**FLUORSPAR AND HYDROFLUORIC ACID**

**A.      Commodity Summary**

In 1994, approximately 73 percent of the reported fluorspar ($CaF_2$) consumed in the United States was used in the production of hydrofluoric acid.  About 10 percent of the fluorspar was used as a fluxing agent in steelmaking, and in iron and steel foundries.  The remaining 17 percent was consumed in aluminum fluoride manufacture, primary aluminum production, glass manufacture, enamels, welding-rod coatings, and other miscellaneous end uses or products.[1]  Fluorspar is sold in three grades:  metallurgical (minimum 85 percent $CaF_2$), ceramic (85-96 percent $CaF_2$), and acid (minimum 97 percent $CaF_2$).[2]  While there are seven active domestic fluorspar mines, the majority of fluorspar used in the U.S. is imported.[3]

Hydrofluoric acid is an aqueous solution of hydrogen fluoride produced by a reaction of fluorspar and sulfuric acid.  Hydrofluoric acid is the feedstock used to produce almost all of the organic and inorganic fluorine-bearing chemicals.  Hydrofluoric acid also is used in aluminum and uranium processing.[4]  As of 1989, three facilities actively produced hydrofluoric acid.  Although several other facilities produce hydrofluoric acid as an intermediate product during the formulation of commercial chemicals or compounds, these facilities are not included as part of the primary hydrofluoric acid industry.  The names and locations of the three hydrofluoric acid production facilities are shown in Exhibit 1.

**EXHIBIT 1**

**SUMMARY OF HYDROFLUORIC ACID PRODUCERS (IN 1989)**

| Facility Name | Location |
|---|---|
| Allied Signal | Geismar, LA |
| E.I. duPont | La Porte, TX |
| Attochemical, N.A. | Calvert City, KY |

**B.      General Process Description**

**1.  Discussion of the Typical Production Processes**

Hydrofluoric acid is produced by reacting acid-grade fluorspar and sulfuric acid in a kiln, and cooling and purifying the product.  This process is described in detail below.

**2.  Generalized Flow Diagram**

Before fluorspar can be used to make hydrofluoric acid, the raw ore must be physically concentrated and purified.  Ceramic and acid grades of fluorspar are concentrated (not shown) by crushing and grinding fluorspar, and purified by froth flotation.  First the fluorspar is crushed and ground.  Then lead and zinc sulfides are preferentially floated away from the fluorspar.  The easily floating fluorspar is removed and sent to the cleaner circuit.  The tailings are discarded and the middling product is reground and passed through a cleaner circuit.  The flotation process yields acid

---

[1] M.M. Miller, "Fluorspar," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 58.

[2] M.M. Miller, "Fluorspar," from Minerals Yearbook. Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 487.

[3] U.S. Bureau of Mines, Randol Mining Directory 1994/1995, Randol International Ltd., Golden, CO, 1994, p. 165.

[4] M.M. Miller, 1994, Op. Cit., p. 58.

grade concentrate, and sometimes lower grade concentrates, which are sold either as ceramic or metallurgical grade fluorspar. Metallurgical grade fluorspar is produced by hand sorting, crushing and screening, and gravity concentration.[5]

Hydrofluoric acid is produced from acid-grade fluorspar ($CaF_2$) which reacts with sulfuric acid in a heated retort kiln to produce hydrogen fluoride gas, as shown in Exhibit 2. The acid grade fluorspar typically contains at least 97 percent calcium fluoride, as well as silica, calcium carbonate, carbon, sulfur, phosphorus pentoxide, chloride, mixed metal oxides, and a trace amount of arsenic. The sulfuric acid generally is between 93 and 99 percent pure. Both sulfuric acid and oleum ($SO_3$) are commonly used.[6] The residue remaining after retorting is calcium sulfate anhydrite, commonly known as fluorogypsum, which is a RCRA special waste. This solid is slurried in process water as it exits the kiln and is transported either to the waste management units[7] or, at the duPont plant, to a production operation for further processing for sale as a byproduct.[8] The process wastewater, the second RCRA special waste generated by this sector, is stored/treated in on-site surface impoundments and then either reused in the process operations or discharged.

The crude product gas is handled differently by the various manufacturers, but cooling and scrubbing are always involved. Exhibit 2 shows the gas being cooled, purified by scrubbing, and condensed. The crude product may be diluted and sold as an approximately 70 percent hydrofluoric acid solution, or distilled to remove any remaining water and impurities, and sold as anhydrous hydrogen fluoride, a colorless fuming liquid. The wastes from the refrigerated condenser go to an acid scrubber. The sulfuric acid used in this process unit is then sent to the acid feed, to react with the fresh fluorspar. The waste stream from the acid scrubber is sent to a water scrubber which generates fluorosilicic acid and gases. The fluorosilicic acid may be recovered or disposed.

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

No new novel processes have been utilized, however, a possible process under investigation involves extracting fluorine as fluorosilicic acid from phosphate rock during the production of phosphoric acid. Also under investigation is the production of calcium fluoride from calcium silicon hexafluoride ($CaSiF_6$) produced by the reaction of fluorosilicic acid and phosphate rock.[9]

---

[5] M.M. Miller, 1992, Op. Cit., pp. 488-89.

[6] "Fluorspar," from Kirk Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. XI, 1994, p. 364.

[7] Allied Signal, Inc., 1989, Public comments from Allied Signal, Inc. addressing the 1989 Proposed Reinterpretation of the Mining Waste Exclusion (Docket No. MW2P00020); November 8, 1989; pg. 1.

[8] At the duPont facility, lime is added when the fluorogypsum is quenched in order to enhance the chemical characteristics of the material for construction applications.

[9] "Fluorspar," 1994, Op. Cit., pp. 367-68.

#### 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 when the beneficiated fluorspar is mixed with concentrated acid in the furnace/kiln where an intense exothermic chemical reaction occurs and significantly alters the chemical structure of the fluorspar. 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.

### C.  Process Waste Streams

### 1.  Extraction and Beneficiation Wastes

Gangue, lead and zinc sulfides, spent flotation reagents, and tailings are likely to be generated by the beneficiation of fluorspar. The lead and zinc sulfides may be processed further to recover the lead and zinc. No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

### 2.  Mineral Processing Wastes

The hydrofluoric acid production process generates several waste streams. Two of these waste streams, fluorogypsum and process wastewater, were classified as RCRA special wastes, and were studied in the July 1990 Report to Congress on Special Wastes from Mineral Processing.

**Fluorogypsum**. This waste is a solid material consisting primarily of fine particles of calcium sulfate, usually less than 0.02 mm in diameter, that is slurried for transport from the kilns to waste management units. Using available data on the composition of fluorogypsum, EPA evaluated whether the waste exhibits any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. Based on analyses of four samples from two facilities (Geismar and Calvert City) and professional judgment, the Agency does not believe the fluorogypsum exhibits any of these characteristics. All eight of the inorganic constituents with EP toxicity regulatory levels were measured in concentrations (using the EP leach test) that were at least two orders of magnitude below the regulatory levels.[10] According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 894,000 metric tons of fluorogypsum are produced annually in the United States.[11] The La Porte, TX plant sells its fluorogypsum for use as a filler for a road base, railroad subbase, and paving material.[12]

**Process wastewater**. This waste is an aqueous liquid, the chemical constituents of which include fluoride, calcium, and sulfate, with smaller amounts of iron and silicon, as well as many trace metals. Using available data on the composition of hydrofluoric acid process wastewater, EPA evaluated whether the wastewater exhibits any of the four characteristics of hazardous waste: corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. Based on available information and professional judgment, the Agency does not believe the wastewater is reactive, ignitable, or EP toxic. All eight of the inorganic constituents with EP toxicity regulatory levels were measured in concentrations (using the EP leach test) that were at most 0.6 times the regulatory levels. Some wastewater samples, however, exhibit the characteristic of corrosivity. Analyses of the pH of hydrofluoric acid process wastewater at the Geismar and Calvert City facilities indicate that the wastewater is corrosive in all of the nine samples analyzed, sometimes with pH values as extreme as 1.00 (for comparison, pH levels below 2.0 are operationally defined as corrosive wastes).[13] According to the Newly Identified Mineral Processing Waste Characterization Data Set, approximately 13.6 million metric tons of process wastewater are produced annually in the United States.[14]

**Sludges**. 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.

**Off-Spec Fluorosilicic acid ($H_2SiF_6$)**. This waste is recovered from the water scrubber, and can be used in water fluoridation after it is recovered. 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, 15,000 metric tons/yr, and 44,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of corrosivity. This waste stream is partially recycled and classified as a by-product.

**APC Dusts**. 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.

---

[10] From the response of Allied Signal, Inc. and Pennwalt Corp. to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities", conducted in 1989.

[11] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Waste Characterization Data Set, Office of Solid Waste, August 1992, p. I-5.

[12] From the response of E.I. duPont to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities," conducted in 1989.

[13] From the response of Allied Signal, Inc. and Pennwalt Corp. to EPA's "National Survey of Solid Wastes from Mineral Processing Facilities", conducted in 1989.

[14] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-5.

**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.

# BIBLIOGRAPHY

"Fluorspar." Kirk Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. XI. 1994. pp. 364-68.

Fulton III, R.B., and G. Montgomery. "Fluorspar." From Industrial Minerals and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 509-522.

Miller, M. M.. "Fluorspar." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995, pp. 58-59.

Miller, M.M., "Fluorspar." From Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 487-500.

MRI Inc. Draft Site Visit Report on Pennwalt Corporation, Calvert City. July 14, 1989.

U.S. Bureau of Mines. Randol Mining Directory 1994/1995. Randol International Ltd. Golden, CO. 1994.

U.S. Environmental Protection Agency. "Fluorspar." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste. 1988. pp. 2-104 - 2-108.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992.

U.S. Environmental Protection Agency. Report to Congress on Special Wastes from Mineral Processing. Volume II. Office of Solid Waste. July 1990. pp. 9-1 - 9-29.

Weiss, N.L., Ed. SME Mineral Processing Handbook. Society of Mining Engineers. New York. 1985. pp. 23-1 - 23-9.