CHAPTER 12.11

Fluorspar

Peter Huxtable

Fluorspar is the name for the naturally occurring mineral fluorite (calcium fluoride, CaF_2). It is the predominant commercial source of fluorine, a nonmetallic element and the lightest of the halogens, and provides 93% of the global demand for fluorine.

Another significant but much smaller (7%) source of fluorine is from phosphate rock (fluorapatite, $Ca_5(PO_4)F$) as fluorosilicic acid (FSA). This is primarily used to produce some (15%) of the alumimun fluoride (AlF_3) used as the flux for aluminum smelting, and in water fluoridation and toothpaste manufacture.

Cryolite (Na_3AlF_6) is a minor source of fluorine found in Greenland, Europe, but minable reserves were depleted by 1962. Other fluorine-bearing minerals are of relatively little significance and include sellaite (MgF_2), topaz ($Al_2SiO_4(FOH)_2$), villiaumite (NaF), and a rare earth bastnaesite ($(Ce,La)(CO_3)F$).

Georgius Agricola described the use of fluorspar as a metallurgical flux in 1556. Fluorspar mining started in England around 1775 and in the United States between 1820 and 1840, and industrial demand increased for fluorspar as a fluxing agent in the late 1880s as the steel industry expanded. In 1886, the development of the electrolytic process for aluminum production led to a further increase in demand.

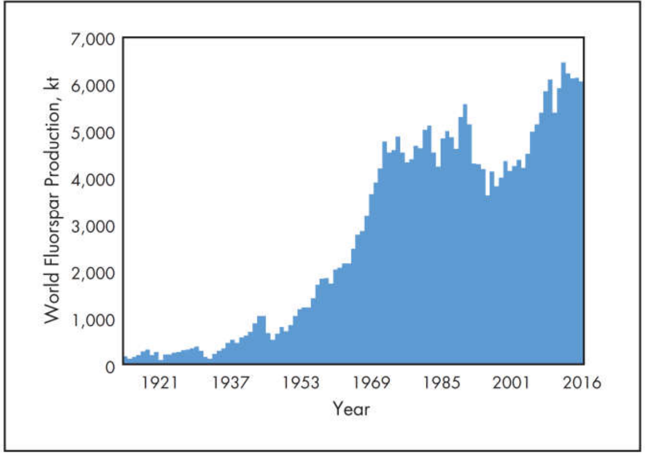
In the 1930s, fluorocarbons were developed using hydrofluoric acid (HF) and were used as refrigerants in household and commercial cooling equipment. This application was greatly expanded in the 1970s and 1980s, and fluorocarbons' use as aerosol propellants was also developed. Concerns about the apparent depletion of the stratospheric ozone layer pointed to the chlorine in chlorofluorocarbons as a primary suspect and led to a phaseout of their use through the international Montreal Protocol treaty of 1987 and subsequent amendments (UNEP 2017). More ozone-friendly replacements—hydrochlorofluorocarbons and hydrofluorocarbons (HFCs)—were developed that contained less chlorine and required more fluorspar to manufacture, although not-in-kind replacements (mainly the more flammable hydrocarbons) replaced all, except for some specialty medical, aerosol applications.

The United Nations Framework Convention on Climate Change in Kyoto (UN 1998) imposed further restrictions on HFCs, perfluorocarbons, and sulphur hexafluoride in 1997 because of their global warming potential (GWP) impact—along with carbon dioxide, methane, and nitrous oxides. These restrictions have become increasingly stringent; the European Union (EU) 2014 F-Gas regulations (EU 2014) became effective in January 2015, and the Significant New Alternatives Policy (SNAP) program from the U.S. Environmental Protection Agency (EPA) became effective in 2016 (EPA 2015). This has led to further developments of almost zero GWP hydrofluoroolefins and low-GWP HFC blends.

The trend in annual world production output since 1913 (Figure 1) shows an average production of 6 Mt from 2009 through 2016.

GEOLOGY, MINERALOGY, AND MINING

Fluorine has an estimated crystal abundance of 0.065%, and among the elements it ranks 13th in order of abundance.



Data from USGS 2016; Roskill 2013, 2015–2016, 2017

Figure 1 World fluorspar production output 1913–2016

Peter Huxtable, Principal, Huxtable Associates, Calver, Derbyshire, United Kingdom

In its pure form, fluorspar contains 51.1% calcium and 48.9% fluorine, and has a specific gravity of 3.18 and a hardness of 4 on the Mohs scale. Pure fluorite melts at 1,378°C and is relatively insoluble in water (0.146 g/L at 25°C). Crystalline fluorspar has a very low index of refraction (1.433–1.435) and low dispersion. It is isotropic and has the unusual ability to transmit ultraviolet light. This makes fluorspar useful in optical systems and high-quality, special-purpose lenses.

Fluorite belongs to the cubic system mineralogically and tends to occur in well-formed isometric crystals, forming cubes and octahedrons. It also occurs in both massive and earthy forms, and as crusts or globular aggregates with radial fibrous texture. Crystalline fluorspar exhibits a great range of colors from colorless to yellow, blue, purple, green, rose, red, bluish and purplish black, and brown.

The natural mineral is commonly associated with other minerals, such as quartz, calcite, barites, galena, siderite, celestite, sphalerite, chalcopyrite, sulfide, or phosphate minerals.

The U.S. Geological Survey (USGS) estimates world reserves in 2017 at 260 Mt (100% CaF_2 basis) with 41 Mt in South Africa, 32 Mt in Mexico, 40 Mt in China, and 22 Mt in Mongolia (USGS 2017). Identified world resources are approximately 500 Mt. In addition, large quantities of fluorine are present in phosphate rock worldwide, estimated at the equivalent of 4.9 billion tons 100% fluorspar equivalent (USGS 2017).

Fluorite occurs in a wide variety of geological environments, with deposition under an extended range of physical and chemical conditions. The deposits occur worldwide, and the average ore grade of sources mined ranges from a low of 8% CaF_2 (Vietnam) to 85% CaF_2 (Mexico). China contributed 65% of world output in 2016 with another 23% from Mexico, Mongolia, South Africa, and Vietnam. The most important modes of fluorite occurrence from an economic view are as follows:

1. Fissure veins commonly occur along faults or shear zones and are found in igneous, metamorphic, and sedimentary rocks. Mineralization occurs as lenses or ore shoots separated by barren zones. Ore shoot widths of 0.5–10 m and lengths of 60–300 m are common, and CaF_2 content typically ranges from 25% to 80%. Vein systems may be several kilometers long and ore presents to depths of 300 m or more below the surface. Important deposits include China, northeast Spain (Osor), Morocco (El Hammam), United States (Rosiclare, Illinois), United Kingdom (Derbyshire), and Italy (Sardinia).
2. Stratiform, manto, or bedded deposits occur in carbonate rocks. Certain beds are replaced along or adjacent to structural breaks such as joints or faults, frequently with sandstone, shale, or clay capping. Well-developed deposits are found in Mexico (northern Coahuila) and South Africa (Zeerust). CaF_2 content ranges from 11% upward.
3. Replacement deposits in carbonate rocks are well developed along contacts with intrusive igneous rocks and include some of the largest and highest grade fluorspar deposits, including those in Mexico (Rio Verde, San Luis Potosi).
4. Stockworks and fillings in shear and breccia zones are generally lower grade, such as those in South Africa (Buffalo); often they are not economic.
5. Fluorspar is a common mineral in *alkaline rock* although not often sufficiently abundant to be economic. Examples can be found in Namibia (Okorusu) and India (Amba Dongar).
6. Concentrations of fluorspar resulting from the weathering of primary vein and replacement deposits are generally sources of metallurgical-grade material. These *residual deposits* can extend to depths of 30 m or more. Examples can be found in Spain (Asturias), Thailand, South Africa (Marico), the United States, and the United Kingdom.
7. Fluorspar occurs in lead–zinc veins in many parts of the world. Economically viable *gangue mineral* deposits average 10%–20% CaF_2.

Table 1 World consumption of fluorspar (kt) by application and grade, 2013–2016

Industry	Acidspar	Metspar	Total
Chemicals	2,300	—	2,300
Steel	—	2,100	2,100
Aluminum	1,400	—	1,400
Other	—	400	400
Total	**3,700**	**2,500**	**6,200**

Data from Roskill 2013, 2015–2016, 2017; Corathers and Machamer 2006

Fluorspar is mined by both open-pit surface and underground methods depending on the geology and location of the deposit. Surface or near-surface deposits are mined using standard open-pit methods ranging from small-scale operations at some of the smaller Chinese mines, to draglines and scrapers, to power shovels. Open-pit methods are employed in China, Kenya, South Africa, Thailand, and Vietnam.

Deeper deposits are extracted using underground techniques by deep-shaft or adit access using rail, haul trucks, or conveyors. Techniques are typically room-and-pillar for bedded deposits, and shrinkage or open stoping for deeper vein deposits.

USES, MARKETING, AND GEOGRAPHIC SOURCES

There are two grades of commercial fluorspar. One is a predominantly metallurgical-grade gravel material (*metspar*) that is typically 85%–92% CaF_2, 5–20 mm in size, and produced by simple crushing and gravity separation. This material is primarily used as a flux in steelmaking, and in smaller quantities in cement clinker and the glass industry.

A higher (>97%) CaF_2 acid-grade product (*acidspar*) is produced by further processing, fine grinding, and froth flotation. This material is used in the chemical industry where the starting point is the manufacture of HF. It is also used as a flux in the production of aluminum after being used to produce AlF_3.

These two grades conform to the international harmonized tariff codes 252922 (acidspar) and 252921 (metspar).

Typical consumption of fluorspar worldwide from 2013–2016 by grade and application is shown in Table 1. The chemical industry is the largest consumer, using 37% of the total, followed by the steel industry with 34% and the aluminum industry with 23%.

Refrigeration and air-conditioning account for around 50% of fluorocarbon production, followed by foam-blowing agents that improve the insulation properties of plastics. These are non-feedstock applications and are subject to environmental controls under the Montreal Protocol (UNEP 2017) and GWP international treaties (UN 1998; EU 2014; EPA 2015). The development of fluorine-based replacements has enabled

Table 2 World production of fluorspar (kt) by country and grade, 2016

Country	Acidspar	Metspar	Total	% Total
China	2,200	1,500	3,700	65.0
Mexico	430	230	660	10.5
Mongolia	10	270	280	5.0
South Africa	220	10	230	4.0
Vietnam	200	—	200	3.5
Spain	110	10	120	2.0
Other	290	270	560	10.0
Totals	**3,460**	**2,290**	**5,750**	**100.0**

Data from Roskill 2013, 2015–2016, 2017

this market to continue to be supplied without reductions in acidspar requirements. Polymer precursors are feedstock fluorocarbons that are not affected by these environmental considerations, and they are the starting blocks for a range of fluoroelastomers and fluoropolymers with outstanding chemical and thermal stability, and are electrically inert and nonflammable. This is a fast-growing area in which polytetrafluoroethylene (PTFE) accounts for 60% of the market. (PTFE includes the nonstick surface coatings on cookware.) Polyvinylidene fluoride is used to manufacture lithium-ion batteries for mobile phones, laptops, and hybrid and electric cars. Diverse industrial applications include electronics, crystal glass, uranium manufacture, and herbicides and detergent manufacture.

The use of fluorspar to produce AlF_3 as a flux for aluminum manufacture is also rapidly increasing because of the high growth rate of aluminum production worldwide. Although about 15% of AlF_3 is produced from by-product FSA, this is not a serious contender for further market erosion of the use of natural fluorspar.

The principal production of fluorspar by leading countries and grade is shown in Table 2. China, North America, and Russia/Commonwealth of Independent States are self-sufficient for their fluorspar needs. Europe has a net import requirement of 0.5 t per year.

Fluorspar prices are not internationally quoted because little material is freely traded and most is either used in-house or sold on long-term supply arrangements and contracts. *Industrial Minerals* magazine quotes typical price ranges of both acidspar and metspar by principal exporter and by main end-use importer (*Industrial Minerals* 2017). Price data are shown in Figure 2 for acidspar wet filtercake exports free on board (fob) China, which is the predominant benchmark for price indications, and for metspar fob Mexico as the main world exporter of the product.

The EU has recognized fluorspar as a critical raw material as a result of its 2008 Raw Materials Initiative (European Commission 2008) and as shown in its latest 2017 update (European Commission 2017). It has also been identified on the British Geological Survey Risk List 2015 (BGS 2015).

PROCESSING

All processing is by physical beneficiation whereby unwanted waste rock (gangue) is separated from the host fluorite by a series of standard techniques tailored to the character of the mined ore feed and the specifications for end use. For acidspar, fine grinding and froth flotation are required to produce the >97% CaF_2 specification material, which adds considerably to the overall processing costs because of high electric power costs and the use of flotation reagents.

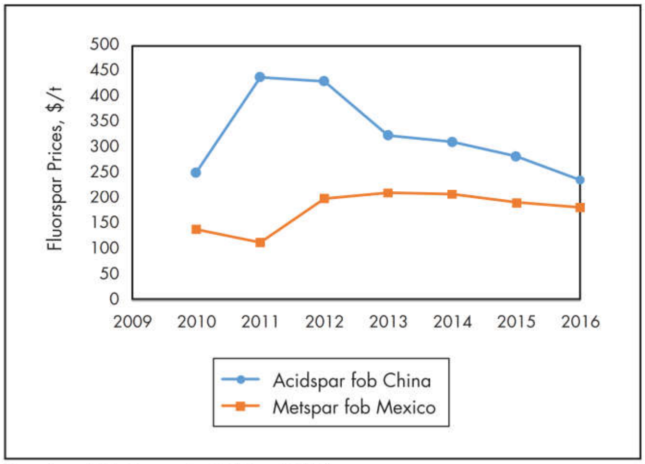
Metspar processing in less-developed countries can be performed by hand-sorting of high-grade lump ore followed by crushing and screening to remove most of the fines. For lower-grade ores or where there is relatively coarse interlocking of minerals, gravity separation using jigs, tables, or heavy media separation is used.

Heavy media cone and drum separators are particularly effective in the size range of 0.5–3.8 cm either for metspar production or to preconcentrate the crude ore for flotation feed. For finer sizes, a heavy media cyclone or a Dynawhirlpool (DWP) is frequently used and the sinks can be sold as metspar, the sands for flotation feed, and the floats for road gravel or concrete aggregate. Ores as low as 8%–10% CaF_2 can be processed this way to produce a flotation feed of 40% CaF_2 or more. Ferrosilicon and magnetite are used as the heavy media solution and cleaned off the surfaces of products with high-pressure water, and recycled through magnetic separators.

Washing plants are also commonly used ahead of flotation to remove any fine clays. Water supply to the plant is often recycled from the process tailings with fresh water input only to the flotation section.

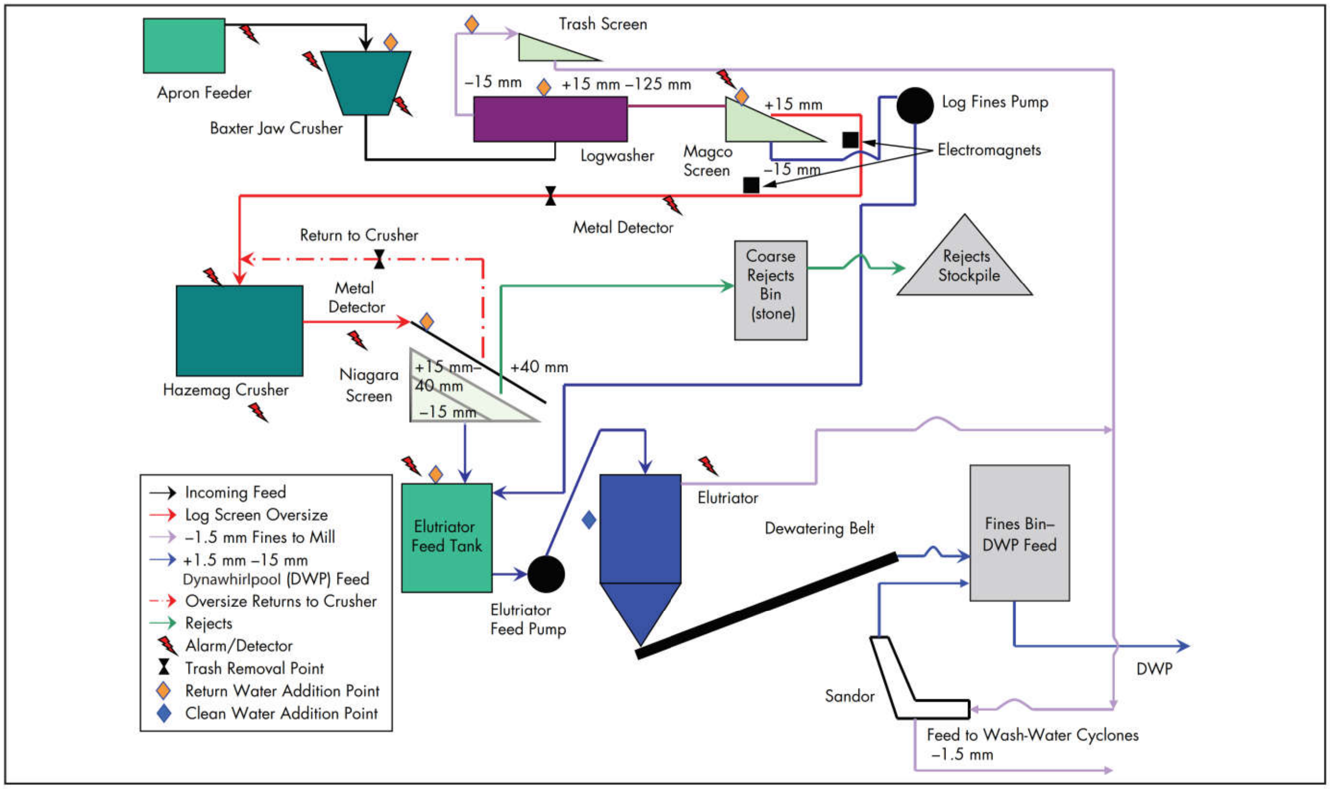
Froth flotation takes advantage of the varying surface properties of different materials enabling separation of valuable product from gangue tailings in flotation cells. Fine grinding in rod or ball mills enables liberation of the fluorite from other minerals present and the host silica or limestone. The circuit is chosen to minimize the generation of extremely fine sizes that are not amenable to efficient flotation recovery.

The flotation feed at suitable pulp density is fed to conditioning tanks where suitable reagents are added and the pH modified with soda ash for optimal recovery. In some operations, the pulp is heated to greater than ambient temperature to improve recovery rates, although the additional cost is not often justified by the potential extra recovery. The pulp is agitated in the presence of injected air and a frother reagent, which creates minute air bubbles that attach preferentially to the desired mineral that has been coated with a collector, a suitable flotation reagent, and is then floated off as a product in a froth. Any metallic sulfides (lead or zinc) in the host ore are removed first using a xanthate or dithiophosphate collector in a circuit before the fluorspar extraction. After rougher



Data from UN Comtrade 2017a, 2017b

Figure 2 Fluorspar world prices, $/t fob source port



Courtesy of British Fluorspar

Figure 3 Cavendish Mill crushing and washing circuit

extraction to maximize recovery, the product goes to cleaner cells to maximize the finished grade of concentrate.

Fluorspar is then extracted in rougher cells using suitable collectors, normally fatty acids (such as oleic), along with quebracho or tannin to depress calcite or dolomite; sodium silicate, starch, or dextrine to depress silicates or any iron; and dichromates to depress any barites in the ore. The rougher concentrate then proceeds to a cleaner circuit, which may include up to six circuits to ensure >97% CaF_2 product and often includes a small regrind mill to liberate interlocking grains of fluorspar and gangue and to maximize recovery—and minimize the levels of calcium carbonate and silica where product specifications typically require less than 1.5% and 1%, respectively. The final concentrate slurry with a pulp density of around 25% solids goes to a thickener where the density is raised to about 55% prior to filtration to produce a filter cake with a moisture below 10%. This material is either shipped directly to the customer or dried first prior to shipment in bulk powder tankers or in 25-kg or 1-t big bags for use by smaller-volume end users.

Tailings disposal from the flotation process is either (1) to a tailings lagoon, direct or via a thickener, or (2) using a filter press or belt filter. Residual waters will recirculate for use in the washing circuits.

The processing of the Cavendish Mill, Glebe Mines, Derbyshire operations (currently owned by British Fluorspar, Ltd., part of the Fluorsid Group) were described in some detail along with process flow sheets at a symposium (Huxtable 1989). The current circuit has evolved, and those changes are shown in Figures 3 through 7.

REFERENCES

Agricola, G. 1556. *De Re Metallica*. Translated by Herbert C. Hoover and Lou Henry Hoover. 1950 edition. New York: Dover Publications.

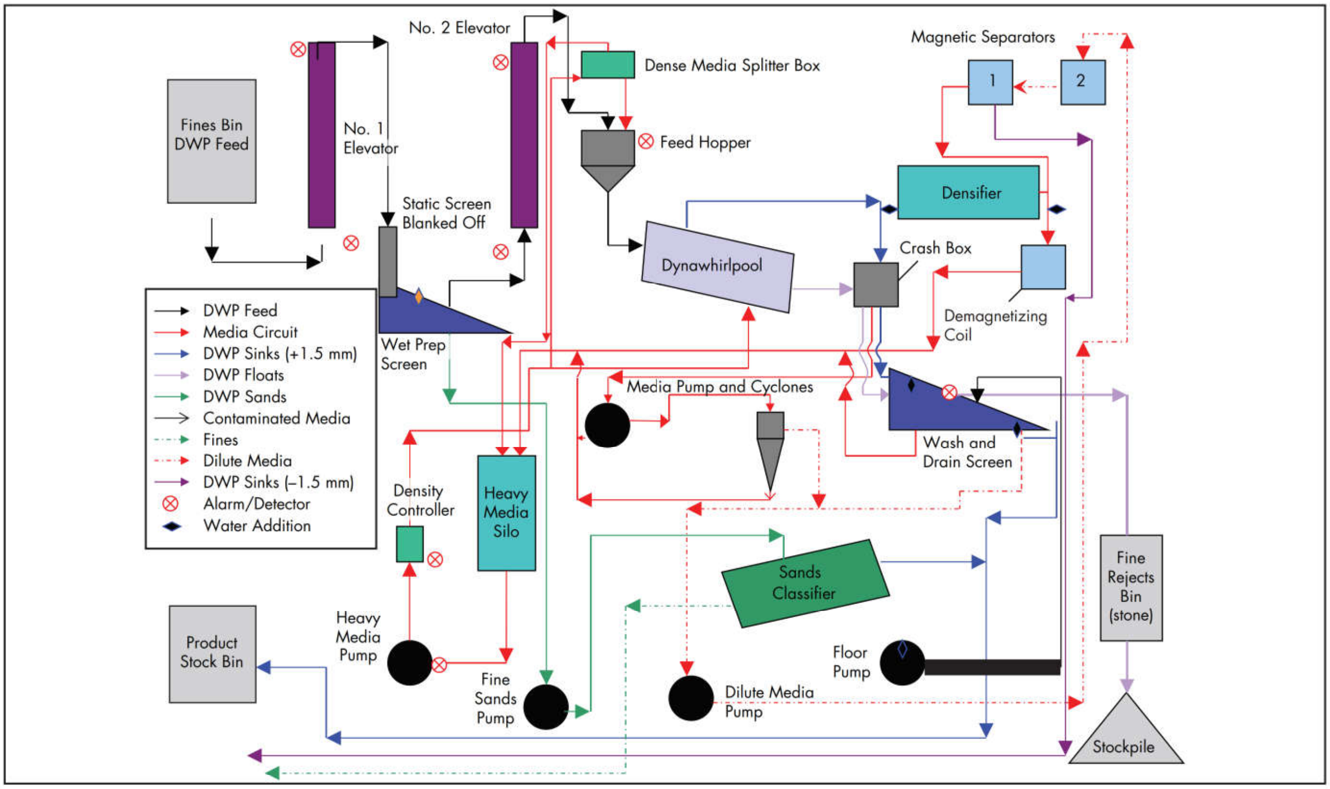
BGS (British Geological Survey). 2015. Risk List 2015: Current supply risk for chemical elements or element groups which are of economic value. Keyworth, UK: National Environment Research Council. www.bgs.ac.uk/downloads/start.cfm?id=3075.

Corathers, L.A., and Machamer, J.F. 2006. Fluorspar. In *Industrial Minerals and Rocks*, 7th ed., Vol. 2. Edited by J.E. Kogel, N.C. Trivedi, J.M. Barker, and S.T. Krukowski. Littleton, CO: SME.

EPA (U.S. Environmental Protection Agency). 2015. Significant New Alternatives Policy (SNAP): SNAP Regulations. https://www.epa.gov/snap/snap-regulations. Accessed August 2017.

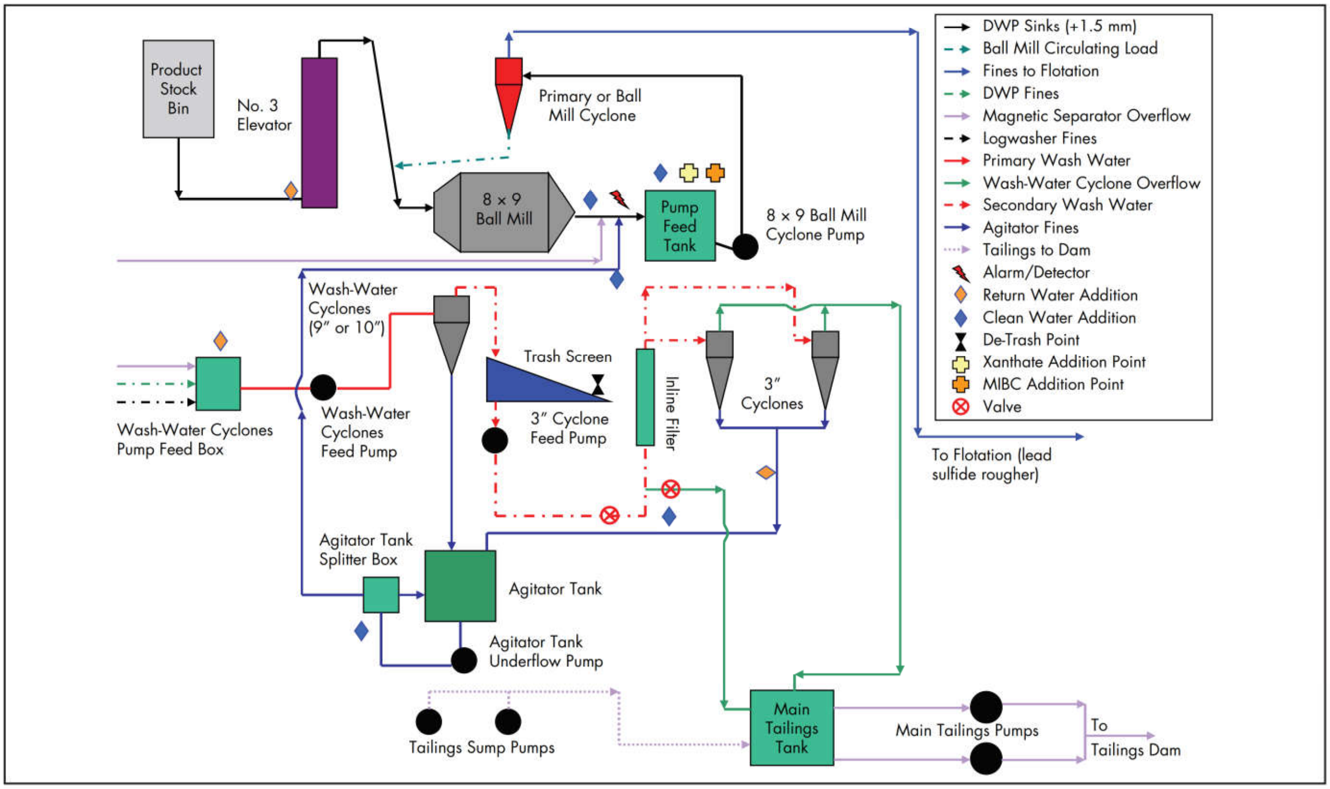
European Commission. 2008. The Raw Materials Initiative—Meeting our critical needs for growth and jobs in Europe. http://ec.europa.eu/growth/sectors/raw-materials/policy-strategy/index_en.htm. Accessed August 2017.

EU (European Union). 2014. Regulation (EU) No. 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No. 842/2006 Text with EEA relevance. http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=uriserv:OJ.L_.2014.150.01.0195.01.ENG. Accessed August 2017.



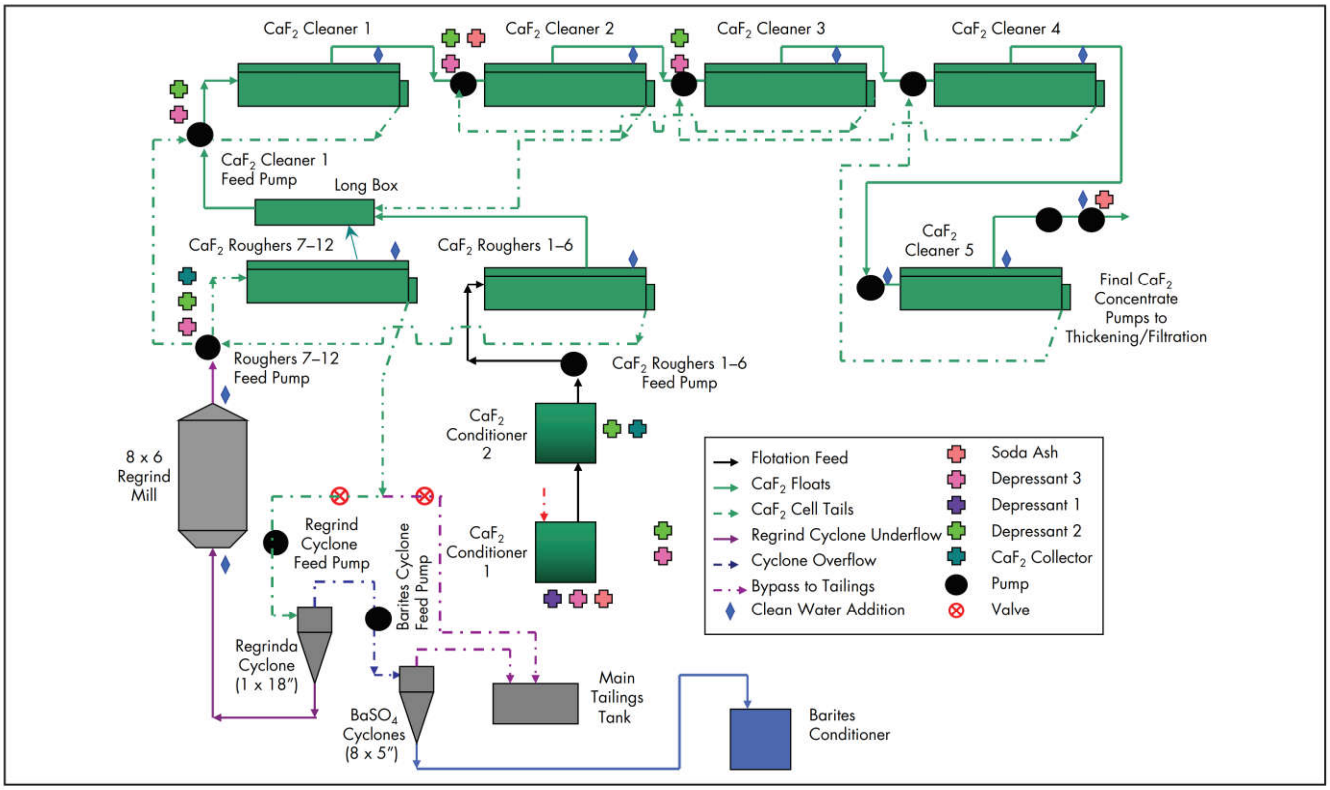
Courtesy of British Fluorspar

Figure 4 Cavendish Mill heavy media separation



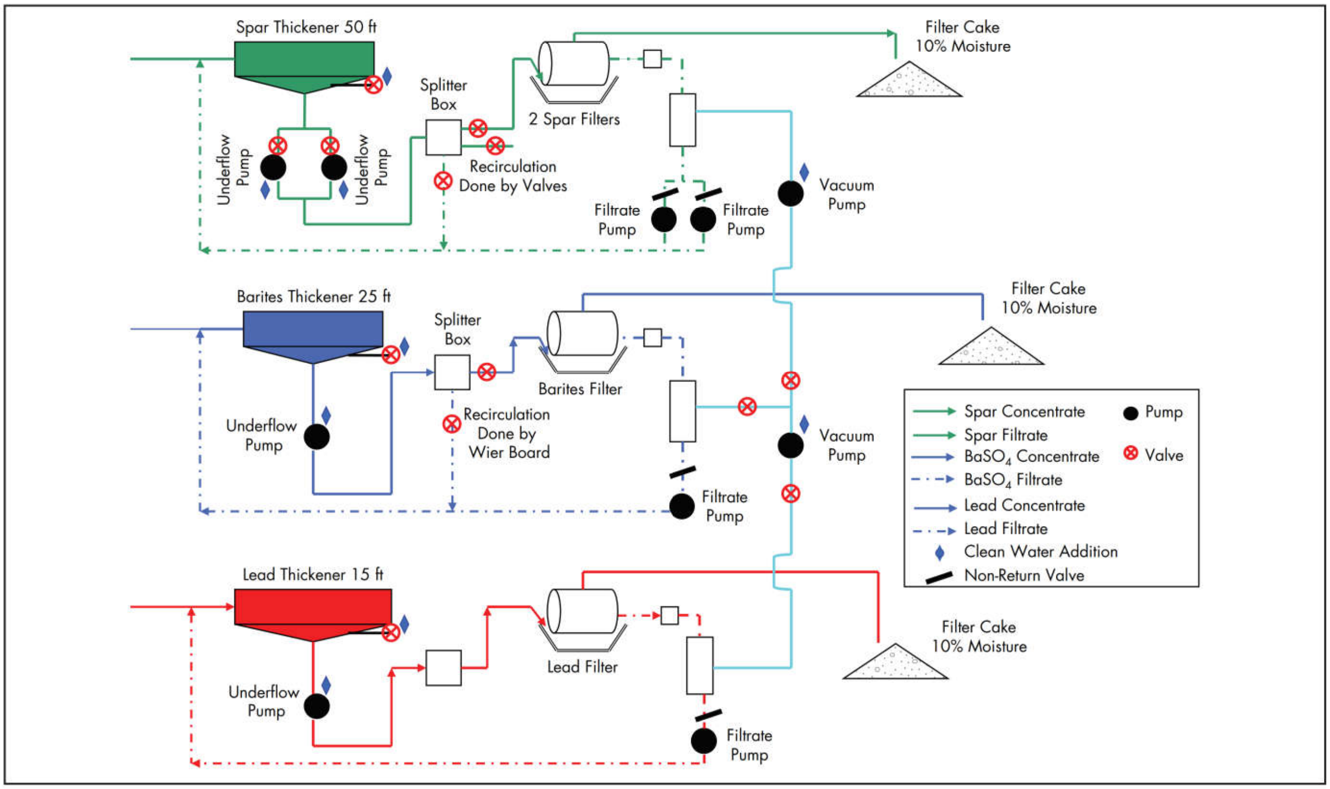
Courtesy of British Fluorspar

Figure 5 Cavendish Mill grinding circuit



Courtesy of British Fluorspar

Figure 6 Cavendish Mill fluorspar flotation°



Courtesy of British Fluorspar

Figure 7 Cavendish Mill thickening and filtration

European Commission. 2017. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the 2017 list of Critical Raw Materials for the EU. http://ec.europa.eu/transparency/regdoc/rep/1/2017/EN/COM-2017-490-F1-EN-MAIN-PART-1.PDF. Accessed October 2017.

Huxtable, P.L. 1989. The one hundred percent solution. In *Proceedings of Mineral Processing in the UK*. London: Institution of Mining and Metallurgy.

Industrial Minerals. 2017. Fluorspar online price information (subscriber only). www.indmin.com/Pricing.html. Accessed August 2017.

Roskill. 2013. *Fluorspar: Global Industry Markets and Outlook*, 11th ed. London: Roskill Information Services Limited.

Roskill. 2015–2016. *Fluorspar: Industry Briefing*. London: Roskill Information Services Limited.

Roskill. 2017. *Fluorspar: Global Industry Markets and Outlook to 2021*, 12th ed. London: Roskill Information Services Limited.

UN (United Nations). 1998. Kyoto Protocol to the United Nations Framework Convention on Climate Change. http://unfccc.int/resource/docs/convkp/kpeng.pdf. Accessed August 2017.

UN Comtrade (United Nations Commodity Trade Statistics Database). 2017a. Acid-grade fluorspar. https://comtrade.un.org/db/mr/daCommoditiesResults.aspx?px=H3&cc=252922. Accessed August 2017.

UN Comtrade (United Nations Commodity Trade Statistics Database). 2017b. Metspar. https://comtrade.un.org/db/mr/daCommoditiesResults.aspx?px=H3&cc=252921. Accessed August 2017.

UNEP (United Nations Environment Programme). 2017. *The Montreal Protocol on Substances That Deplete the Ozone Layer,* 10th ed. http://ozone.unep.org/en/treaties-and-decisions/montreal-protocol-substances-deplete-ozone-layer. Accessed August 2017.

USGS (U.S. Geological Survey). 2016. Fluorspar. In *Historical Statistics for Mineral and Material Commodities*. Washington, DC: USGS.

USGS (U.S. Geological Survey). 2017. Fluorspar. In *Mineral Commodity Summaries*. Washington, DC: USGS.