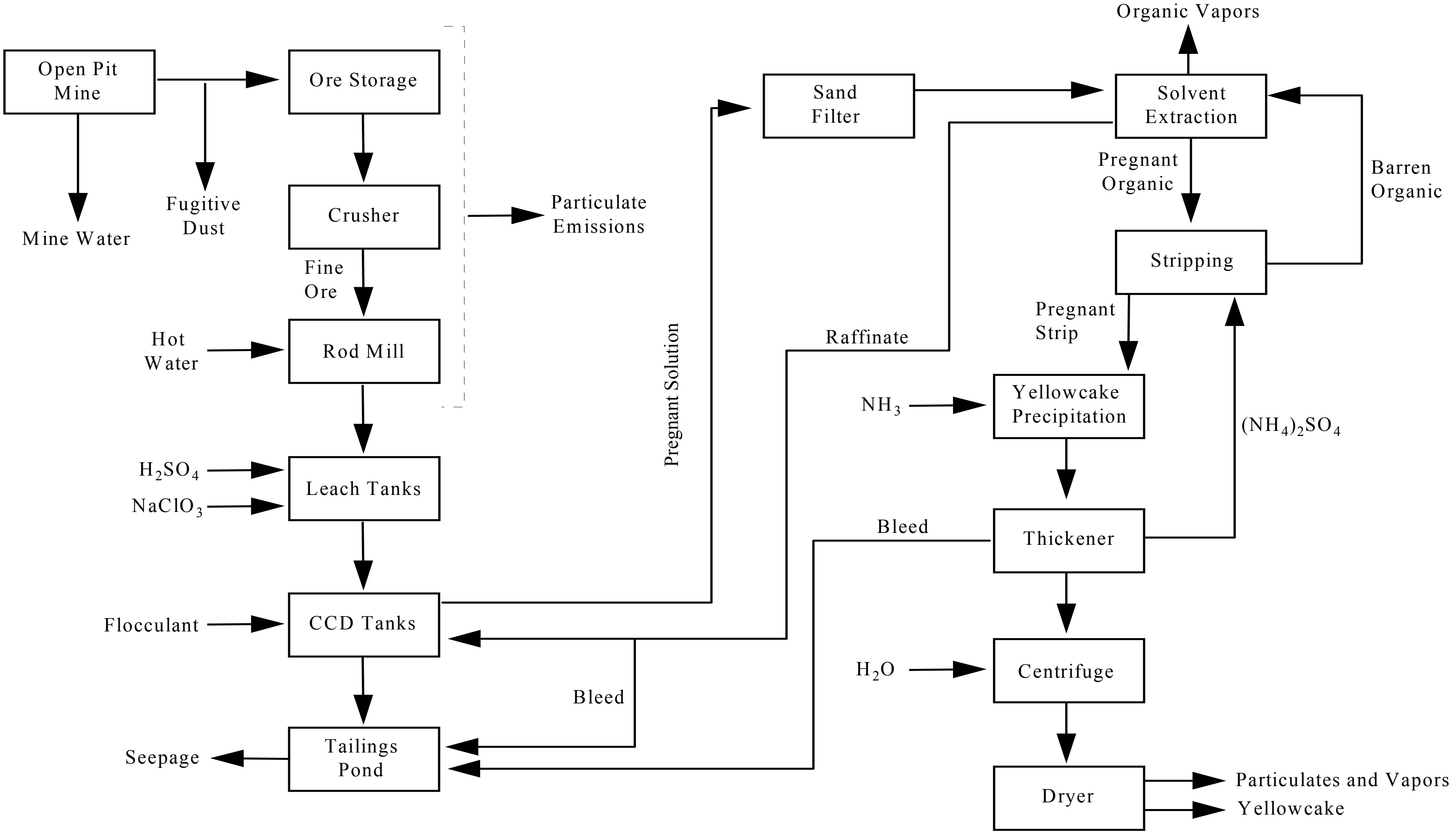


EXHIBIT 2

ACID LEACH PROCESS FLOW CHART FOR ACID-LEACH PROCESS 2

(Adapted from: Assessment of Environmental Aspects of Uranium Mining and Milling, U.S. EPA, 1976, p. 38.)

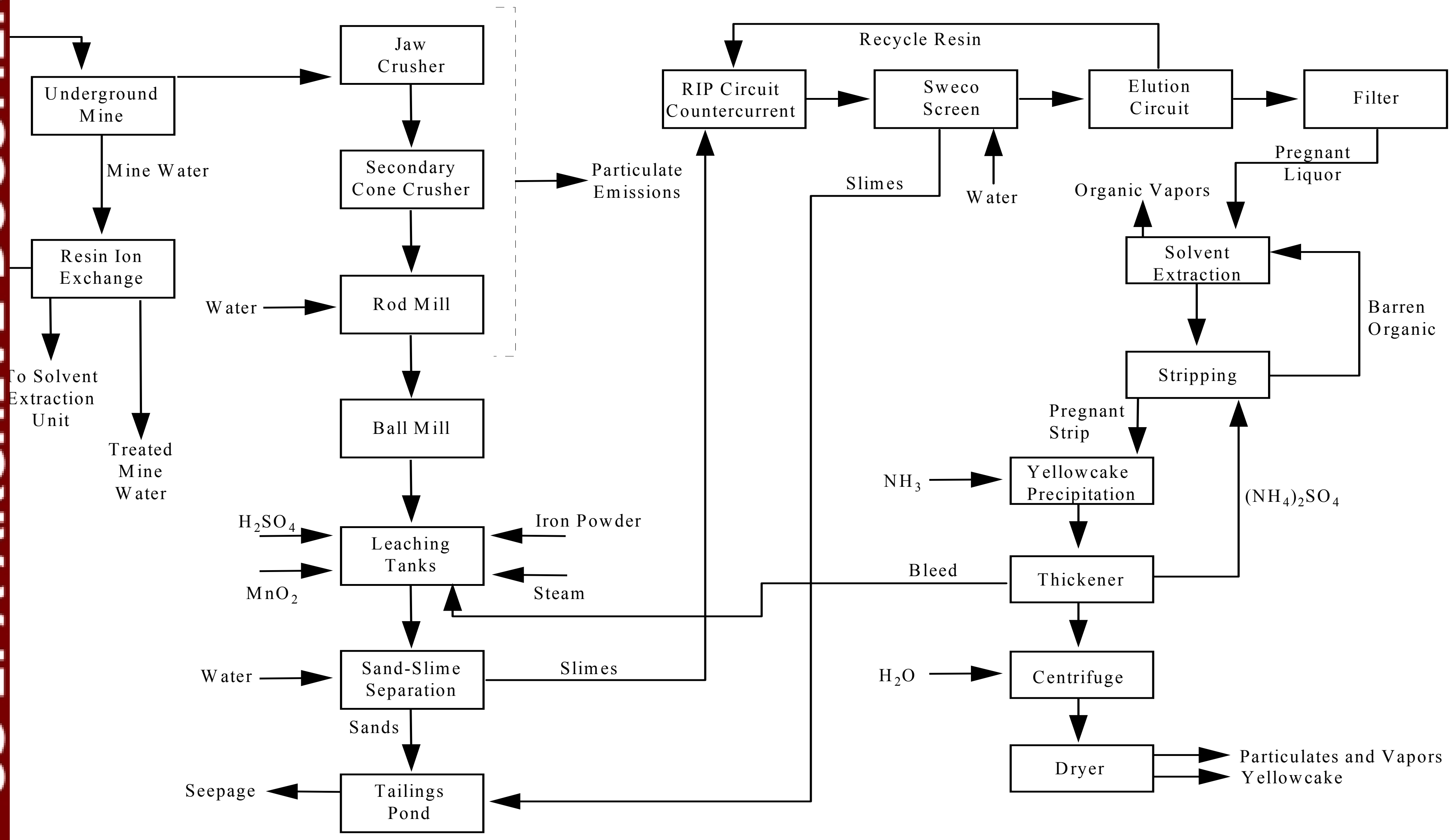


EXHIBIT 3

ALKALINE LEACH PROCESS FLOW CHART FOR AN UNDERGROUND MINE

(Adapted from: Assessment of Environmental Aspects of Uranium Mining and Milling, U.S. EPA, 1976, p. 41.)

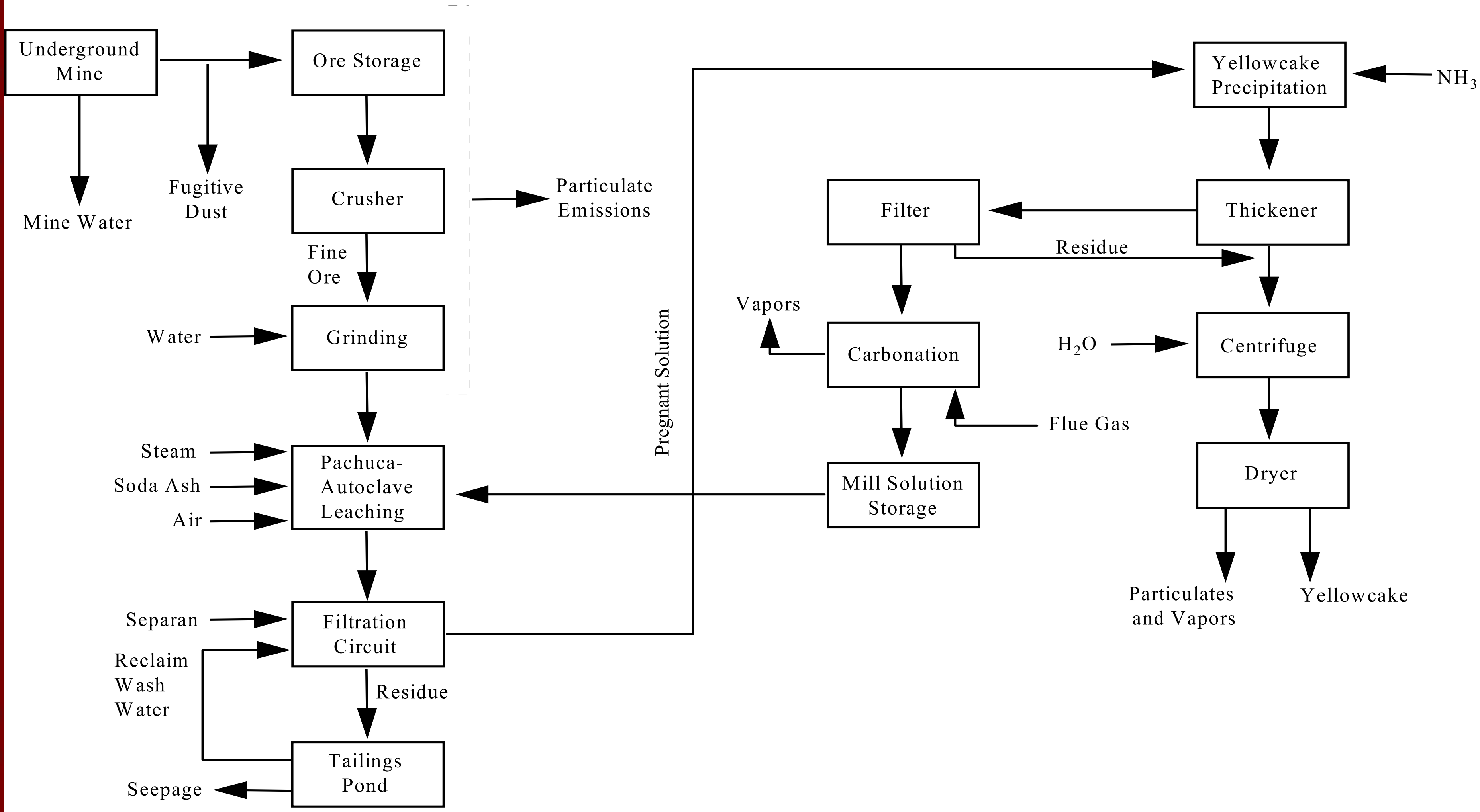
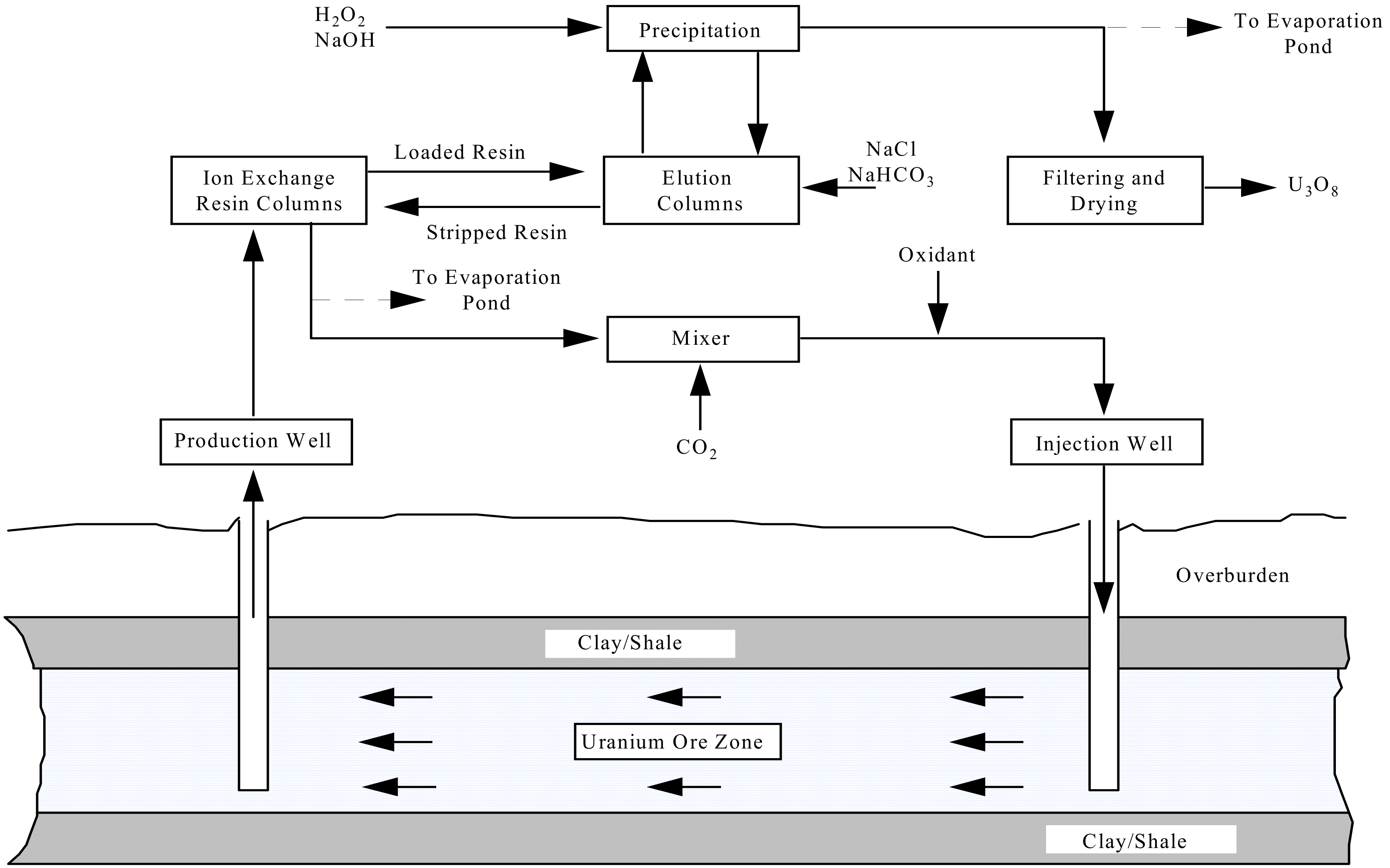


EXHIBIT 4

URANIUM *IN SITU* LEACH PROCESS

(Adapted from: DOE, Decommissioning of U.S. Uranium Production Facilities, 1995, p. 31.)



Solvent Extraction

Solvent extraction is typically employed by conventional milling operations. The pregnant leach solution is mixed in tanks with the solvent. Normally, the solvents are organic compounds that can combine with either solute cations or solute anions. The uraniferous ions preferentially move from the aqueous pregnant leach solution into the organic solvent as the two are mixed and agitated. After the uraniferous compounds have been extracted, the barren lixiviant (raffinate) is typically sent to the CCD tanks.[15,16] After the solute exchange has taken place, the pregnant solvent extraction liquor is stripped using various agents such as nitrates, chlorides, sulfates, carbonates, and acids. The pregnant stripping liquor is then pumped to the precipitation step while the stripped organic solvent is recycled to the beginning of the solvent extraction circuit.

Ion Exchange

Ion exchange operations, used by most if not all *in situ* operations and some mills, make use of organic compounds to perform solute concentration. Generally, fixed organic resins contained within a column are used to remove uraniferous compounds from the leach solution by ion exchange. As thepregnant leach solution passes through the ion exchange resins, the uraniferous compounds bind to the resins. The barren leach solution is recycled back to the leaching circuit. After adsorption, the uraniferous compounds attached to the resins are released (eluted) by passing a concentrated chloride salt solution through the loaded resins. The pregnant elute liquor can then be directed to the precipitation circuit. The liquor may be acidified slightly to prevent the premature precipitation of uraniferous compounds.[17]

Yellowcake Production

Concentrated uraniferous ions from solvent extraction or ion exchange units are precipitated out of solution to produce yellowcake. Uranium is usually precipitated from acid solutions by neutralization with ammonia or magnesia.[18] Hydrogen peroxide may also be added to an acid pregnant stripping liquor or pregnant elution liquor to precipitate uranium peroxide. All forms of the uraniferous precipitate are known as yellowcake.

Alkaline pregnant stripping liquors or pregnant elution liquors typically contain uranyl carbonates. Prior to the precipitation of the uranyl ions, the carbonate ions are destroyed by adding hydrochloric acid. The carbonates are converted to carbon dioxide, which is vented off. The acidified solution is neutralized with an alkali or treated with hydrogen peroxide to precipitate the uraniferous compounds. The yellowcake is separated from the precipitation solution by filtration. Thickeners may be used in conjunction with filtration units. The filtered yellowcake is then dried and/or calcined and packaged for shipping. The supernatant generated from the precipitation and dewatering circuits can be recycled to the respective solvent extraction or ion exchange stripping solutions.[19]

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[15] Kennecott Corporation. Op. Cit.

[16] Rio Algom Mining Corp. Op. Cit.

[17] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 22-23.

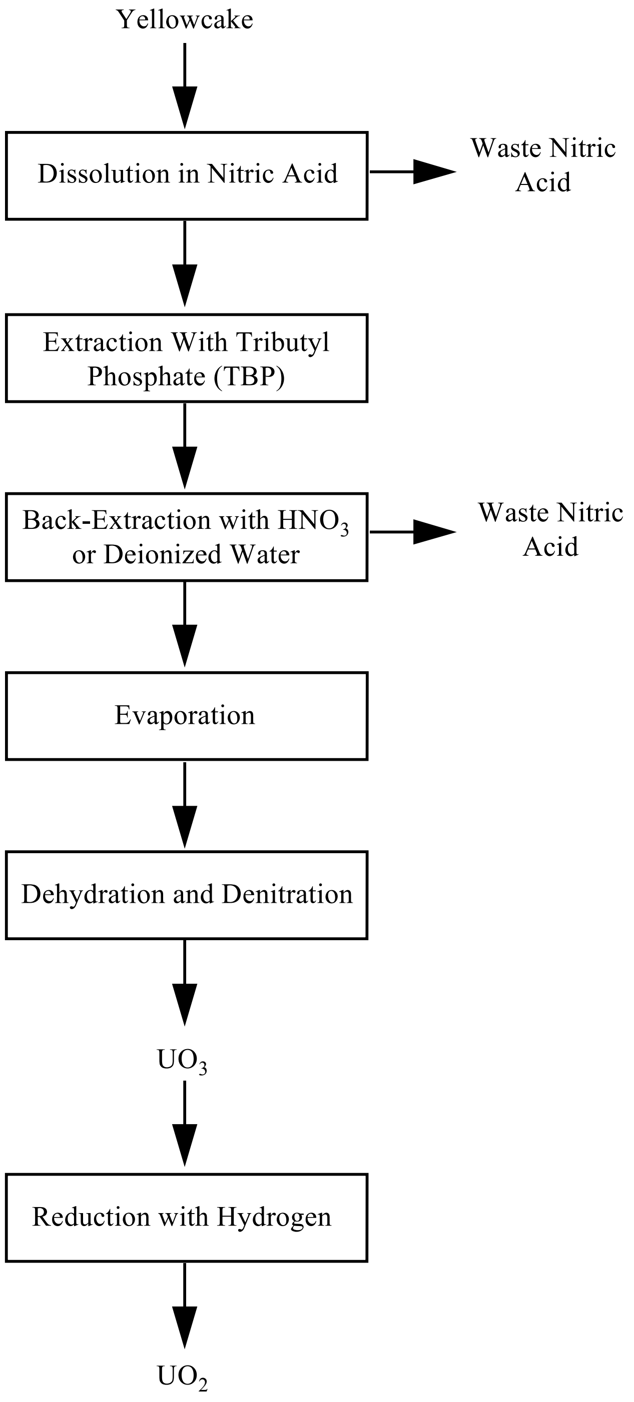
[18] "Uranium and Uranium Compounds," 1983, Op. Cit., p. 522.

[19] U.S. Environmental Protection Agency, January 1995, Op. Cit., p. 23.

EXHIBIT 5

PRODUCTION OF URANIUM DIOXIDE

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 523.)



Conversion and Purification Processes

Production of UF_4. The crude product from the refineries is purified to a degree that is usable in nuclear applications. The purified material is converted to uranium dioxide (UO_2) as shown in Exhibit 5. UO_2 is then converted to uranium tetrafluoride (UF_4) based on the following reaction:

$$UO_2(s) + 4HF(g) \text{ ---> } UF_4(s) + 2H_2O(g)$$

The process used to convert UO_2 to UF_4 is shown in Exhibit 6. Uranium tetrafluoride is then converted to either uranium metal or uranium hexafluoride (UF_6), the basic compound for isotope separation.

Production of UF_6. Uranium hexafluoride is prepared by direct fluorination of UF_4 with elemental fluorine in a fluorination tower based on the following reaction:

$$UF_4(s) + F_2(g) \text{ ---> } UF_6(g)$$

Solid UF_4 is fed through suitable locks into the top of the fluorination tower. Filtered and preheated fluorine is introduced into the side of the tower. Unreacted UF_4 is collected in a hopper at the bottom. This material is periodically removed and recycled.

Production of Uranium Metal. Uranium metal is produced by reduction of UF_4 by the Ames process as shown in Exhibit 7. The reduction process is carried out in a bomb. A charge consisting of anhydrous UF_4 powder and magnesium chips is placed into the bomb. The charge is covered with MgF_2 powder, and the bomb is closed with a screwed-on flange cover. The charge is ignited spontaneously by heating, and the reduction of the UF_4 proceeds at a temperature of 700 °C.[20]

Uranium-235 Enrichment

Most nuclear reactors built for the generation of electric power are based on uranium fuel enriched in ^{235}U. Normally for such reactors, ^{235}U is enriched from a concentration of 0.7 percent to approximately 2-3 percent. The processes used to produce enriched uranium include the gaseous-diffusion process, centrifugal isotope separation, and electromagnetic separation.

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

An improved Eluex process for uranium extraction was developed in 1957 and later improved by the U.S. Bureau of Mines.[21,22] In this process, a stage of uranium solvent extraction is coupled with each stage of resin elution rather than the elution and solvent extraction operations being conducted separately. The improved system reduces the number of stages, retention time, and resin inventory to about one-fourth or one-fifth that of other circuits.

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[20] "Uranium and Uranium Compounds," 1983, Op. Cit., pp. 523-528.

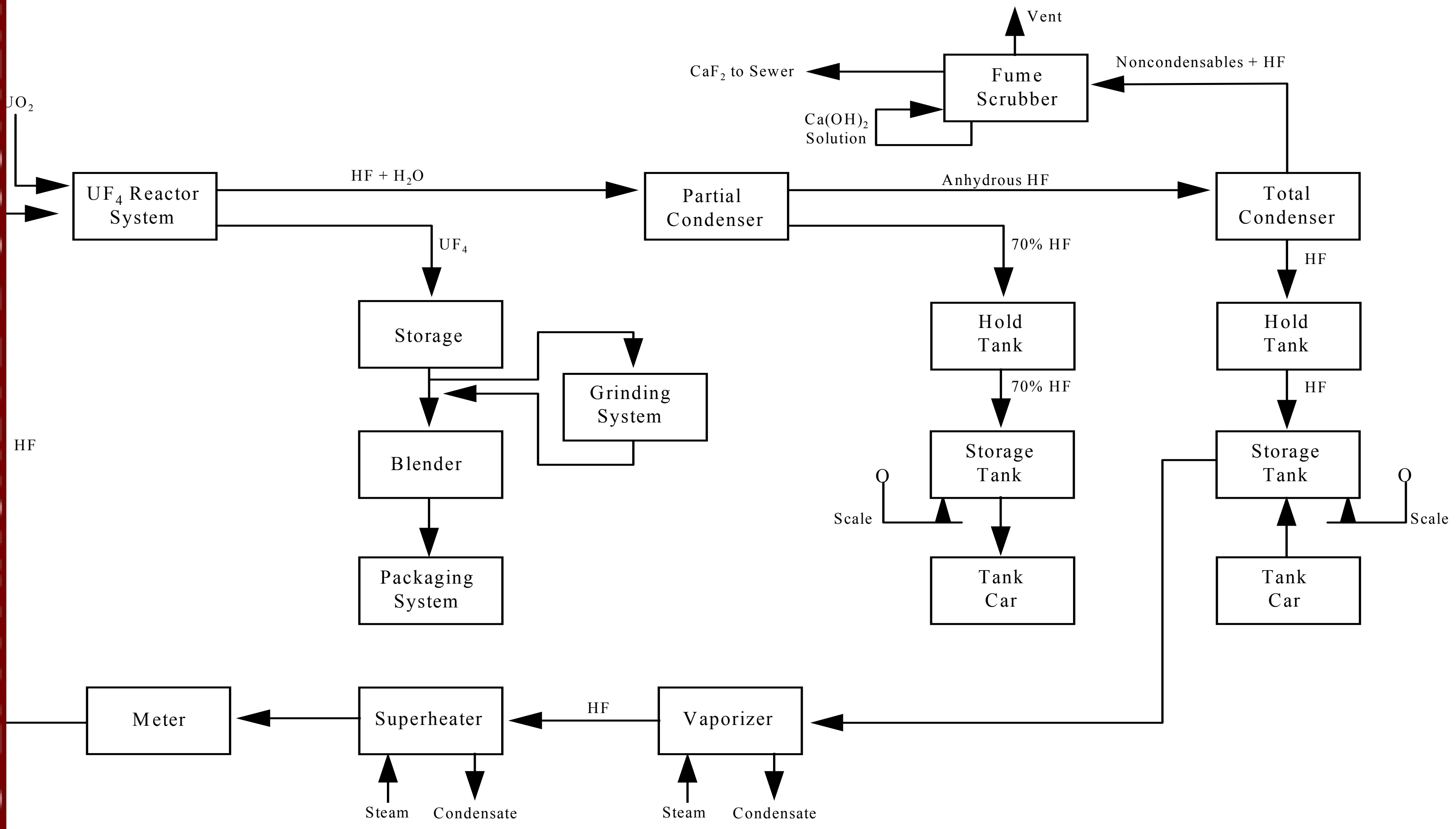
[21] Kennecott Corporation. Op. Cit.

[22] Rio Algom Mining Corp. Op. Cit.

EXHIBIT 6

FLOW SHEET FOR UF$_4$ PRODUCTION

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 527.)

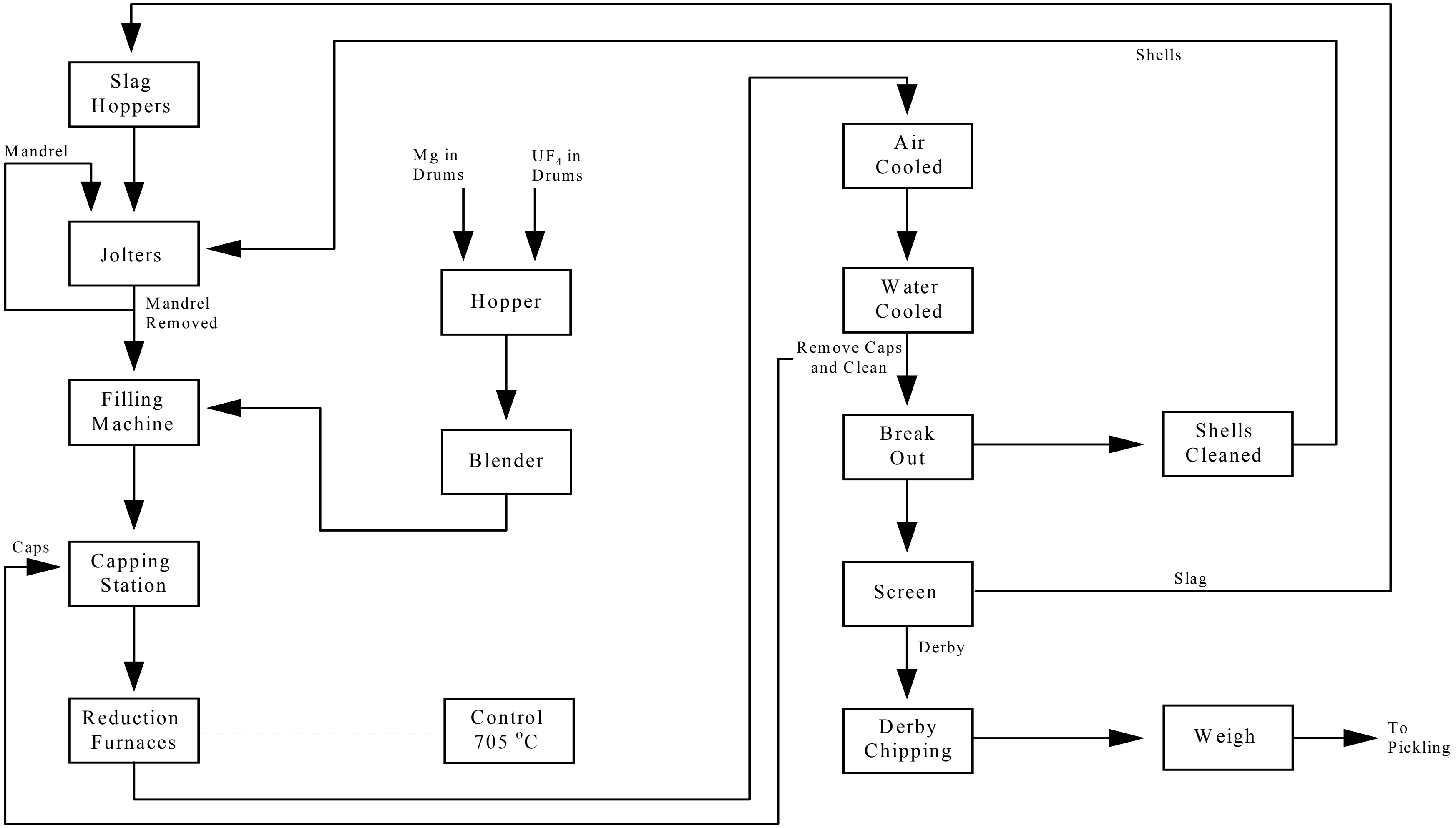


SOURCE: "Uranium and Uranium Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, p. 527.

EXHIBIT 7

THE AMES PROCESS

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 530.)



Source: "Uranium and Uranium Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, p. 530.

A flotation technique also has been developed to extract uranium from seawater. Uranium is present in seawater in concentrations of 2.9 to 3.3 micrograms per liter. Sea water is the lowest grade but the most abundant source of uranium. However, it is unlikely that this source of uranium would be considered unless ore reserves become depleted.

4. Beneficiation/Processing Boundary

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

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

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between yellowcake production and the conversion/purification processes. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where yellowcake (uranium oxide) is chemically oxidized to uranium dioxide. 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

Wastes and materials generated by uranium mining operations include waste rock, tailings, spent extraction/leaching solutions, particulate emissions, organic vapors, and refuse.[23]

Waste rock and overburden are deposited in waste rock piles or dumps. During the late 1970s, the largest open pit uranium mines produced an average of 40 million metric tons of overburden annually. Underground mines produced an average of 2,000 metric tons per year of waste rock during the same time period. Limited data indicate

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[23] U.S. Environmental Protection Agency, Assessment of Environmental Aspects of Uranium Mining and Milling, December 1976, pp. 36-43.

that waste rock contained higher levels of arsenic, selenium, and vanadium than background levels. Constituents of concern for waste rock and ore piles include low concentrations of radionuclides as well as sulfur-bearing minerals that, under certain conditions, may generate acid and, thus, leach metals.[24]

Most wastes generated by conventional mills are disposed of in tailings impoundments. These wastes, disposed of in the form of a slurry, include tailings (reground and pulped waste rock from the leaching process), gangue (including dissolved base metals), spent beneficiation solutions, and process water bearing carbonate complexes (alkaline leaching), sulfuric acid (acid leaching), sodium, manganese, and iron. Two acid- and alkaline-leach mills were reported to generate approximately 7,400 and 3,200 to 10,900 m^3/day of tailings, respectively. The tailing pond seepage from the acid-leach mill had a mean pH of 1.7 and contained high concentrations of dissolved solids (31,780 ppm), radium-226 (127 ppm), and dissolved metals (including lead, nickel, chromium, arsenic, and selenium). The tailing pond decant from the alkaline-leach mill contained high concentrations of arsenic (4 - 5 ppm), selenium (17 - 20 ppm), vanadium (24 - 27 ppm), uranium (55 - 960 ppm), and radium-226 (30 - 667 ppm).[25] The generation rate for tailing pond seepage was estimated to be 1,800 m^3/day at the facility mentioned above. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 17,000 mt/yr, 3,833,500 mt/yr, and 7,650,000 mt/yr, respectively for the tailing pond seepage.

In situ bleed solutions and lixiviant leaching solutions constitute the major wastes directed to lined evaporation ponds. These solutions consist of barren lixiviant and usually have high levels of radium; other contaminants (metals, salts) are limited to what may have been solubilized by the lixiviant. Barium chloride is added to the ponds, which in the presence of radium, forms a barium-radium-sulfate precipitate. This precipitate forms the majority of sludges in the evaporation ponds. These sludges, which may contain metals, sulfates, chlorides, and amines, are either disposed of at an NRC-licensed disposal facility or deposited in the tailings impoundment. In certain locations, where climatic conditions limit the use of evaporation, treated bleed solutions are land applied.[26]

Reverse osmosis brines, generated during the *in situ* leaching process, typically contain high concentrations of salts (total dissolved solids) and may have radionuclide (including naturally occurring radionuclides) concentrations that exceed NPDES discharge limits. These wastes, along with laboratory wastes and other wastes, are typically injected into Class I deep disposal wells permitted under the Underground Injection Control (UIC) program. These deep disposal wells are used as an alternative source of disposal at operations that usually do not operate a tailings impoundment.[27,28]

Ion exchange resins are occasionally replaced. Spent resins from *in situ* operations are disposed of at an NRC-licensed disposal facility. Conventional mills typically dispose of the spent resins in the tailings impoundments. The contribution of spent resins to the volume of a tailings impoundment is minimal compared to the volumes of tailings.[29] No information regarding the types of contaminants present in spent ion exchange resins was found.

Waste solutions are generated during acid/alkaline leaching, solvent extraction, stripping, and precipitation. Stripping solution could contain nitrates, chlorides, sulfates, hydroxides or acids. Constituents that could accumulate in the precipitation circuit are primarily anions - sulfates, chlorides, and possibly carbonates. Spent acids from

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[24] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 30-37.

[25] Werthman P., and K. Bainbridge, 1980, Op. Cit., pp. 249-250.

[26] Kennecott Corporation. Op. Cit.

[27] Kennecott Corporation. Op. Cit.

[28] Uranium Resources, Inc. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[29] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 30-37.

leaching and wash waters from the washing of leached ore solids are generated at an approximate rate of 1,000 gallons per ton of ore processed and are discharged to the tailings ponds. In addition to radionuclides, solvent extraction solutions include phosphoric acids, amines, and ammonium salts. Process water from alkaline leaching is generated at a rate of 250 gallons per ton of ore processed and is discharged to the tailings pond.[30] The supernatant generated from precipitation and dewatering circuits can be recycled to the respective solvent extraction or ion exchange stripping solutions.

Solvent extraction generates by-products (as defined in Section 11e(2) of the Atomic Energy Act), including waste acids, barren lixiviant, slimes, and waste solvents. These materials are not considered solid wastes and are excluded from RCRA regulation at 40 CFR 261.4(a)(4).[31,32,33] Although no published information regarding generation rates for these materials was found, we used the methodology outlined in Appendix A of this report to estimate low, medium, and high annual generation rates (see Exhibit 8).

2. Mineral Processing Wastes

Although no published information regarding waste generation rates or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate low, medium, and high annual waste generation rates (see Exhibit 9).

10 CFR Part 61 provides the Nuclear Regulatory Commission with complete authority to regulate radioactive waste defined as by-product material at a land disposal facility. The following wastes, therefore, may not be subject to RCRA if they are not mixed hazardous wastes. It is unclear at this time if all wastes generated at in-situ uranium mines are NRC by-product wastes. RCRA clearly has jurisdiction over mixed hazardous and radioactive wastes.

Production of UO_2

Waste Nitric Acid from the Production of UO_2. Waste nitric acid is produced during dissolution of yellowcake in nitric acid and during back-extraction. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of corrosivity. This waste was formerly classified as a spent material.

Production of UF_4

Waste Calcium Fluoride. Waste calcium fluoride, which typically contains elevated concentrations of radionuclides resulting from yellowcake production, is regulated by the Nuclear Regulatory Commission.[34] 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.

Vaporizer Condensate. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

Superheater Condensate. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

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[30] Clark, D., Op. Cit, pp. 50 - 51.

[31] Kennecott Corporation. Op. Cit.

[32] Rio Algom Corp. Op. Cit.

[33] Uranium Resources, Inc. Op. Cit.

[34] Rio Algom Corp. Op. Cit.

EXHIBIT 8

Estimated By-Product Generation Rates

By-Product Material[35]	Generation Rate (metric tons/yr)		
	Low	Medium	High
Waste Acids from Solvent Extraction	1,700	9,350	17,000
Barren Lixiviant	0	1,700	17,000
Slimes from Solvent Extraction	1,700	9,350	17,000
Waste Solvents	0	0	1,700

EXHIBIT 9

Estimated Waste Generation Rates

Waste Stream	Waste Generation Rate (metric tons/yr)		
	Low	Medium	High
Waste Nitric Acid from Production of UO_2[36]	1,700	2,550	3,400
Vaporizer Condensate	1,700	9,350	17,000
Superheater Condensate	1,700	9,350	17,000
Slag	0	8,500	17,000
Uranium Chips from Ingot Production	1,700	2,550	3,400

Ames Process

Slag. We used best engineering judgment to determine that this waste may exhibit the characteristic of ignitability. This waste is fully recycled and was formerly classified as a by-product.

Uranium Chips from Ingot Production. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of ignitability. This waste was formerly classified as a by-product.

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[35] These materials, generated during uranium beneficiation from the solvent extraction process are not considered solid wastes and are excluded from RCRA regulation at 40 CFR part 261.4(a)(4).

[36] This waste is not considered by the Agency as a mineral processing waste, but a related waste.

D. Non-uniquely Associated Wastes.

No non-uniquely associated waste streams have been identified in the uranium sector. However, standard ancillary hazardous wastes may include vehicular emissions including particulates, sulfur oxides, carbon monoxide, and hydrocarbons. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and some waste oil and other lubricants.

E. Summary of Comments Received by EPA

New Factual Information

Three commenters provided new information and clarifications of existing information related to the uranium sector that the Agency has included in this report. (COMM40, COMM66, COMM72)

Sector-specific Issues

One commenter raised an specific issue relating to the use of the term solvent extraction in conventional uranium milling operations. The commenter stated that the operation does not use halogenated hydrocarbons or degreasers, but instead uses mostly kerosene with isodecanol and tertiary amine. The commenter suggested that a better term for solvent extraction would be liquid ion exchange. EPA rejects this argument because the term “solvent extraction” does not imply use of halogenated solvents. (COMM40)

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