

US EPA ARCHIVE DOCUMENT

ZIRCONIUM AND HAFNIUM

A. Commodity Summary

Zirconium and hafnium occur most commonly in nature as the mineral zircon and less commonly as baddeleyite. Zircon is used both for its properties as a mineral and as an ore of zirconium and hafnium. Zircon is a byproduct from the mining and processing of heavy mineral sands for rutile and ilmenite. Zirconium and hafnium occur together in ores at ratios of about 50:1.¹

Zircon sand is produced at two mines in Florida. Zirconium metal is extracted from imported zircon sand by two domestic producers, one in Oregon and the other in Utah. Exhibit 1 presents the names and locations of facilities associated with the production of zirconium/hafnium.

The two metals can remain unseparated for all uses except nuclear applications. Because of the extremely opposite absorption characteristics for thermal neutrons in nuclear reactor cores, the zirconium-cladded fuel rods must be hafnium free. The strong-absorbing hafnium, if present, would decrease the relative transparency of the zirconium cladding, and the reactor's efficiency. For this reason, hafnium is used in reactor control rods to regulate the fission process via neutron absorption. Hafnium is also used as an additive in superalloys, as refractory and cutting tool coatings, and in oxide and nitride forms. Nuclear fuel rod cladding accounts for most of zirconium's use. Zircon refractories and foundry sands are used primarily in the production of finished metal and glass products.²

B. Generalized Process Description

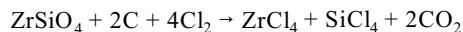
1. Discussion of Typical Processes

Zircon is mined from a shoreline deposit in Green Cove Springs, FL and from the Trail Ridge deposit in north central Florida. Sand ores are mined with dredges, bulldozers, and elevating scrapers. The production processes used at primary zirconium and hafnium manufacturing plants depend largely on the raw material used. Six basic operations may be performed: (1) sand chlorination, (2) separation, (3) calcining, (4) pure chlorination, (5) reduction, and (6) purification. Plants that produce zirconium and hafnium from zircon sand use all six of these process steps. Plants which produce zirconium from zirconium dioxide practice reduction and purification only. Exhibit 2 presents a process flow diagram for primary zirconium and hafnium production. These processes are described in further detail below.³

2. Generalized Process Flow Diagram

Sand Chlorination

After drying, concentrated zircon sand is mixed with coke, ground, and fed continuously to the top of a fluidized bed chlorinator. The basic sand chlorination reaction is as follows:



¹ Thomas E. Garner, "Zirconium and Hafnium Minerals," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 1159-1164.

² Ibid.

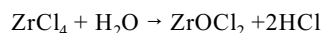
³ U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Vol. IX, Office of Water Regulations and Standards, May 1989, pp. 5081-5106.

EXHIBIT 1

SUMMARY OF ZIRCONIUM/HAFNIUM MINING AND PROCESSING FACILITIES

Facility Name	Location	Operations/Products
Du Pont	Trail Ridge, FL	Mining, extraction
RGC	NE Florida	Mining, extraction
Teledyne	Albany, OR	Metals, and alloys
Western Zirconium	Ogden, UT	Metals, and alloys

Crude zirconium tetrachloride and silicon tetrachloride are condensed from the off-gases. ("Crude zirconium tetrachloride" is a mixture of zirconium tetrachloride and hafnium tetrachloride.) The crude zirconium tetrachloride is then hydrolyzed with water and the resulting solution is filtered to remove suspended solids. The reaction is as follows⁴:



Separation

Iron is removed from the zirconium-hafnium solution from the feed makeup step by extraction. The iron free zirconium and hafnium solution is passed through a series of liquid-liquid extractions, stripping, and scrubbing steps to separate zirconium from hafnium. Liquid-liquid extraction, using methyl isobutyl ketone (containing thiocyanate) as a solvent, separates zirconium from hafnium by preferentially extracting hafnium into the solvent phase. The zirconium ions are "complexed" with the ammonium thiocyanate and the hafnium is preferentially extracted by the MIBK. The solvent, MIBK, and the complexing agent, ammonium thiocyanate, are recovered by steam stripping and recycled to the process.⁵ (According to a facility representative from Teledyne Wah Chang in Albany, Oregon, there is no ammonium thiocyanate bleed stream.⁶)

Hafnium is stripped from the solvent to the aqueous phase by acidification and the recovered solvent is recycled, after treatment, within the separation operations. The hafnium solution is reacted with ammonium hydroxide to precipitate hafnium hydroxide. The precipitate is recovered by filtration and the residual wastewater discharged to treatment. After drying, the hafnium hydroxide is either stored or calcined to produce hafnium dioxide.⁷

Zirconium is recovered from the aqueous zirconium stream through chemical treatment and further extraction with methyl isobutyl ketone. Zirconium is precipitated and filtered as zirconium sulfate. The filter cake can be either sent to calcining or repulped with ammonium hydroxide. Ammonium hydroxide is added to convert the zirconium sulfate to zirconium hydroxide and to remove trace metals

⁴ Ibid.

⁵ J.H. Schemel, ASTM Manual on Zirconium and Hafnium, American Society for Testing and Materials, 1977, pp. 58-59.

⁶ Personal communication between ICF Incorporated and Chuck Knoll, Manager of Environmental Affairs, Teledyne Wah Chang, Albany, Oregon, October 24, 1994.

⁷ U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 5081-5106.

EXHIBIT 2

PRIMARY ZIRCONIUM AND HAFNIUM PRODUCTION

Graphic Not Available.

Source: Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, 1989, Vol. 9, pp. 5081-5106.

from the zirconium product. The precipitate is filtered to remove water and sent to the calcining furnace for further processing.⁸

Calcining

From this point on in the process, zirconium and hafnium are processed separately but identically. The hafnium and zirconium filter cakes are calcined to produce hafnium oxide and zirconium oxide, respectively. Scrubber water from calciner emission control operations is recycled to the separation process to recover zirconium and hafnium.⁹

Pure Chlorination

Pure chlorination is essentially the same process as sand chlorination. The pure zirconium or hafnium oxide is mixed with fine coke and reacted with chlorine to produce the tetrachloride gas. The pure zirconium or hafnium tetrachloride is then recovered in condensers.¹⁰

Reduction

The zirconium tetrachloride and hafnium tetrachloride are reduced to their respective metals in a batch process using magnesium in a reduction furnace. The tetrachloride is added to magnesium in a retort furnace where it is converted to zirconium or hafnium metal and magnesium chloride. Off-gases from the furnace pass through a water scrubber before being released. The scrubber blowdown is recycled to the separation process to recover zirconium and hafnium.¹¹

Zirconium oxide is mixed with magnesium metal powder and placed in a steel cylinder. The cylinder is then placed in a furnace and retorted. Once initiated, the reaction becomes self-sustaining. Zirconium metal sponge and magnesium oxide are produced.¹²

Zirconium oxide can also be used to produce zirconium-nickel alloys. The process is similar to the magnesium reduction operation except that calcium hydride is used as the reducing agent in the furnace and nickel is added directly to the mixture of zirconium oxide and calcium.¹³

Purification

When zirconium or hafnium metal is produced by magnesium reduction of the tetrachloride, a crude metal regulus with magnesium chloride is formed in the furnace. The magnesium chloride is separated from the zirconium or hafnium regulus to produce zirconium or hafnium sponge.¹⁴

A different purification process is used when zirconium metal or zirconium-nickel alloys are produced by magnesium reduction of zirconium oxide. The zirconium sponge is removed from the reduction cylinder and pulverized. The impurities are leached out with acid, and the purified metal is rinsed with water. The product is then dried and sold as metal or alloy powder.¹⁵

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

⁸ Ibid.

⁹ Ibid.

¹⁰ Ibid.

¹¹ Ibid.

¹² Ibid.

¹³ Ibid.

¹⁴ Ibid.

¹⁵ Ibid.

A less complicated method may be found to separate hafnium from zirconium and to refine the hafnium. A new process is being developed where zirconium and hafnium are separated by fractional distillation of the zirconium tetrachloride. Such a process would eliminate the liquid-liquid extraction and associated precipitation, calcination, and rechlorination steps currently used.¹⁶

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 in Section B.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between ore preparation and sand chlorination because it is where a significant change to the metal 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 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.

¹⁶ Timothy Adams, "Zirconium and Hafnium," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 941-956.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Sand Drying Wet Air Pollution Control (APC)

Wastewater.

Monazite inclusions within the zircon grains and/or ionic substitution of uranium, thorium, radium, and/or actinium for the zirconium and/or hafnium within the mineral lattice result in some radioactive contamination.¹⁷

2. Mineral Processing Wastes

Sand Chlorination

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

Silicon tetrachloride purification wet APC wastewater. Silicon tetrachloride purification requires wet air pollution control. That process practices 96 percent recycle of the scrubberwater before discharging it. The existing treatment for this wastewater consists of chemical precipitation and sedimentation. This waste is discharged at a rate of 7,498 l/kg of zirconium dioxide and hafnium dioxide produced.¹⁸

Sand chlorination off-gas wet APC wastewater. After zircon ore is chlorinated, crude zirconium-tetrachloride and silicon tetrachloride are separated and recovered from the off-gases using a series of condensers. Wet air pollution control equipment is used to remove residual chlorine gas and particulates from the condenser off-gases. While one plant has achieved zero discharge of this wastewater stream using evaporation ponds, other plants discharge this stream after dechlorination, chemical precipitation, and sedimentation. Extensive recycle of scrubber liquor is practiced. This waste is generated at a rate of 16,540 to 43,470 l/kg of zirconium dioxide and hafnium dioxide produced.¹⁹

Sand chlorination area-vent APC wastewater. Ventilation vapors from the sand chlorination area are routed to wet air pollution control equipment before being released to the atmosphere. At one plant, which reports a separate waste stream for area-vent scrubbers, the wastewater generated is discharged after dechlorination, chemical precipitation, and sedimentation. That plant reported recycling 96 percent of this wastewater. This waste is discharged at a rate of 8,524 l/kg of zirconium dioxide and hafnium dioxide produced.²⁰

Feed makeup wet APC wastewater. This wastewater is characterized by treatable concentrations of suspended solids, zirconium, cyanide, and a low pH. Feed makeup steps are intended to remove suspended solids from crude zirconium-hafnium tetrachloride. This process uses wet scrubbing systems to control emissions. A high rate of recycle and reuse (92 to 100 percent) of the feed makeup scrubber liquor is achieved prior to discharge. Chemical precipitation and sedimentation is practiced for this waste stream. This waste is discharged at a rate of 5683 l/kg of hafnium dioxide and zirconium dioxide produced.²¹

¹⁷ Joseph M. Gambogi, "Zirconium and Hafnium," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 1487-1494.

¹⁸ U.S. Environmental Protection Agency, 1989, Op.Cit., pp. 5081-5106.

¹⁹ Ibid.

²⁰ Ibid.

²¹ Ibid.

Separation

Existing data and engineering judgement indicate that the wastes listed below from separation do not exhibit characteristics of hazardous wastes. Therefore, the Agency did not evaluate these materials further.

Hafnium filtrate wastewater. Separated hafnium is precipitated from solution and filtered before being sent to the calcining furnace. The filtrate can be reused in the separation process to recover its zirconium content or disposed of in evaporation ponds.²²

Zirconium filtrate wastewater. Separated zirconium is precipitated from solution and filtered before being sent to the calcining furnace. This wastestream is not recycled or reused. When this wastewater is discharged, it is treated by ammonia steam stripping, chemical precipitation, and sedimentation. This waste is generated at a rate of 37,640 to 39,900 l/kg of zirconium dioxide and hafnium dioxide produced.²³

Iron extraction (methylisobutyl ketone) steam stripper bottoms. MIBK is recovered from the iron extraction wastewater stream using a steam stripper, from which the bottoms are discharged. When this stream is discharged, it is treated by ammonia steam stripping, chemical precipitation, and sedimentation.²⁴

Ammonium thiocyanate bleed stream. Ammonium thiocyanate is recycled to the process. As stated before, according to a facility representative from Teledyne Wah Chang in Albany, Oregon, there is no ammonium thiocyanate bleed stream.

Calcination

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

Caustic wet APC wastewater. Wet air pollution control systems are used to clean the off-gases from the calcining furnaces. A high rate, 90 percent, of recycle or reuse of the discharge from the water scrubbers in the separations process is achieved. When the blowdown from this operation is discharged it is treated by dechlorination, chemical precipitation, and sedimentation. This waste is discharged at a rate of 1,539 to 8,997 l/kg of hafnium dioxide and zirconium dioxide produced.²⁵

Filter cake/sludge. Zirconium and hafnium filter cakes are calcined to produce zirconium oxide and hafnium oxide, respectively.

Furnace residue.

Pure Chlorination

Wet APC wastewater. Pure chlorination is similar to sand chlorination except that the chlorination of zirconium oxide and hafnium oxide is carried out in separate reactors at lower temperatures. The scrubbers used for reactor off-gases and area ventilation vapors discharge a wastewater stream. This stream may be recycled and the blowdown is treated by dechlorination, chemical precipitation, and sedimentation before being discharged. It contains zirconium and chlorine as well as suspended solids. This waste is discharged at a rate of 38,317 l/kg of zirconium and hafnium produced.²⁶ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

Reduction

²² Ibid.

²³ Ibid.

²⁴ Ibid.

²⁵ Ibid.

²⁶ U.S. Environmental Protection Agency, 1989, Op. Cit., pp. 5081-5106.

Reduction area-vent wet air pollution control wastewater. The plants that reduce zirconium and hafnium tetrachloride to metal use scrubbers for area ventilation vapors. The scrubber liquor is recycled before it is discharged after treatment by chemical precipitation and sedimentation. This waste is discharged at a rate of 3,686 l/kg of zirconium and hafnium produced.²⁷ 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.

Purification

Leaching rinse water from zirconium or hafnium metal production. After leaching with acid to remove impurities, the zirconium and hafnium metals are rinsed with water, dried, and packaged for sale. Treatment for this stream may consist of pH adjustment before discharge.²⁸ 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 200 metric tons/yr, 1,000,000 metric tons/yr, and 2,000,000 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 is classified as a spent material.

Leaching rinse water from zirconium and hafnium alloy production. After leaching with acid to remove impurities, the zirconium and hafnium alloys are rinsed with water, dried, and packaged for sale.²⁹ 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 34,000 metric tons/yr, 42,000 metric tons/yr, and 51,000 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 is classified as a spent material.

Spent acid leachate from zirconium and hafnium metal production. When zirconium and hafnium metals are purified by leaching, the resulting leachate is not reused or recycled. Existing treatment for this wastewater stream may consist of pH adjustment before discharge.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 1,600,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity.

Spent acid leachate from zirconium and hafnium alloy production. When zirconium and hafnium alloys are purified by leaching, the resulting leachate is not reused or recycled. Existing treatment for this wastewater stream may consist of pH adjustment before discharge.³¹ 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 850,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity.

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

Zirconium chip crushing wet APC wastewater. The zirconium sponge formed by reduction is removed from the reduction container and crushed. Scrubbers, installed for air pollution control in the crushing operation, generate a wastewater. Zero discharge of this wastewater is achieved by 100 percent recycle of the scrubber liquor.³²

Magnesium recovery off-gas wet APC wastewater. Scrubbers, installed for air pollution control in the magnesium recovery area, discharge a wastewater which is characterized by treatable concentrations of magnesium and solids. The scrubber liquor may be recycled prior to treatment which consists of chemical precipitation and

²⁷ Ibid.

²⁸ Ibid.

²⁹ Ibid.

³⁰ Ibid.

³¹ Ibid.

³² Ibid.

sedimentation followed by discharge. This waste is discharged at a rate of 20,733 l/kg of zirconium and hafnium produced.³³

Magnesium recovery area vent wet APC wastewater. Ventilation air from the magnesium recovery area passes through a wet scrubber prior to being released to the atmosphere. The scrubber liquor is recycled prior to discharge and treatment consists of chemical precipitation and sedimentation. This waste is discharged at a rate of 11,518 l/kg of zirconium and hafnium produced.³⁴

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 (e.g., petroleum naphtha), 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.

³³ Ibid.

³⁴ Ibid.

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