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% 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]

Ilmenite (FeTiO3) is the most abundant titanium-bearing mineral and is comprised of about 43% to 65% titanium dioxide (TiO2). A second major mineral form of titanium is rutile, a crystalline, high-temperature polymorph of TiO_2, containing about 95% 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% 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, or chloride-ilmenite process. The sulfate process, used at only 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, resulting in expensive 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 purified to form TiO_2 pigment. A third 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. Each of these processes is described in more detail below.

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

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

[3] J. Gambogi, 1993, <u>Op. Cit.</u>, p. 1.

[4] U.S. Environmental Protection Agency, "Titanium," from <u>1988 Final Draft Summary Report of Mineral Industry Processing Wastes</u>. 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	Chloride	Rutile
		Sulfate	Slag
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 clarified, yielding 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 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 (i.e., fluidized bed reactor) in

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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.

the presence of 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 can also 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]

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

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

[7] U.S. Environmental Protection Agency, "Titanium Tetrachlorid 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

Graphic Not Available.

Source: U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-221.

EXHIBIT 4

CHLORIDE PROCESS FOR TITANIUM DIOXIDE PRODUCTION

Graphic Not Available.

Source: U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-223.

EXHIBIT 5

CHLORIDE-ILMENITE PROCESS FOR TITANIUM DIOXIDE PRODUCTION

Graphic Not Available.

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% 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.

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

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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.

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

EXHIBIT 6

KROLL PROCESS FOR TITANIUM SPONGE PRODUCTION

Graphic Not Available.

Source: U.S. Environmental Protection Agency, 1988, Op. Cit., p. 3-224.

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 can also be crushed to create titanium powder.

<u>Titanium Ingot</u>

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) Process(es)

The United States Bureau of Mines is actively researching new processes to produce titanium alloys, with a focus on developing a continuous process to produce titanium powder for metallurgical applications. The Bureau is also conducting research on improving 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 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

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

[15] J. Gambogi, 1993, <u>Op. Cit.</u>, p. 4.

[16] "Titanium and Titanium Alloys," 1981, <u>Op. Cit.</u>, p. 116.

[17] J. Gambogi, 1993, <u>Op. Cit.</u>, p. 4.

[18] J. Gambogi, 1993, <u>Op. Cit.</u>, p. 8.

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, 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.

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. Waste sludge is also 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 1 million metric tons per facility annually. (Volume data are unavailable for this waste stream due to confidential business information [CBI] designation.) The waste did pass the low hazard criterion for special waste status.[20]

Waste Acids

Waste acids are generated when titania hydrate, generated by vacuum-evaporation and hydrolysis of titania sulfate, is filtered prior to washing. At 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] The volume of this waste stream generated annually is unavailable due to CBI designation, but it did pass the high volume criterion for special waste status of 1 million metric tons per facility annually. 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 slurry and 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

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

[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.

being discharged through an NPDES outfall and the solids disposed in a landfill. In addition, the chloride and chloride-ilmenite processes generate several other waste streams, ferric chloride and ferric chloride sludge, scrubber water and solids, and vanadium oxychloride.

Waste Acids

Waste acids 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 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 are generated annually.[23] We used best engineering judgement to determine that this waste may be partially recycled and may exhibit the characteristics of toxicity (chromium, selenium, and lead) and corrosivity. This waste is classified as a spent material. Data for this wastestream are presented in Attachment 1.

Waste Solids

Waste solids from the chloride and the chloride-ilmenite processes are generated in the chlorination step as a combined acids/solids slurry and are classified as a mineral processing special waste. The combined waste acids and solids are treated by a solids/liquids separation process, and the resulting chloride process waste solids (a special waste) are landfilled, while the chloride process waste acids are deep-well injected. Approximately 414,000 metric tons of waste solids are generated annually.[24]

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 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 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 judgement 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 is classified as a by-product. Data for this wastestream 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 24,000 metric tons/yr, 30,000 metric tons/yr, and 36,000 metric tons/yr, respectively. 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.

Two scrubber water wastestreams are generated in the chloride process, as described below. Data describing these wastestream 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.[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 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

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

[24] <u>Ibid</u>.

[25] U.S. Environmental Protection Agency, <u>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</u>, EPA 440/1-89-019.9, Office of Water Regulations and Standards, May 1989, p. 4861.

to commingling of numerous wastestreams.) We used best engineering judgement 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.[26] 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 judgement 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 judgement 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 $TiCl_4$ 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 wastestreams.) Existing data (Attachment 1) and engineering judgement 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 sludges and solids resulting from the treatment of the wastewaters described above. Sludge/solids are disposed in on- or off-site landfills. Approximately 420,000 metric tons are generated annually.[27] We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity (chromium). Data describing this wastestream 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 has 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 judgement to determine that this waste may be recycled and may exhibit the characteristics of toxicity (chromium and lead). This waste is classified as a spent material. Data describing this wastestream are presented in Attachment 1.

Spent Surface Impoundment Solids

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[26] Ibid.

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

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.[28] We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity (chromium and lead). Data describing this wastestream 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 judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

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.[29] 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 wastestreams.) 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.

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.[30] 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 judgement 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.[31] 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 wastestreams.) 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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[28] Ibid.

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

[30] Ibid.

[31] Ibid.

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

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.[33] 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 judgement 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.[34] 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 judgement 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 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 wastestreams 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 wastestreams.) 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.

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 judgement to determine that this waste may be recycled and may exhibit the characteristic of reactivity with water. This waste is 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 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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[32] U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 4863.

[33] Ibid.

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

Ingot production generates six 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.[35] 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 judgement 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 is classified as a spent material. Data describing this wastestream 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.[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 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 judgement 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, supended solids, and metals.[37] 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 judgement 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 judgement 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.[38] 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 judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Finishing Scrap

Finishing scrap is generated in the melting or milling operations used to convert titanium sponge into ingots.

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

[36] Ibid.

[37] Ibid.

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

Scrap is generally recycled back into the melting or milling operation and is not regarded as a solid waste.[39] 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 judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

D.   Ancillary Hazardous 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), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

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[39] Ibid.

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