

US EPA ARCHIVE DOCUMENT

CHROMIUM, FERROCHROMIUM, AND FERROCHROMIUM-SILICON

A. Commodity Summary

Chromite ore, the starting material for chromium metal, alloys, and other chromium products, is not produced in the United States.¹ The metallurgical and chemical industry consumed 93 percent of the imported chromite ore used domestically in 1994; the refractory industry consumed the remainder. The major end uses of chromium metal and ferroalloys were stainless and heat-resisting steel (78 percent), full-alloy steel (8 percent), superalloys (2 percent) and other miscellaneous uses (12 percent).² Exhibit 1 summarizes the producers of chromium products in 1992. Only a small amount of the chromite is processed to produce ductile chromium; the rest is used in an intermediate form.³

EXHIBIT 1

SUMMARY OF PRODUCERS OF CHROMIUM PRODUCTS (IN 1992)^a

Facility Name	Location	Industry
American Chrome & Chemicals Inc.	Corpus Christi, TX	Chemical
Elkem AS, Elkem Metals Co.	Marietta, OH	Metallurgical
Elkem AS, Elkem Metals Co.	Alloy, WV	Metallurgical
General Refractories Co.	Lehi, UT	Refractory
Harbison-Walker Refractories ^b	Hammond, IN	Refractory
Macalloy Corp.	Charleston, SC	Metallurgical
National Refractories and Mining Corp.	Moss Landing, CA	Refractory
National Refractories and Mining Corp.	Columbiana, OH	Refractory
North American Refractories Co. Ltd.	Womelsdorf, PA	Refractory
Occidental Chemicals Corp.	Castle Hayne, NC	Chemical
Satra Concentrates Inc.	Steubenville, OH	Metallurgical

^a - Papp, John. "Chromium," Minerals Yearbook Volume 1. Metals and Minerals 1992. United States Bureau of Mines, 1992. p. 355.

^b - a division of Dresser Industries Inc.

Ferrocromium, an alloy of iron and chromium, is used as an additive in steel making. There are three major grades of ferrocromium: low carbon, high carbon, and charge grade. In the past, low carbon ferrocromium was required by steel makers to keep the carbon content of steel low. However, improved ladle refining techniques such as argon oxygen decarburization, have allowed the steel industry to use high carbon ferrocromium, which is less expensive.⁴

¹ John Papp, "Chromium," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, p. 43.

² Ibid, p. 42.

³ "Chromium and Chromium Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. VI, 1993, p. 230.

⁴ John Papp, "Chromium," Minerals Yearbook Volume 1. Metals and Minerals 1992, U.S. Bureau of Mines, 1992, p. 325.

Ferrochromium-silicon is used in the metallurgical industry to produce stainless, alloy, and tool steels and cast irons.⁵ Ferrochromium-silicon is a smelted product of chromite ore; silicon is added during the smelting process. Although a high silicon ferrochromium is sometimes produced as an intermediate in the production of low carbon ferrochromium, no ferrochromium-silicon has been produced in the United States since 1982, and it is unlikely to be produced domestically again.^{6,7} Ferrochromium-silicon typically contains 34 to 42 percent chromium, 38 to 45 percent silicon and 0.05 to 0.06 percent carbon.⁸

B. Generalized Process Description

1. Discussion of Typical Production Processes

Chromite ore is prepared for processing using several methods, depending on the ore source and the end use requirements. Course clean ore is hand sorted, while fine clean ore is gravity separated. Lumpy ore mixed with host rock may require heavy-media separation. If the chromite mineral occurs in fine grains intermixed with host rock, crushing, gravity separation and magnetic separation may be used.⁹ Chromite ore is typically beneficiated before it is sold, hence many of these operations may not be conducted in the United States.¹⁰ Exhibit 2 is a conceptual diagram of chromite ore processing. Either ferrochromium or sodium chromate is produced, and may be sold or further processed to manufacture other chromium compounds, as well as chromium metal.

2. Generalized Process Flow Diagram

Ferrochromium

Ferrochromium is made by smelting chromite ore in an electric arc furnace with flux materials (quartz, dolomite, limestone, and aluminosilicates) and a carbonaceous reductant (wood chips, coke, or charcoal.) Lumpy ore may be fed directly to the furnace, while finer ore must be agglomerated before it is added to the furnace. In efficiently operated smelters, furnace dust is collected and resmelted, and slag is crushed and processed to recover chromium. The chromium content of the ferrochromium is determined by the chromite ore's chromium to iron ratio.¹¹ The production of low carbon ferrochromium requires

⁵ John Papp, "Chromium," Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 141.

⁶ Personal Communication between ICF Incorporated and John Papp, U.S. Bureau of Mines, March 1994.

⁷ "Chromium and Chromium Alloys," 1993, Op. Cit., p. 232.

⁸ Ibid., p. 234.

⁹ John Papp, 1992, Op. Cit., p. 327.

¹⁰ John Papp, "Chromite," Industrial Minerals and Rocks, 6th Ed., Society for Mining, Metallurgy, and Exploration, 1994, p. 210.

¹¹ John Papp, 1992, Op. Cit., p. 328.

EXHIBIT 2

CONCEPTUAL DIAGRAM OF CHROMITE ORE PROCESSING

Graphic Not Available.

top blowing with oxygen. Aluminum, or more frequently, silicon is used as the reducing agent. Extremely low carbon ferrochromium is made by the simplex process, in which high carbon ferrochromium and oxidized ferrochromium are heated under high vacuum. The carbon and oxygen form carbon monoxide, leaving a pure ferrochromium with a carbon content of about 0.01 weight percent.¹²

Sodium Chromate and Dichromate

Sodium chromate and dichromate are produced at two facilities by a hydrometallurgical process during which ground chrome ore and soda ash are mixed (lime and/or leached calcine are sometimes added as well), roasted in an oxidizing atmosphere, and leached with weak chromate liquor or water, as shown in Exhibit 3.¹³ The resulting leach liquor is separated from the remaining leach residue. At the American Chrome and Chemicals facility, the roasting/leaching sequence is repeated, that is, two complete chromium extraction cycles are performed prior to removal of the residue. The leach residue is then treated, as discussed below. The treatment residue from this operation is classified as a RCRA special waste; it is disposed on-site at both facilities.¹⁴ The leach solution contains unrefined sodium chromate; this liquor is neutralized and then filtered (not shown) to remove metal precipitates (primarily alumina hydrate).¹⁵ The alumina-free sodium chromate may be marketed, but the predominant practice is to convert the chromate to the dichromate form. Occidental Chemicals Corp. uses a continuous process that involves treatment with sulfuric acid, evaporation of sodium dichromate, and precipitation of sodium sulfate (see left output stream from leaching and precipitation operation in Exhibit 3.) Sodium sulfate may be sold as a byproduct or disposed. American Chrome and Chemicals uses carbon dioxide (CO₂) to convert the chromate to dichromate (see right output stream from leaching and precipitation operation in Exhibit 3.) This process confers the advantage of not generating a sludge. The dichromate liquor may be sold as 69 percent sodium dichromate solution or returned to the evaporators, crystallized, and sold as a solid.¹⁶

Chromium Oxide

Sodium dichromate can be converted into both anhydrous chromic oxide and hydrated chromic oxide.¹⁷ To produce anhydrous chromic oxide (not shown), sodium dichromate, sulfur and wheat flour are blended with water, and the resultant slurry is heated in a kiln. The material recovered from the kiln is slurried with water, filtered, washed, dried, ground to size, screened and packaged. To produce hydrated chromic oxide (not shown), sodium dichromate solution and boric acid are blended and heated in a kiln. The reacted material is slurried with water and washed. Most of the washwater from the process is treated with sulfuric acid to recover boric acid. A waste stream containing boric acid and sodium sulfate leave the boric acid recovery unit. The product with some of the final washwater is filtered, rewashed, dried, ground, screened and packaged.¹⁸

Chromium Metal

¹² "Chromium and Chromium Alloys," 1993, *Op. Cit.*, p. 232.

¹³ *Ibid.*, p. 275.

¹⁴ American Chrome and Chemicals and Occidental Chemical, 1989. Company Responses to the "National Survey of Solid Wastes from Mineral Processing Facilities", U.S. EPA, 1989.

¹⁵ Marks, et al., editors, *Encyclopedia of Chemical Technology*, Wiley Interscience, New York, NY, 1978, pp. 93-94.

¹⁶ U.S. Environmental Protection Agency, *Report to Congress on Special Wastes from Mineral Processing*, Volume II, Office of Solid Waste, July 1990, p. 4-2.

¹⁷ Processing of either form of chromic oxide, as well as chromium metal are not primary mineral processing, and are therefore outside the scope of this report. Brief descriptions of these processes have been included for completeness.

¹⁸ Versar, Inc., *Multi-Media Assessment of the Inorganic Chemicals Industry*, Vol. II, Prepared for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, August 1980, pp. 3-13 - 3-16.

Chromium metal can be made either pyrometallurgically or electrolytically. In the pyrometallurgical method (not shown), chromium oxide (Cr_2O_3) reacts with aluminum powder in a refractory lined vessel after being ignited with barium peroxide and magnesium powder. Chromium metal may also be made from the oxide by reduction with silicon in an electric arc furnace. The chromium from this process is similar to that obtained by the aluminothermic process, except the aluminum content is lower and the silicon content may approach 0.8 percent. Chromium may also be made by reducing chromium oxide briquets with carbon at low pressure and temperatures of 1,275 to 1,400°C.¹⁹

Exhibit 4 shows the production of electrolytic chromium by the chrome alum process conducted at the Elkem Metals Company's Marietta Plant. High carbon ferrochromium is ground and leached with a hot solution of reduced anolyte, chrome alum mother liquor, and makeup sulfuric acid. Cold mother liquor is added, and the slurry is filtered to remove the undissolved solids, which are mostly silica. The filtrate is conditioned at elevated temperature for several hours to convert the chromium to the non-alum form. The filtrate is then cooled to 5°C, allowing a crude ammonium sulfate to crystallize. This iron salt is further treated to form technical ferrous ammonium sulfate, which can be sold as fertilizer and other purposes. The filtrate is clarified and aged, allowing ammonium chrome alum to precipitate. The slurry is filtered, and the chrome alum is dissolved in hot water. The chrome alum solution is clarified and fed to the electrolysis cell. After the electrolysis is complete, the cathodes are removed, washed, and the metal is removed by air hammers. The metal is crushed, washed, and dehydrogenated.²⁰

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

Research is being conducted to investigate the feasibility of using plasma smelting both worldwide, as a more efficient way of processing ferrochromium, and in the United States, to utilize low quality chromium bearing ores.²¹

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.

Ferrochromium

EPA determined that for ferrochromium, mineral processing first occurs when the chromite ore undergoes smelting in an electric arc furnace and the physical/chemical structure of the chromite ore is significantly altered. Therefore, because EPA has determined that all operations following the initial "processing" step in the production

¹⁹ "Chromium and Chromium Alloys," 1993, Op. Cit., pp. 232-234.

²⁰ Ibid., pp. 234-236.

²¹ J.E. Goodwill, "Developing Plasma Applications for Metal Production in the USA," Iron and Steelmaking, 17, No. 5, 1990, p. 352.

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.

Sodium Chromate/Dichromate

EPA determined that for sodium chromate/dichromate, mineral processing occurs at the "leaching" sequence of the process because the ore is vigorously attacked (digested) with a concentrated acid to significantly change the physical structure of the ore. 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.

Chromium Oxide

Since chromium oxide is produced from sodium dichromate, all of the wastes generated during chromium oxide production are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the sodium chromate/dichromate section above.

Chromium Metal

Since chromium metal is produced from either ferrochromium or chromium oxide, all of the wastes generated during chromium oxide production are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the ferrochromium and chromium oxide sections above.

EXHIBIT 4

C. Process Waste Streams

1. Extraction and Beneficiation Wastes

Wastes from the extraction and beneficiation of chromite may include gangue, and tailings. No information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

2. Mineral Processing Wastes

The following waste streams have been associated with the production of sodium dichromate, ferrochromium, and ferrochromium-silicon.

Sodium Dichromate Production

Treated roast/leach residue is classified as a RCRA special waste. We note, however, that prior to treatment, the roast/leach residue is not a RCRA special waste. Treatment of the leach residue consists of treating the residue slurry with either a ferrous or sulfide ion to reduce hexavalent chromium followed by treatment with sulfuric acid to lower the pH level. American Chrome and Chemicals pumps the leach residue directly to a dedicated treatment unit, in which sulfuric acid and sodium sulfide are used to induce the desired chemical changes in the residue, while at Occidental Chemicals Corp., the untreated residue is pumped to a wastewater treatment plant which receives, and apparently combines, several other influent streams prior to treatment with several different chemical agents. At both plants, the treated residue is pumped in slurry form to disposal surface impoundments.²²

The treated residue from roasting/leaching of chrome ore, is a solid material, though it typically is generated as a slurry containing particles between 2 mm and about 0.08 meters (3 inches) in diameter. The treated roast/leach residue is composed primarily of metallic oxides, such as those of iron, aluminum, silicon, magnesium, and chromium, as well as sulfates.²³ Using the available data on the composition of treated roast/leach residue, EPA evaluated whether the residue exhibited any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. The limited available data indicated that the waste did not exhibit any of the four hazardous waste characteristics.

According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 102,000 metric tons of treated leach residue are produced annually in the United States.²⁴

Ferrochromium

Dust or Sludge was a listed hazardous waste that has been remanded, therefore, the agency did not evaluate this material further. Data from the Newly Identified Mineral Processing Waste Characterization Data Set indicate the following constituents above detection limits for untreated and treated K091 (baghouse dust): aluminum, antimony, chromium, magnesium, manganese, molybdenum, nickel, selenium, thallium, vanadium, and zinc. Other EP toxicity leachate analyses indicated many of the same constituents, as well as lead and silver. In addition, the data set indicated that organics were found in the dust or sludge, but did not list them by name or concentration.²⁵ The data set also indicated that approximately 3,000 metric tons of dust or sludge are produced annually in the United States.²⁶ Additional data is provided in Attachment 1.

²² U.S. Environmental Protection Agency, 1990, Op. Cit., p. 4-2.

²³ Occidental Chemical Corp., Company Responses to the "National Survey of Solid Wastes from Mineral Processing Facilities", U.S. EPA, 1989.

²⁴ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Vol. I, Office of Solid Waste, August 1992, p. I-3.

²⁵ Ibid, pp. 15-1 - 15-10.

²⁶ Ibid, p. I-4.

ELECTROLYTIC CHROMIUM METAL PRODUCTION

Slag and Residues - According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 47,000 metric tons of slag and residue are produced annually in the United States, and the available data do not indicate that the waste is hazardous.²⁷

Ferrochromium-silicon

Dust or Sludge was a listed hazardous waste that has been remanded, therefore, the Agency did not evaluate this material further.²⁸ According to the Newly Identified Mineral Processing Waste Characterization Data Set, there is no domestic production of ferrochromium-silicon currently. Additional data is provided in Attachment 1.

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 tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

²⁷ Ibid.

²⁸ Ibid.

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