

US EPA ARCHIVE DOCUMENT

SYNTHETIC RUTILE

A. Commodity Summary

Synthetic rutile (TiO_2) is manufactured through the upgrading of ilmenite ore to remove impurities (mostly iron) and yield a feedstock for production of titanium tetrachloride through the chloride process. The chemical composition of synthetic rutile is similar to that of natural rutile, but differs in physical form. Synthetic rutile concentrates are composed of very fine crystals and are porous, whereas natural rutile grains are composed of single crystals.¹

Since 1977, Kerr-McGee Chemical Corporation has produced synthetic rutile at its Mobile, Alabama plant; it is the only U.S. producer of synthetic rutile today. Because of its purity in comparison with ilmenite, rutile and synthetic rutile are the preferred feedstocks for production of titanium tetrachloride intended for sponge and metal production. The development of processes to produce synthetic rutile was necessitated by the small quantity of economic reserves of natural rutile worldwide.² Thus, despite the fact that the U.S. has large reserves of ilmenite, the majority of sponge produced is manufactured from imported rutile and synthetic rutile, primarily from Australia and Malaysia.³

Because it is relatively free of impurities, less wastes are generated using rutile and synthetic rutile to produce titanium tetrachloride and titanium dioxide pigment than with ilmenite. The process of converting ilmenite to synthetic rutile generates 0.7 tons of waste per ton of product, and the chloride process generates about 0.2 tons of waste per ton of TiO_2 product using rutile as a feedstock. In comparison, direct chlorination of ilmenite generates approximately 1.2 tons of waste (primarily ferric chloride) per ton of TiO_2 .⁴

B. Generalized Process Description

1. Discussion of Typical Production Processes

Several processes using oxidation, reduction, leaching, and/or chlorination have been developed to remove iron from low-grade, beach sand ilmenite and produce synthetic rutile having 90 to 97% TiO_2 and very low levels of impurities. These processes can be organized in three categories:

- (1) Processes in which the iron in the ilmenite ore is completely reduced to metal and separated either chemically or physically;
- (2) Processes in which the iron is reduced to the ferrous state and chemically leached from the ore; and
- (3) Processes in which selective chlorination is used to remove the iron.⁵

Kerr-McGee uses the Benelite Cyclic process, in which hydrochloric acid is used to leach iron from reduced ilmenite. The plant has an annual capacity of almost 91,000 metric tons. The plant recycles most of its waste streams and reportedly discharges no liquid wastes.⁶

2. Generalized Process Flow Diagram

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

² U.S. Environmental Protection Agency, Technical Background Document: Development of the Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes, Office of Solid Waste, August 1989, p. B-39.

³ J. Gambogi, 1993, Op. Cit., pp. 5, 18.

⁴ J. Gambogi, "Rutile," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 141.

⁵ J. Gambogi, 1993, Op. Cit., p. 3.

⁶ D. Carr, ed., Industrial Minerals and Rocks, Society for Mining, Metallurgy, and Exploration, Inc., 1994, p. 1085.

Benelite Cyclic Process

In the Benelite Cyclic process (Exhibit 1), developed by the Benelite Corporation of America, raw ilmenite sand containing 54 to 65% TiO₂ is roasted with heavy fuel oil in a rotary kiln at 870° C. The fuel oil functions as a reducing agent, converting ferric iron (Fe³⁺) in the ilmenite to the ferrous (Fe²⁺) state. The fuel oil is burned at the discharge end of the kiln, and the resulting gases are passed through a cyclone and an incinerator to remove solids and unreacted hydrocarbons.⁷

The reduced ilmenite is then batch-digested in rotary-ball digesters with 18-20% HCl at 140° C. Ferrous oxide in the ilmenite is converted to soluble ferrous chloride, and the TiO₂ portion of the ilmenite is left as a solid. Spent acid liquor, which contains excess HCl and ferrous chloride, is sent to an acid regeneration circuit. The TiO₂ solids are washed with water and filtered and calcined at 870° C, yielding synthetic rutile with approximately 94% TiO₂. Exhaust gases from the calciner are treated to remove solids and acidic gases before they are released to the atmosphere.⁸

In the acid regeneration circuit, the spent acid liquor is sent to a preconcentrator where one-fourth of the water in the liquor is evaporated. The concentrated liquor is sprayed through atomizers, causing the droplets to dry out, yielding HCl gas and ferric oxide powder. The gas is cycloned and then sent to an absorber to remove HCl for reuse. The ferric oxide powder is slurried with water to create the waste stream iron oxide slurry.

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

High-grade synthetic rutile (98% TiO₂) has been generated through batch-scale and continuous rotary kiln carbothermic metallization of ilmenite, followed by treatments such as catalytic rusting, acidic chloride leaching, and oxidation-leaching.⁹

4. Beneficiation/Processing Boundary

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

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

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

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between screening/cleaning of sand and reduction in a rotary kiln. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the ilmenite ore occurs. Therefore, because EPA has determined that all operations following the initial "processing"

⁷ U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40.

⁸ U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40.

⁹ A. Damodaran, et al., "On Extraction of High Grade Synthetic Rutile from Indian Ilmenite," The Minerals, Metals & Materials Society, 1992, p. 1079.

step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Beach/alluvial sands containing ilmenite 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.¹⁰

2. Mineral Processing Wastes

The **Benelite Cyclic process** for manufacturing synthetic rutile generates three mineral processing wastes, as described below.

Air Pollution Control Dust/Sludges

Air pollution control (APC) dust/sludges are generated by the cycloning of off-gases from the roasting step to remove solids. Solids are also removed from off-gases from the calcining step. Off-gases from the spray roaster used in the acid regeneration circuit are also cycloned to remove entrained solids,

¹⁰ U.S. Environmental Protection Agency, "Titanium," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. p. 3-219.

EXHIBIT 1

BENELITE CYCLIC PROCESS FOR SYNTHETIC RUTILE PRODUCTION

Graphic Not Available.

Source: Kerr-McGee Corp., Comments on Notice of Proposed Rulemaking, U.S. Environmental Protection Agency, April 17, 1989, submitted May 31, 1989.

and subsequent gases from the absorber are scrubbed. APC dust/sludge is believed to be recycled back into the production process (possibly to the roasting step) and is not regarded as a solid waste.¹¹ This waste stream has a reported waste generation rate of 30,000 mt/yr. Although no published information regarding characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (cadmium and chromium).^{12,13} This waste stream is fully recycled and is classified as a sludge.

Spent Iron Oxide Slurry

Iron oxide slurry is the primary waste stream generated in the production of synthetic rutile; it is generated in the acid regeneration circuit. Approximately one-half metric ton of slurry is generated for every metric ton of synthetic rutile. The disposal method for this waste is unknown.¹⁴ This waste stream has a reported waste generation rate of 45,000 mt/yr. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity (cadmium and chromium). This waste is classified as a by-product.

Spent Acid Solution

Spent acid solution is generated in the digestion step. Spent acid liquor, which contains excess HCl and ferrous chloride, is sent to an acid regeneration circuit to recover HCl for recycle back to the digester. This waste stream is generally recycled back into the process and is not regarded as a solid waste.¹⁵ This waste stream has a reported waste generation rate of 30,000 mt/yr. Although no published information regarding characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (cadmium and chromium) and corrosivity. This waste stream is classified as a spent material.

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.

¹¹ D. Carr, ed., 1994, Op. Cit., p. 1085.

¹² U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-39.

¹³ U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, August 1992, p. I-6.

¹⁴ U.S. Environmental Protection Agency, 1989, Op. Cit., p. B-40 - B-41.

¹⁵ Ibid.

BIBLIOGRAPHY

- Carr, D., ed. Industrial Minerals and Rocks. Society for Mining, Metallurgy, and Exploration, Inc. 1994. p. 1085.
- Damodaran, A., P. Mohan Das, P. Sai, and G. Surender. "On Extraction of High Grade Synthetic Rutile from Indian Ilmenite." The Minerals, Metals & Materials Society. 1992. p. 1079.
- Gambogi, J. Annual Report: Titanium-1992. U.S. Bureau of Mines. December 1993.
- Gambogi, J. "Rutile." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 140-141.
- Kerr-McGee Corp. "Comments on Notice of Proposed Rulemaking, U.S. Environmental Protection Agency, April 17, 1989." Submitted May 31, 1989.
- U.S. Environmental Protection Agency. "Titanium." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp. 3-217 - 3-227.
- U.S. Environmental Protection Agency. Technical Background Document: Development of the Cost, Economic, and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes. Office of Solid Waste. August 1989. pp. B-39 - B-41.
- U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992.