TITANIUM TETRACHLORIDE PRODUCTION BY THE CHLORIDE ILMENITE PROCESS

Technical Background Document Supporting the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes

Office of Solid Waste
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TECHNICAL BACKGROUND DOCUMENT

TITANIUM TETRACHLORIDE PRODUCTION BY THE CHLORIDE ILMENITE PROCESS

1. Background and Purpose

This document presents EPA's factual basis for proposing to withdraw a waste generated in the production of titanium tetrachloride by the chloride-ilmenite process from the RCRA Mining Waste Exclusion. The waste in question, titanium tetrachloride waste acids (which implicitly includes iron chloride), was one of numerous mineral processing wastes that was made conditionally exempt from RCRA Subtitle C requirements under the Bevill Amendment to RCRA, and later codified at 40 CFR Part 261.4(b)(7). In 1989, following a study of the nature and characteristics of this waste, EPA determined that titanium tetrachloride waste acids (and therefore iron chloride) did not qualify for the Mining Waste Exclusion.[1]

In contrast to wastes from beneficiation operations, mineral processing wastes were required to meet two criteria in order to continue to qualify for the Mining Waste Exclusion: (1) the waste had to be a low hazard waste; and (2) it had to be generated in large volumes, defined as greater than 45,000 metric tons per year per facility for a solid waste or 1 million metric tons per year per facility for a liquid waste (averaged across the commodity sector). EPA's findings indicated that titanium tetrachloride waste acids exhibited the characteristic of EP toxicity[2] for chromium, making them a hazardous waste, and were generated in annual volumes of less than 1 million metric tons per facility; therefore, the Agency concluded that titanium tetrachloride waste acids, implicitly including iron chloride, should be withdrawn from the Mining Waste Exclusion.

Du Pont, which is the sole generator of the iron chloride waste in question, filed a lawsuit against EPA claiming that its process was different than the conventional chloride process and, therefore, that its wastes (including iron chloride) should be considered separately for Bevill status.[3] Du Pont claimed that EPA had ignored the information provided in Du Pont's written comments on several notices of proposed rulemaking addressing the Exclusion[4], and that the Agency had not provided an adequate justification for its decision. The federal D.C. Circuit Court of Appeals, in reviewing EPA's decision to withdraw titanium tetrachloride waste acids from the Mining Waste Exclusion, found that the Agency had not provided an adequate, reasonable justification in the public record to support its action.

The purpose of this technical background document is to provide a description of the Du Pont chloride-ilmenite process and the generation of the iron chloride waste, and to provide EPAs' evaluation of this the process. This evaluation serves as the technical basis for EPA's response to the Court's directives regarding the regulatory status of the iron chloride waste.

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[1] 54 FR 36592.

[2] Based upon the regulatory standard in effect and available data as of September 1989. EPA believes that the waste in question would exhibit the hazardous waste characteristic of toxicity if tested using the currently applicable testing method (the TCLP).

[3] *Solite Corporation v. U.S. Environmental Protection Agency*, Case No. 89-1629, argued September 16, 1991, decided December 31, 1991, United States Court of Appeals for the District of Columbia Circuit (952 F.2d 473).

[4] Comments submitted to RCRA docket Nos. F-88-MWEP-FFFFF (10/29/88 NPRM), F-89-MWRP-FFFFF (4/17/89 NPRM), and F-89-MW2P-FFFFF (9/15/89 NPRM).

2. Commodity Summary

Ilmenite ($FeTiO_3$) is the most abundant titanium-bearing mineral and is comprised of about 43% to 65% titanium dioxide (TiO_2). 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 available commercially at present, but deposits of anatase-bearing ore are being developed in Brazil.[5] Titanium minerals are found in hard rock deposits and in beach and alluvial sands commonly know as "beach sands." Other sources of titanium include titaniferous slags (70-85% TiO_2) made by electric furnace smelting of ilmenite with carbon.

Titanium (Ti) metal is valued 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 1993, about 75 percent of titanium metal produced was used in jet engines, airframes, and space and missile applications.[6] 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 in oxide form (TiO_2) as a white pigment for paints, rubber, paper, and plastics.[7]

Titanium dioxide pigment is manufactured through either the sulfate, the chloride, or the chloride-ilmenite process. The sulfate process, used at only two U.S. plants, involves 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 the need for expensive treatment by neutralization before disposal of the wastes.

In the more commonly used chloride process, rutile, synthetic rutile, or high-purity ilmenite is chlorinated to form titanium tetrachloride, which is purified and oxidized to form TiO_2 pigment. Titanium tetrachloride is currently manufactured at nine plants in the United States for conversion to titanium dioxide pigment.[8] (Titanium tetrachloride is also manufactured as an intermediate product in the production of titanium sponge (metal), which is cast into ingots for further processing and alloying.) Of these nine plants, six utilize the traditional chloride process.

In contrast to production operations at these plants, Du Pont employs a proprietary chloride-ilmenite process at three of its plants in which ilmenite ore is directly used to produce high-purity titanium tetrachloride. Du Pont describes the process as a "simultaneous beneficiation/processing operation." Because ilmenite contains significant quantities of iron, use of this process requires removal of the iron from the titanium value, in the form of iron (ferric) chloride. Du Pont has claimed that the iron chloride waste is generated through the removal of iron from the ilmenite ore before the physical structure of the ore is destroyed in the subsequent chlorination step of the chloride-ilmenite process. This process, conducted exclusively by Du Pont at its Edgemoor, DE and New Johnsonville, TN plants and at its DeLisle plant in Pass Christian, MS, is described in more detail below after a description of the conventional chloride process.

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

[6] J. Gambogi, "Titanium and Titanium Dioxide," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1994, p. 184.

[7] J. Gambogi, 1993, Op. Cit., p. 1.

[8] J. Gambogi, 1993, Op. Cit., p. 13.

3. Production Processes

In this section, EPA provides brief descriptions of the two major process routes for producing titanium tetrachloride. These descriptions provide the basis for the application of the Agency's definitions of mineral beneficiation and processing, which is presented below in Section 4.

3.1 Chloride Process

In the chloride process, rutile or high-grade ilmenite is converted to titanium tetrachloride ($TiCl_4$) gas. The conversion takes place in a chlorinator (i.e., fluidized bed reactor) in 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, though static-bed systems also can be used.[9] The chief reaction products are volatile metal chlorides, including $TiCl_4$, which are collected. The non-volatile chlorides and the unreacted solids that remain in the chlorinator are wasted, forming the special waste stream "chloride process waste solids."[10] The gaseous raw 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 a major acidic liquid waste stream through fractional condensation.[11] 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. 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.[12]

3.2 Chloride-Ilmenite Process

In the chloride-ilmenite process, ilmenite, which, even at high grade, has a substantially lower TiO_2 content (approximately 65%) than rutile, is converted to $TiCl_4$. The ilmenite ore used in the process contains a much larger amount 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 fluid bed reactor 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 within a four step production process, there is a two-step reaction sequence referred to as "selective chlorination," consisting of a beneficiation step and a processing step. Both of these first two steps occur in the chlorinator. In the first step, ilmenite ore is reacted with the chlorine gas and coke. Within seconds, the chlorine reportedly reacts with the iron oxide in the ilmenite ore, producing gaseous iron chlorides that are subsequently condensed (in step 3) in a spray condenser to form iron chloride waste acids, which are either sold as product or disposed as the waste stream "titanium tetrachloride waste acids." The initial step is the beneficiation portion of the process, according to Du Pont. This step also reportedly yields enriched ilmenite

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

[10] U.S. Environmental Protection Agency, "Titanium Tetrachloride Production," from Report to Congress on Special Wastes from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, p. 13-3.

[11] U.S. Environmental Protection Agency, 1988. "Titanium," from Summary Report of Mineral Industry Processing Wastes (Final Draft). p. 3-222.

[12] Ibid.

ore consisting of more than 95% TiO_2 and having the same basic particle structure as the original ilmenite ore feed.[13] Du Pont contends that

> [T]he first phase of the chlorination step produces sand grains that are virtually unchanged from the original mineral, except for a change in color as a result of the removal of iron. Thus, this phase, which generates most of the waste from the Du Pont process, produces nothing more than a high grade beneficiate.[14]

In the second 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. Du Pont contends that this step is the mineral processing portion of the operation. The $TiCl_4$ is condensed and further refined to remove contaminants in step 4 of the process. These contaminants are then combined with the iron chloride waste stream generated at step 3.[15]

4. Application of Definitions of Mineral Beneficiation and Processing

By classifying the first phase of its chloride-ilmenite process as beneficiation, Du Pont is seeking to include the iron chloride waste generated through steps 1 and 3 of the process within the Mining Waste Exclusion. Du Pont bases its classification on its belief that the "beneficiation" step renders the structure of the ilmenite ore intact and essentially unchanged after the initial reaction with chlorine gas and coke.[16] Based on this criterion alone, Du Pont concludes that because the ore structure remains essentially unchanged, the initial step constitutes beneficiation. According to the preamble of EPA's final rule on the Mining Waste Exclusion, however,

> Most beneficiation processes, at least those immediately upstream from the initial processing operation in a production sequence, generate high volume solid waste streams that are essentially earthen in character. Despite the fact that valuable constituents have been removed, the remaining material is often physically and chemically similar to the material (ore or mineral) that entered the operation, except that particle size reduction has often occurred. Processing operations, in contrast, generate waste streams that generally bear little or no resemblance to the materials that entered the operation. These operations most often destroy the physical structure of the mineral, producing products and waste streams that are not earthen in character.[17]

Based upon detailed evaluation of the information submitted by Du Pont, EPA has found that in the initial step, chlorine gas is reacted with the solid ore, inducing significant chemical changes in the ore and forming a new chemical compound, ferric chloride. The reaction forming this new compound is the first of two that fundamentally alter the physical and chemical nature of the mineral feedstock. Indeed, the reaction of chlorine with iron and the changes in

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[13] 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.

[14] 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.

[15] Ibid.

[16] Letter from Aldo Morell, Du Pont, to Van E. Housman and George B. Wyeth, U.S. Environmental Protection Agency, May 12, 1995, p. 1.

[17] 54 FR 36619.

the ore that it induces are very similar to the subsequent reaction between chlorine and titanium and its impacts upon the mineral feedstock. Both of these reactions occur in the same vessel using the same reagent and reaction conditions, and both contribute to the physical and chemical destruction of the ore.

In terms of the nature of the waste in question, the ferric chloride waste acids do not resemble the ore feedstock entering the operation, and instead are much more similar to typical mineral processing wastes such as metallurgical acid plant blowdown than to beneficiation wastes such as mill (flotation) tailings. In this example, the removal of iron as an impurity from the titanium ore is directly analogous to the removal of sulfur and heavy metal impurities during the primary smelting of base metals such as lead and copper. Furthermore, ferric chloride is a highly corrosive material. While EPA has not collected analytical testing data for this waste in order to apply the hazardous waste test for corrosivity, it is known generally that $FeCl_3$ in solution has corrosive properties[18]. Data submitted by Du Pont to the Agency in 1990[19] show, in fact, that the liquid iron chloride waste has a pH below zero and exhibits the hazardous waste characteristic of toxicity for cadmium, lead, and silver. Published information[20] also shows that Du Pont markets the ferric chloride solution that it produces from titanium tetrachloride production as a wastewater and drinking water treatment reagent. Clearly, this material more closely resembles a concentrated chemical product or waste than a typical earthen beneficiation waste such as flotation tailings.

Finally, it is worthy of note that, according to EPA's codified definitions, chlorination constitutes beneficiation only when it is used in preparation for a leaching operation that does not produce a final or intermediate product that does not undergo further beneficiation or processing.[21] In the case of Du Pont's process, the first step of the "simultaneous beneficiation/processing" operation is followed not by a leaching step but by further chlorination (destructive chlorination, in this case). In other words, notwithstanding Du Pont's technical arguments, no part of the production sequence involving the reaction of ilmenite ore with chlorine in the fluid bed reactor falls within EPA's established and codified definition of beneficiation. Accordingly, all wastes associated with this production sequence are mineral processing wastes. Furthermore, because the liquid wastes from this operation are not high volume (whether considered separately or as part of the larger $TiCl_4$ industry), they are not eligible for retention within the Mining Waste Exclusion.

In response to Du Pont's most recent submission concerning the chloride-ilmenite process and the wastes that it generates[22], EPA believes that the central point is that within one reaction vessel and set of reaction conditions, a beneficiated ore is treated so aggressively that solid metals are *vaporized*. The fact that more than one gaseous (metal chloride) stream emerges from this operation is irrelevant, as is the fact that one stream is a product and the other (primarily) is a waste. While the Agency recognizes that it has previously suggested that the Kerr-McGee synthetic rutile plant is a beneficiation operation, EPA wishes to clarify that

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[18] A five percent solution of $FeCl_3$ has a pH of 1.7 at equilibrium (Kirk-Othmer Encyclopedia of Chemical Technology, Third Ed., vol. 13. John Wiley and Sons, New York, 1981. p. 773.).

[19] Letter from C. Goldstein, Covington & Burling, Washington, D.C., to Randolph L. Hill, U.S. Environmental Protection Agency, Office of General Counsel, December 13, 1990, Table IVB.

[20] American Chemical Society, 1991. Chemcyclopedia 1992. p. 171, and ERT Hazardous Substances Database. 1995.

[21] 40 CFR 261.4(b)(7).

[22] Morell, Op Cit., p. 1.

volatilization of metals in a primary mineral production sequence constitutes mineral processing.

5. Conclusions

In this technical background document, EPA has provided the relevant facts for determining whether iron chloride waste generated by Du Pont's chloride-ilmenite process constitutes an exempt beneficiation waste or a non-exempt mineral processing waste. Du Pont asserts that the initial step of its process involves beneficiation rather than processing on the basis that the ore structure remains physically intact following chlorination of the iron in the ore. EPA concludes, however, that due to the significant physical and chemical changes that are induced in the feedstock (and the generation of a new chemical compound) in the first step, and the similarity of these changes to those induced by the second step, it is most appropriate to consider the entire sequence a mineral processing operation. Furthermore, EPA disagrees with Du Pont's recent assertion that the Agency and Du Pont are in agreement that the chloride-ilmenite operation involves beneficiation.[23] As a final and definitive point on this question, the form of chlorination employed by Du Pont in this process is not included within EPA's definition of beneficiation. Accordingly, the chloride-ilmenite process is defined as mineral processing. Hence, because the iron chloride wastes are not high volume, they are non-exempt mineral processing wastes.

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[23] Morell, Op Cit., p. 2.

BIBLIOGRAPHY

Derkics, D. "Notes of the October 24, 1989 Meeting with Representatives of E.I. Du Pont de Nemours & Company." U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Memorandum submitted to Mining Waste Docket No. F-89-MW2P-FFFFF. 1989. 5 pp.

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

Gambogi, J. "Titanium and Titanium Dioxide." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1994. pp. 184-185.

Goldstein, C. Letter to Randolph L. Hill, U.S. Environmental Protection Agency, Office of General Counsel, from C. Goldstein, Covington & Burling, Washington, D.C. November 16, 1990. 7 pp.

Goldstein, C. Letter to Randolph L. Hill, U.S. Environmental Protection Agency, Office of General Counsel, from C. Goldstein, Covington & Burling, Washington, D.C. December 13, 1990. 15 pp.

Morell, Aldo. Letter to Van E. Housman and George B. Wyeth, U.S. Environmental Protection Agency, from A. Morell, Du Pont, Wilmington, DE. May 12, 1995. 3 pp.

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. "Titanium Tetrachloride Production." From Report to Congress on Special Wastes from Mineral Processing. Vol. II. Office of Solid Waste. July 1990. pp. 13-1 - 13-31.