

US EPA ARCHIVE DOCUMENT

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.

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.	Genee, 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

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

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

Source: U.S. Environmental Protection Agency, 1989, p. 4359

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 fluotantalate 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

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

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.

¹⁸ Ibid.

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

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.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1983, p. 552.
ELECTRON BEAM MELTING

EXHIBIT 3
EXHIBIT 4
EXHIBIT 5

FERROCOLUMBIUM PRODUCTION

VACUUM ARC MELTING

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) Process(es)

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 in Section B.

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 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

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.

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.

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 characteristics 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 characteristics 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,

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.

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.

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 is classified as 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.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents, tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include sanitary sewage, and waste oil and other lubricants.

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.

BIBLIOGRAPHY

- Brown, R.E., and G.F. Murphy. "Ferroalloys." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. p. 265.
- Cunningham, L.D. "Columbium." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 185-196.
- Cunningham, L.D. "Columbium (niobium)." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 48-49.
- Cunningham, L.D. "Columbium (niobium) and Tantalum." From Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 435-460.
- Cunningham, L.D. "Tantalum." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1994. pp. 170-71.
- Cunningham, L.D. "Tantalum." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 811-822.
- Gaballah, I, 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.
- "Niobium and Niobium Compounds." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XV. 1982. pp. 823-827.
- Personal Communication between ICF incorporated and Chuck Knoll, Teledyne Wah Chang, Albany, OR. November 1994.
- Personal Communication between ICF Incorporated and Larry D. Cunningham, U.S. Bureau of Mines. November 1994.
- Sutill, Keith R. "Greenbushes Lithium Generates A New Source of Income." Engineering and Mining Journal, 188, No. 11. 1987. pp. 40-43.
- "Tantalum and Tantalum Compounds." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. XXIII. 1983. pp. 547-553.
- U.S. Environmental Protection Agency. "Columbium and Tantalum." From 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes. Office of Solid Waste. 1988. pp. 3-80 -3-87.
- 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.
- U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992.
- 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.
- Weiss, Norman L., Ed. "Columbium and Tantalum." SME Mineral Processing Handbook. Volume II. Society of Mining Engineers. 1985. p.27-3.