

## CALCIUM FLUORIDE

### 1. Introduction

Fluorine chemistry began with observations by Georgius Agricola as early as 1529 that fluorspar lowers the melting point of minerals and reduces the viscosity of slags. This property of fluxing (Latin *fluere*, to flow) is the origin of the name fluorine. The term fluorspar correctly describes ores containing substantial amounts of the mineral fluorite [14542-23-5],  $\text{CaF}_2$ , but the word fluorspar is often used interchangeably with fluorite and calcium fluoride.

Calcium fluoride [7789-75-5] has the formula  $\text{CaF}_2$  and a molecular weight of 78.07, and it is 51.33% calcium and 48.67% fluorine. Calcium fluoride occurs in nature as the mineral fluorite or fluorspar. It is prepared from the reaction of  $\text{CaCO}_3$  and HF.

### 2. Occurrence

Significant mining of fluorspar began in England about 1775 and in the United States after 1820. Substantial use of fluorspar began about 1880 in the basic open-hearth process for making steel (qv). Large increases in demand came with the need for fluorides in the aluminum industry, starting about 1900. A large fluorine chemicals industry based on hydrogen fluoride made from fluorspar followed in production of refrigerants (see REFRIGERATION AND REFRIGERANTS) (1930), alkylation (qv) catalysts for gasoline (1942), materials for nuclear energy (ca 1942), aerosol propellants (see AEROSOLS) (ca 1942), fluoroplastics (ca 1942), and fluorocarbons for soil-repellant surface treatments (early 1950s). Fluorspar is used directly in the manufacture and finishing of glass (qv), in ceramics (qv) and welding (qv) fluxes, and in the extraction and processing of nonferrous metals (see METALLURGY, EXTRACTIVE).

In the geochemistry of fluorine, the close match in the ionic radii of fluoride (0.136 nm), hydroxide (0.140 nm), and oxide ion (0.140 nm) allows a sequential replacement of oxygen by fluorine in a wide variety of minerals. This accounts for

the wide dissemination of the element in nature. The ready formation of volatile silicon tetrafluoride, the pyrohydrolysis of fluorides to hydrogen fluoride, and the low solubility of calcium fluoride and of calcium fluorophosphates have provided a geochemical cycle in which fluorine may be stripped from solution by limestone and by apatite to form the deposits of fluorspar and of phosphate rock (fluorapatite [1306-01-0]), approximately  $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ , which are the world's main resources of fluorine (1).

On average, fluorine is about as abundant as chlorine in the accessible surface of the earth including oceans. The continental crust averages about 650 ppm fluorine. Igneous, metamorphic, and sedimentary rocks all show abundances in the range of 200–1000 ppm. Fluorspar is still the principal source of fluorine for industry.

Fluorspar deposits are commonly epigenetic, ie, the elements moved from elsewhere into the rock. For this reason, fluorine mineral deposits are closely associated with fault zones. In the United States, significant fluorspar deposits occur in the Appalachian Mountains and in the mountainous regions of the West but the only reported commercial production in 1993 was from the faulted carbonate rocks of Illinois.

Worldwide, large deposits of fluorspar are found in China, Mongolia, France, Morocco, Mexico, Spain, South Africa, and countries of the former Soviet Union.

**2.1. Supply.** Soon after World War II, stockpiling of fluorspar began upon recommendation by the Strategic Material Committee and the Army and Navy Munitions Board. It was decided that this stockpile must be sufficient to sustain United States consumption for at least three years in the case of a national emergency. Domestic output of fluorspar is entirely dependent on sales of material from this stockpile. During the 2002, fiscal year, there were no fluorspar sales authorized to be sold from the national stockpile (2). For fiscal year 2003, 54,400 tons of metallurgical-grade and 10,900 tons of acid-grade are authorized to be sold (2). A global-scale shortage of calcium fluoride could be prevented by (1) use of fluorspar reserves currently considered not to be economically workable, (2) prospecting and discovery of new deposits, and (3) production from hydrofluoric acid and fluorosilicic acid. Processes for synthesis have been proposed, but none have been utilized industrially. In 1997, imports of fluorspar increased almost 4% compared to 1996. From 1995 to 1998, the United States imported approximately 66% of its fluorspar, typically 96.5–97.5%  $\text{CaF}_2$ , from China, 23% from South Africa, and 11% from Mexico (3).

In 1993, Illinois was the only state reporting production of acid-grade fluorspar, typically 96.5–97.5%  $\text{CaF}_2$ , and accounted for 100% of all reported shipments. Ozark-Mahoning Company, a wholly owned subsidiary of Elf Atochem North America, Incorporated, operated three deep mines and a flotation mill in Hardin County, Ill.. A limited amount of metallurgical-grade gravel was produced by Hastie Mining, also located in Hardin County, Ill. (11). Since 1997, there has been no domestic mine production of fluorspar (3). Since 1997, there has been no domestic mine production of fluorspar (3). World mine production, reserves, and reserve base for 2001–2002 are shown in Table 1.

Table 1. World Mine Production, Reserves, and Reserve Base of Fluorspar,  $\times 10^3$  t<sup>a</sup>

Country	Mine production		Reserves <sup>c</sup>	Reserve base <sup>c</sup>
	2001	2002 <sup>b</sup>		
United States	NA <sup>d</sup>	NA <sup>d</sup>	NA <sup>d</sup>	6,000
China	2,450	2,450	21,000	110,000
France	110	110	10,000	14,000
Italy	45	50	6,000	7,000
Kenya	108	95	2,000	3,000
Mexico	635	640	32,000	40,000
Mongolia	200	200	12,000	16,000
Morocco	75	95	NA <sup>d</sup>	NA <sup>d</sup>
Namibia	83 <sup>e</sup>	86 <sup>e</sup>	3,000	5,000
Russia	190	190	moderate	18,000
South Africa	286	240	41,000	80,000
Spain	130	130	6,000	8,000
other countries	220	240	100,000	170,000
<i>World total (may be rounded)</i>	<i>4,530</i>	<i>4,530</i>	<i>230,000</i>	<i>480,000</i>

<sup>a</sup> From Ref. 3.<sup>b</sup> Estimated.<sup>c</sup> Measured as 100% calcium fluoride.<sup>d</sup> Not available.<sup>e</sup> Data are reported in wet tons.

### 3. Properties

Some of the important physical properties of calcium fluoride are listed in Table 2. Pure calcium fluoride is without color. However, natural fluorite can vary from transparent and colorless to translucent and white, wine-yellow, green, greenish blue, violet-blue, and sometimes blue, deep purple, bluish black, and brown. These color variations are produced by impurities and by radiation damage (color centers). The color of fluorite is often lost upon heating, sometimes with luminescence. Mineral specimens are usually strongly fluorescent, and the mineral thus gives its name to this phenomenon. Specimens vary from well-formed crystals (optical grade) to massive or granular forms.

The crystal structure of fluorite gives its name to the fluorite crystal type. The lattice is face-centered cubic (fcc), where each calcium ion is surrounded by eight fluoride ions situated at the corners of a cube, and each fluoride ion lies within a tetrahedron defined by four calcium ions (23). The bonding is ionic. The unit cell (space group  $O_h^{5/}$ ) can be pictured as made up of eight small cubes, each containing a fluoride ion, and the eight forming a cube with a calcium ion on each corner and one in the center of each face (Fig. 1). The lattice constant is 0.54626 nm at 25°C (24). The habit is usually cubic, less frequently octahedral, rarely dodecahedral. Cleavage on the [111] planes is perfect. The crystals are brittle with flat-conchoidal or splintery fracture. Luster is vitreous, becoming dull in massive varieties.

Systems of metal oxides with calcium fluoride usually have a simple freezing point composition diagram, commonly exhibiting a eutectic point and no

Table 2. Physical Properties of Calcium Fluoride

Property	Value	Reference
formula weight	78.08	
composition, wt %		
Ca	51.33	
F	48.67	
melting point, °C	1402	4
boiling point, °C	2513	5
heat of fusion, kJ/mol <sup>a</sup>	23.0	6
heat of vaporization at bp, kJ/mola	335	7
vapor pressure at 2100°C, Pa <sup>b</sup>	1013	7
heat capacity, $C_p$ , kJ/(mol · K) <sup>a</sup>		
solid at 25°C	67.03	8
solid at mp	126	9
liquid at mp	100	9
entropy at 25°C, kJ/(mol · K) <sup>a</sup>	68.87	8
heat of formation, solid at 25°C, kJ/mol <sup>a</sup>	−1220	8
free energy of formation, solid at 25°C, kJ/mol <sup>a</sup>	−1167	8
thermal conductivity, crystal at 25°C, W/(m · K)	10.96	10
density, g/mL		
solid at 25°C	3.181	11
liquid at mp	2.52	12
thermal expansion, average 25 to 300°C, K <sup>−1</sup>	$22.3 \times 10^{-6}$	13
compressibility, at 25°C and 101.3 kPa (=1 atm)	$1.22 \times 10^{-8}$	14
hardness		
Mohs' scale	4	
Knoop, 500-g load	158	15
solubility in water, g/L at 25°C	0.146	16
refractive index at 24°C, 589.3 nm	1.43382	17
dielectric constant at 30°C	6.64	18
electrical conductivity of solid, ( $\Omega \cdot \text{cm}^{-1}$ )		
at 20°C	$1.3 \times 10^{-18}$	19
at 650°C	$6 \times 10^{-5}$	20
at mp	3.45	21
optical transmission range, nm	150 to 8000	22

<sup>a</sup>To convert J to cal, divide by 4.184.<sup>b</sup>To convert Pa to mm Hg, multiply by  $7.5 \times 10^{-3}$ .

abnormal lowering of the melting point (25). When silicates are present, the systems become more complicated and a striking decrease in the viscosity of the glassy melts is observed. The viscosity most likely decreases because of depolymerization of chains or networks of SiO<sub>4</sub> tetrahedra via the replacement of oxide ion by the singly charged fluoride ion, which is close in both size and electronegativity to oxide ion (1). The benefits of calcium fluoride as a metallurgical flux result from both the freezing point depression and the decrease in slag viscosity.

Although stable at ambient temperature, calcium fluoride is slowly hydrolyzed by moist air at about 1200°C, presumably to CaO and HF. Calcium fluoride is not attacked by alkalis or by reactive fluorine compounds but is decomposed by hot, high-boiling acids, as in the reaction with concentrated sulfuric acid, which is the process used to produce hydrogen fluoride. Calcium fluoride is slightly soluble in cold dilute acids and somewhat more soluble in solutions of aluminum halides.

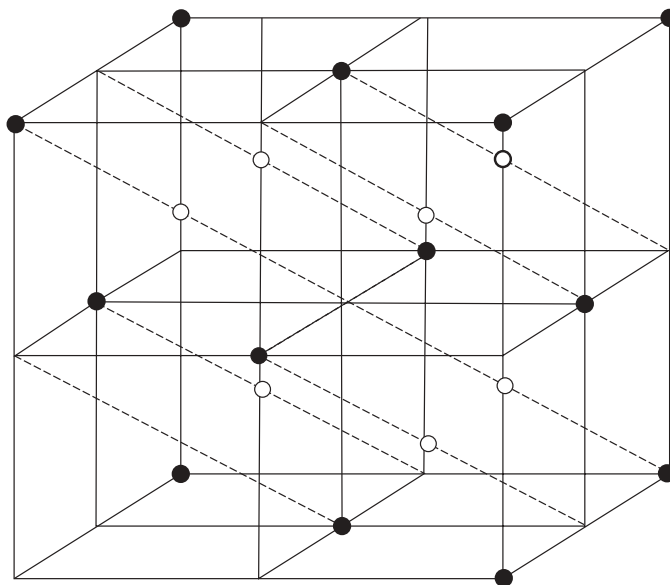


Fig. 1. Structure of fluorite where ● is Ca and ○ is F (3).

## 4. Mining

For a deposit to be economically workable, the  $\text{CaF}_2$  content must be, on average, 20%. Underground mining procedures are used for deep fluorspar deposits, and open-pit mines are used for shallow deposits or where conditions do not support underground mining techniques (see MINERAL RECOVERY AND PROCESSING).

Fluorspar occurs in two distinct types of formation in the fluorspar district of southern Illinois and Kentucky: in vertical fissure veins and in horizontal bedded replacement deposits. A 61-m bed of sandstone and shale serves as a cap rock for ascending fluorine-containing solutions and gases. Mineralizing solutions come up the faults and form vein ore bodies where the larger faults are plugged by shale. Bedded deposits occur under the thick sandstone and shale roofs. Other elements of value associated with fluorspar ore bodies are zinc, lead, cadmium, silver, germanium, iron, and thorium. Ore has been mined as deep as 300 m in this district.

**4.1. Beneficiation.** Most fluorspar ores as mined must be concentrated or beneficiated to remove waste. Metallurgical-grade fluorspar is sometimes produced by hand-sorting lumps of high grade ore. In most cases the ore is beneficiated by gravity concentration with fluorspar and the waste minerals, having specific gravity values of  $>3$  and  $<2.8$ , respectively. In preconcentration of fluorspar, barite and valuable sulfide minerals are separated from waste as the higher density valuable minerals sink while the waste floats and is discarded. This preconcentration can enrich ores as low as 14% to a concentration of 40%. Multistage froth flotation (qv) is used to take this preconcentrate and produce acid and ceramic grades of fluorspar as well as zinc and lead sulfides. In this

process air bubbles are forced through a suspension of pulverized ore, which float the ore into a froth that is continuously skimmed off. After flotation, the fluor-spar products are filtered and dried in rotary kilns.

## 5. Preparation

$\text{CaF}_2$  is manufactured by the interaction of  $\text{H}_2\text{SiF}_6$  with an aqueous carbonate suspension (26–29); by the reaction of  $\text{CaSO}_4$  with  $\text{NH}_4\text{F}$  (30); by the reaction of  $\text{HF}$  with  $\text{CaCO}_3$  in the presence of  $\text{NH}_4\text{F}$  (31); by reaction of  $\text{CaCO}_3$  and  $\text{NH}_4\text{F}$  at 300–350°C followed by calcining at 700–800°C (32); by reaction of  $\text{NH}_4\text{F}$  and  $\text{CaCO}_3$  (33–38); and from the thermal decomposition of calcium tri-fluoroacetate (39).

High purity  $\text{CaF}_2$  is obtained from micro- and ultrafiltration (qv) of raw materials and then crystallization of  $\text{CaF}_2$  (40) from the reaction of  $\text{CaCO}_3$  and the product of  $\text{H}_2\text{SiF}_6$  and  $\text{NH}_3$  (41). High purity  $\text{CaF}_2$  having particles of 0.0005–0.5 mm is produced from the reaction of  $\text{NaF}$ ,  $\text{KF}$ , or  $\text{NH}_4\text{F}$  and  $\text{CaCO}_3$  with a particle size distribution of 0.01–0.05 mm (42). High purity  $\text{CaF}_2$  is also prepared from the reaction of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{F}$  or a mixture of  $\text{NH}_4\text{HF}_2$  and  $\text{NH}_4\text{F}$  (43) and obtained by heating impure  $\text{CaF}_2$  with 10–15%  $\text{HCl}$  at 95–100°C (44). Very pure calcium fluoride for the manufacture of special glasses is made by the reaction of hydrofluoric acid with precipitated calcium carbonate. Acicular (whisker-form)  $\text{CaF}_2$  particles have been manufactured by continuous feeding of an aqueous  $\text{Ca}(\text{OH})_2$  solution into water containing  $\text{CO}_2$  and subsequent reaction with  $\text{HF}$  (45). Coarse grain  $\text{CaF}_2$  crystals can be prepared by several routes (46–59).  $\text{CaF}_2$  can be is crystallized from a wastewater containing fluoride by adding  $\text{CaCl}_2$  (60). Calcium fluoride can be produced from waste  $\text{H}_2\text{SiF}_6$  from phosphate product operations and from treating fluoride solution from industrial wastewater with  $\text{KOH}$  and then with lime (61).

The large amount of fluorine values released from phosphate rock in the manufacture of fertilizers (qv) gives a strong impetus to develop fluorine chemicals production from this source (see PHOSPHORIC ACID AND THE PHOSPHATES). Additional incentive comes from the need to control the emission of fluorine-containing gases. Most of the fluorine values are scrubbed out as fluorosilicic acid,  $\text{H}_2\text{SiF}_6$ , which has limited usefulness. A procedure to convert fluorosilicic acid to calcium fluoride is available (62).

## 6. Shipment

Truck, rail, barge, and ship are all methods used to transport fluor-spar. The different grades are shipped in different forms: metallurgical grade as a lump or gravel; acid grade as a damp filtercake containing 7–10% moisture to facilitate handling and reduce dust.

## 7. Economic Aspects

In looking at trends for fluor-spar use over the past ca 25 years, domestic production has declined since 1976. Pertinent statistics on the United States production

Table 3. U.S. Pertinent Statistics for Fluorspar,  $\times 10^3$  t<sup>a</sup>

Statistics—United States	1998	1999	2000	2001	2002 <sup>b</sup>
production:					
finished, all grades <sup>c</sup>			NA <sup>d</sup>	NA <sup>d</sup>	NA <sup>d</sup>
fluorspar equivalent from phosphate rock	118	122	119	104	126
imports for consumption					
acid grade	462	419	484	495	466
metallurgical grade	41	59	39	27	36
total fluorspar imports	503	478	523	522	502
fluorspar equivalent from hydrofluoric acid plus cryolite	204	192	208	176	189
exports <sup>e</sup>	24	55	40	21	25
shipments from government stockpile	110	131	106	65	13
consumption					
apparent <sup>f</sup>	591	615	601	543	472
reported	538	514	512	536	562
stocks, yearend, consumer and dealer <sup>g</sup>	468	373	289	221	240
employment, mine and mill, number			5	5	5
net import reliance as a percentage of apparent consumption	100	100	100	100	100

<sup>a</sup> From ref. 3.<sup>b</sup> Estimated.<sup>c</sup> Shipments.<sup>d</sup> Not available.<sup>e</sup> Exports are all general imports re-exported or National Defense Stockpile material exported.<sup>f</sup> Excludes fluorspar equivalent of fluosilicic acid, hydrofluoric acid, and cryolite.<sup>g</sup> Industry stocks for three largest consumers, fluorspar distributors, and committed National Defense Stockpile material.

and consumption of fluorspar are given in Table 3 (2,3). Thus, the United States has relied on imports for more than 80% of its fluorspar needs. However, foreign sources are more than adequate. The principal sources are China, Mexico, and South Africa. Foreign producers are able to offer fluorspar at a lower price than that produced domestically because of lower operating costs. Imports from Mexico have declined in part because Mexican export regulations favor domestic conversion of fluorspar to hydrogen fluoride for export to the United States. Statistics for the United States exports by country are given in Table 4 (2).

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## 8. Grades and Specifications

Ceramic-grade and acid-grade fluorspars (ceramic-spar and acid-spar) have the typical analysis shown in Table 5. Both types are usually finely ground, the bulk

Table 4. U.S. Exports of Fluorspar<sup>a</sup>

Country	2000		2001	
	Quantity, t	Value, \$ <sup>b</sup>	Quantity, t	Value, \$ <sup>b</sup>
Canada	18,100	2,930,000	15,800	2,410,000
Dominican Republic	62	9,090		
Italy	13,200	1,210,000		
Mexico	4,520	441,000	3	2,510
Taiwan	3,310	592,000	5,020	733,000
other <sup>c</sup>	647	146,000	374	101,000
<i>Total</i>	<i>39,800</i>	<i>5,330,000</i>	<i>21,200</i>	<i>3,240,000</i>

<sup>a</sup> From ref. 2, data are rounded to no more than three significant digits; may not add to totals shown.

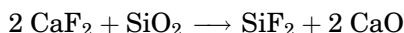
<sup>b</sup> Free alongside ship values at U.S. ports.

<sup>c</sup> Includes Australia, Belgium, France, India, Israel, Japan, the Netherlands, Saudi Arabia, Switzerland, and Venezuela.

Source: U.S. Census Bureau.

of the powder passing a 0.23 mm (65 mesh) screen with 22–81% held on a 44  $\mu$ m (325 mesh) screen. In acid-spar, at least 85–97% calcium fluoride is present with impurities being limited to 1–1.5% silica and 0.03–0.10% sulfide or free sulfur. Ceramic-spar is marketed in different levels: 95–97% CaF<sub>2</sub> (No. 1), 93–95% CaF<sub>2</sub>, and 85–93% CaF<sub>2</sub> (No. 2). Specifications on impurities vary but allow a maximum amount of 2.3–3% silica, 1–1.5% calcite, and 0.12% ferric oxide and trace amounts of lead.

Metallurgical fluorspar (met-spar) is sold as gravel, lump, or briquettes. It contains 60–85% effective calcium fluoride. In the United States, the effective value is usually quoted, determined by subtracting 2.5 times the SiO<sub>2</sub> content of the ore from the calcium fluoride content (1). This allows for the fluorine-consuming reaction:



Expressed as effective CaF<sub>2</sub>, the specification is usually 70% minimum. Impurities are usually limited to 0.3% sulfide or free sulfur, 0.25–0.50% lead, and minor amounts of phosphorus.

Table 5. Analyses of Ceramic- and Acid-Grade Fluorspar, wt %<sup>a</sup>

Assay	Ceramic	Acid
CaF <sub>2</sub>	90.0–95.5	96.5–97.5
SiO <sub>2</sub>	1.2–3.0	1.0
CaCO <sub>3</sub>	1.5–3.4	1.0–1.5
MgO		0.15
B		0.02
Zn		0.02
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.10
P <sub>2</sub> O <sub>5</sub>		0.03
BaSO <sub>4</sub>		0.2–1.3
R <sub>2</sub> O <sub>3</sub> <sup>b</sup>	0.15–0.25	0.1–0.3

<sup>a</sup> Refs. 64 and 65.

<sup>b</sup> R<sub>2</sub>O<sub>3</sub> is any trivalent metal oxide, eg, Al<sub>2</sub>O<sub>3</sub>.



In steel making, the preferred form of fluorspar flux is a washed gravel, 0.6–5 cm in diameter, containing less than 3% water and assaying 60–80% effective  $\text{CaF}_2$  units. The higher  $\text{CaF}_2$  ranges are hard to supply in large amounts from some sources of fluorspar. The use of fluorspar briquettes and pellets in the steel industry has declined, but these are still preferred by some producers. The briquettes contain 25–90%  $\text{CaF}_2$ , are frequently made to customer specifications, and may include fluxing agents and recycled steel mill wastes. Binders used include molasses, lime, and sodium silicate.

Optical-grade calcium fluoride, for special glasses and for growing single crystals, is also supplied in purities up to 99.99%  $\text{CaF}_2$ . This grade is especially low in transition elements.

## 9. Health and Safety Factors

Fluorite is not classified as a hazardous material. However, every precaution should be taken to prevent contact of calcium fluoride with an acid since formation of hydrofluoric acid will result. Because of the low solubility of calcium fluoride, the potential problem of fluoride-related toxicity is reduced. However, ingesting large amounts may cause vomiting, abdominal pain, and diarrhea. Water saturated with calcium fluoride has a fluoride concentration of 8.1 ppm as compared to the recommended water fluoridation level of 1 ppm fluoride ion. However, because the solubility of calcium fluoride in stomach acid is higher, continued oral ingestion of calcium fluoride could produce symptoms of fluorosis. The adopted TWA limit for fluorides as F is  $2.5 \text{ mg/m}^3$  (66).

Beneficiation facilities require air and water pollution control systems, including efficient control of dust emissions, treatment of process water, and proper disposal of tailings. In handling finished fluorspar, operators must avoid breathing fluorspar dust and contacting fluorspar with acids. Inhalation may cause irritation to the respiratory tract. Symptoms may include coughing and shortness of breath. Upon contact with the skin a mild irritation or redness may result. Protective gloves, safety goggles, and full-body covering are recommended. Proper disposal of spills and the use of respirators and other personal protective equipment must be observed. Spills should be placed in a suitable container for reclamation or disposal, using a method that does not generate dust.

Shipping and storage containers, when empty, can be hazardous as they will contain residues. Calcium fluoride should be kept in a tightly closed container, stored in a cool, dry, ventilated area.

## 10. Environmental Concerns

Plants sensitive to fluorides have been shown to show signs of injury at concentrations of  $1.0\text{--}4.0 \text{ } \mu\text{g}$  of fluoride/ $\text{m}^3$  over a 24-h period of exposure or at  $0.5\text{--}1.0 \text{ } \mu\text{g}$  of fluoride over a one month period of exposure. Cattle consuming a diet containing 40 ppm of fluoride or more developed symptoms of fluorosis: dental defects, bone lesions, lameness, and reduced appetite. The results were weight loss and diminished milk yield (67).

Naturally occurring fluorides are not considered to be health hazards. However, fluorides used in pesticides may cause severe illness or death if ingested. Fluorocarbons are very stable but do pose a health hazard: burning can result in the release of phosgene gas, which is toxic; some fluorocarbons as gases can replace the normal air supply in confined spaces if more dense than air, resulting in suffocation.

## 11. Uses

Fluorspar is considered to be a commodity of strategic and commercial importance as the United States import reliance is high and fluorspar is necessary in steel and aluminum production. Fluorspar is also the primary source of fluorine and its compounds. Table 5 shows the United States imports for consumption of calcium fluoride by country (2). Over 80% of reported fluorspar consumption is used in the manufacture of hydrofluoric acid and 20% in the steel and iron industry. Fluorspar is the starting material for the production of HF. See Table 6 for U.S. consumption by end use.

An estimated 90% of reported fluorspar consumption went to the manufacture of hydrofluoric acid and aluminum fluoride. The remaining 10% of the reported fluorspar consumption was used as a flux in steel making, in iron and steel foundries, for primary aluminum production, glass manufacture, enamels, welding rod coatings, and other uses or products.

Fluorspar is marketed in several grades. The three principal grades of fluorspar are acid, ceramic, and metallurgical. The specifications (discussed under Grades and Specifications) for the different grades are fairly well defined,

Table 6. U.S. Reported Consumption of Fluorspar, by End Use, t<sup>a,b,c</sup>

End use or product	Containing more than 97% calcium fluoride		Containing not more than 97% calcium fluoride		Total	
	2000	2001	2000	2001	2000	2001
hydrofluoric acid and aluminum fluoride	474,000	429,000	16	1,100	474,000	430,000
metallurgical <sup>d</sup>	W	21,300	15,900	43,700	15,900	65,000
other <sup>e</sup>	13,600	23,700	8,650	17,000	22,200	40,700
<i>Total</i>	<i>487,000</i>	<i>474,000</i>	<i>24,500</i>	<i>61,800</i>	<i>512,000</i>	<i>536,000</i>
stocks (consumer), December 31 <sup>f</sup>	48,300	71,100	25,700	NA	73,900	NA

<sup>a</sup> Ref. 2.

<sup>b</sup> NA Not available. W Withheld to avoid disclosing company proprietary data.

<sup>c</sup> Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>d</sup> Data for 2000 include consumption for basic oxygen and electric arc furnaces; 2001 data include consumption for all metallurgical uses.

<sup>e</sup> Includes acid grade used in enamel, glass and fiberglass, steel castings, welding rod coatings, and data represented by symbol W.

<sup>f</sup> Because of a change in survey methodology, the 2001 stocks data are only available for hydrofluoric acid and aluminum fluoride.

although some variation is allowed. There has been a general movement toward the use of higher quality fluorspar by many of the consuming industries.

$\text{CaF}_2$  is used for prisms in spectrometers and for cell windows (especially for aqueous solutions), where transparency to visible and ultraviolet radiation is a requirement.

Acid-grade fluorspar is used primarily as a feedstock in the manufacture of hydrofluoric acid and to produce aluminum fluoride. HF is the primary feedstock for the manufacture of most organic and inorganic chemicals containing fluorine. Two companies reported calcium chloride consumption for the production of HF. The largest use of HF is for the production of various fluorocarbon chemicals: hydrofluorocarbons (HFC), hydrochlorofluorocarbons (HCFC), and fluoropolymers. Most of the  $\text{AlF}_3$  produced is used in aluminum reduction cells using acid-grade fluorspar.

Ceramic-grade fluorspar is used in the production of glass and enamel (68–70) to make welding rod coatings and as a flux in the steel industry (71).

Metallurgical-grade fluorspar is primarily used as a fluxing agent by the steel industry (71). Calcium fluoride is added to slag to make it more reactive, increasing the fluidity of the slag (by reducing its melting point) and thus increasing the reactivity. Reducing the melting point of the slag brings lime and other fluxes into solution allowing the absorption of impurities. Methods for producing large-volume crystals from calcium chloride for use in photolithography, optics, excimer lasers, wafers, and computer chips have been reported (72,73).

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