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FLUORSPAR

Introduction:

Fluorspar, known in works on mineralogy as "fluorite," is a mineral important to several industries. Its greatest use is in the steel industry, where it is essential as a flux; therefore it is most important in the war program. In the chemical industry, it is the basic material from which hydrofluoric acid is made, and in the ceramic industry it is used in the manufacture of opal glass and enamels. Perfect crystals of fluorspar are of value in the making of optical instruments. Although the physical properties of fluorspar are of importance to the optical industry, in most of its uses fluorspar is employed for its chemical properties, specifically, for its low melting point and its fluxing ability. In fact, the name fluorspar is derived from the Latin word "fluere" which means "to flow."

In industry, fluorspar is frequently referred to as "spar."

History:

The first recorded use of fluorspar was in 1529 when Agricola wrote of its use as a flux. In these early days, the mineral was thought indispensable to smelting operations. Early in the 19th century, however, when improvements had been made in metallurgical methods and equipment, limestone took the place of the rare and costly fluorspar, except in the smelting of highly refractory ores.

Fluorspar was first used by prehistoric folk or by the Indians who took advantage of its beautiful colors and its transparency in the making of jewelry and ornaments. It was produced commercially in the United States for the first time in 1837 when it was mined from a topaz vein near Trumbull, Connecticut, and used in the smelting of copper ores. The mineral at that time sold for \$60 per ton. Although the presence of fluorspar in the Illinois-Kentucky district was recognized for several years previously, the first mining of the now-famous deposits began in 1842; the first shipments were made in 1871. The Royal mines in western Kentucky furnished the ore, which was ground at the mines and then shipped to glass works in Baltimore.

In the United States, the manufacture of glass and of hydrofluoric acid absorbed the greatest tonnages of the available fluorspar until 1898. Then as the mineral was needed as a flux and cleansing agent in the basic open-hearth process for steel, fluorspar began to show its importance to the steel industry. Within a few years this new process absorbed a greater tonnage of fluorspar than the older uses; in recent years the tonnage used in the making of steel has soared to 80 percent of the total yearly domestic production.

Even before the first world war, the nation depended upon the Illinois-Kentucky field for the bulk of its fluorspar. With the beginning of World War I, a great demand arose for fluorspar, and small deposits all over the country were developed and mined for this mineral. After the end of the war, however, many small mine owners found further mining unprofitable. Since 1918, at least 90 percent of our domestic supply of fluorspar has been derived from the Illinois-Kentucky field, with about 5 percent coming from Colorado.

Physical and chemical properties:

The chemical composition of fluorspar is CaF_2 , calcium fluoride. It represents a hardness of 4 in Mohs' scale, being harder than calcite (3) and softer than apatite (5). Fluorspar crystallizes in the isometric system, often forming perfect cubes, and also having excellent octahedral cleavage. Its specific gravity is 3.18, and its melting point lies between 1270° and 1387° C.; pure calcium fluoride melts at 1387° C. The fracture surface is conchoidal or splintery. When the mineral is crystalline, its luster is vitreous; when granular, it is dull or earthy.

Fluorspar ranges in color from the clear, colorless crystal through many shades of yellow, green, brown, pink, violet, and purple. The reason for the differences in color is not known. The mineral may be transparent, translucent, or opaque, depending upon the form in which it is found. It is rarely contaminated with impurities, and is usually found as a mass of very pure crystalline material, with vugs containing aggregates of cubical crystals. It may also be found in granular form, varying from fine to coarse. Other forms are banded veins or fibrous masses with radiating structure. Some specimens of fluorspar will fluoresce under an ultraviolet light, while others exhibit phosphorescence when heated or scratched.

Fluorspar can be differentiated from calcite by its failure to effervesce when treated with dilute hydrochloric acid.

Geological associations:

Fluorspar is found under widely different conditions and in all kinds of rocks. It is most abundant in veins and in sedimentary formations, but is also found in small quantities in granite, syenite, pegmatite, gneiss, and schist, and may appear even in volcanic rocks. It may be associated with calcite, barite, quartz, galena, and sphalerite. It is a common gangue mineral of ore deposits, particularly those of lead and zinc ores formed under moderate to low temperatures and pressures. Frequently it is not feasible to determine whether a deposit of this sort may be worked primarily for the lead and zinc or for the fluorspar "gangue."

Lindgren (Mineral Deposits, 4th ed.) considers fluorspar to be one of a group which he terms "persistent" minerals. These, he says, seem to be less sensitive than others to physical conditions and recur in very different environments. Fluorspar is found in ore deposits formed by magmatic separation, contact metamorphism, and deposition in veins as a result of circulating hydrothermal solutions. It is also found, together with galena and sphalerite, at moderate to shallow depths in sedimentary rocks. Some geologists consider these latter deposits to have their origin in rising magmatic solutions, while others believe that circulating meteoric waters furnished the materials for the deposits.

The following discussion of the conditions under which fluorspar is found has been derived largely from U. S. Bureau of Mines Bulletin 244.

1. Almost all the important deposits of fluorspar are either in or near fault zones. They are either vein fillings, replacements of the wall rock, replacements of sedimentary beds (particularly limestones) near fault fissures, or fillings of solution cavities near faults. Weathering of the more soluble minerals of the vein may produce residual deposits of fluorspar called "gravel-spar."

2. Almost all the important deposits of fluorspar are found in limestones or calcite veins. Calcareous beds seem to favor the formation of large, rich deposits of the spar. In the Illinois-Kentucky field where the faults cut calcareous beds, such as limestones and limy shales and sandstones, or where the faults were originally filled with calcite, the deposits of fluorspar are widest and best. However, where the faults cut through highly siliceous beds, the deposits pinch and decrease in value.

Although most deposits of fluorspar in igneous rocks are of small extent, at Wagon Wheel Gap, Colorado, the fluorspar occurs in Tertiary volcanic rocks, forming the largest and most persistent deposit known in igneous rocks. That there is lime in this area, however, is shown by the fact that the Wagon Wheel Gap vein, if projected, would cut a deposit of travertine not far away.

3. Almost all the important deposits of fluorspar either show, or are found near, evidences of igneous activity. Such evidences may take the form of intrusive dikes, hot mineral springs, or similar features. It seems probable that, in most deposits of fluorspar, the fluorine, together with the other elements that form the vein, was brought up by ascending hot magmatic solutions. The calcium fraction of the fluorspar may have been brought up in the same solutions or may have been derived from the calcareous beds cut by the fault. It is not to be assumed, however, that all deposits of fluorspar were formed in this way.

In large deposits the fluorspar tends to be white and gray, while in the smaller veins and in siliceous rocks the fluorspar may be green and purple, particularly near the surface. The reason for this variation in color is not known.

Deposits in the United States:

The fluorspar-producing area which for years has furnished the United States with at least 90 percent of her needs, and which is probably the greatest fluorspar deposit in the world, is an area about 40 miles square straddling the Ohio River in Illinois and Kentucky. The field is underlain by nearly horizontal Paleozoic sedimentary beds cut by many steeply dipping normal faults and by dikes of altered volcanics. The fluorspar is found either in veins occupying the nearly vertical fault fissures or in horizontal, tabular bodies or lenses.

Most of the production of fluorspar from this area has come from the vein deposits. The total production is estimated at more than 2,500,000 tons. The veins, ranging in width from a fraction of an inch to 30 feet, are composed mainly of fluorspar and calcite. Fluorspar has been found more than 720 feet underground in Illinois, and at depths greater than 400 feet in Kentucky. At depth, however, the fluorspar may decrease in amount and give way to calcite. The veins probably underwent two periods of deposition: first, vein filling, and second, replacement of calcareous material of the wall rock.

The tabular or lenticular deposits, known as "bedding," "bedded," or "blanket," deposits, have produced more than 100,000 tons of fluorspar, and reserves may be estimated at many times this tonnage. Fluorspar, in light and dark colored bands, has replaced the upper beds of the Fredonia limestone of Mississippian age near Cave In Rock, Illinois. A roof of nearly impervious shale prevented the further ascension of hot mineralizing solutions which rose along minor fissures. The solutions were forced to spread out fan-wise beneath this stratum, replacing the limestones with fluorspar. The Cave In Rock district lies just east of the highly faulted zone in which the vein deposits of fluorspar are so notable. The fluorspar-forming solutions may have spread from these major fractures to the smaller outlying faults. The tabular deposits range in thickness from a few inches to more than 12 feet; the average thickness mined is about 4 feet. Vugs containing aggregates of perfectly formed fluorspar crystals have been found in these bedded deposits.

Fluorspar is mined on its own account at several places in Colorado, including Wagon Wheel Gap, Jamestown, North Gate, and Brown Canyon. It is also found in metaliferous ore deposits as a gangue mineral. A basic open-hearth steel plant at Pueblo furnished the first major market for Colorado spar.

According to Minerals Yearbook, 1941, shipments of fluorspar from 1870, when production began, to 1941 total 4,848,000 short tons. Of this tonnage, Illinois furnished 56 percent and Kentucky, 36 percent. Colorado has shipped approximately 5 percent of this total.

Fluorspar is found and mined in many other places in the United States, but none has reached the prominence of the Illinois-Kentucky field. Central Kentucky, New Hampshire, and Tennessee boast a small production of the mineral. In the western United States, much of the fluorspar is found in igneous rocks, and, although many of these deposits are too low in value to permit mining, commercial production has been reported in Arizona, California, Nevada, New Mexico, Utah, and Washington.

Foreign deposits:

On the American continent, fluorspar is mined in Canada, Newfoundland, Mexico, and Argentina. On the European continent, it is produced in England, France, Germany, Spain, and Italy. The English deposits are found in Derbyshire, Durham, Cornwall, Devon, and North Wales. In Derbyshire, the veins, which cut Paleozoic limestones, average 6 feet in width. They were mined originally for lead, the fluorspar gangue being left in waste heaps. Later, however, the fluorspar was extracted from this waste material. Fluorspar is abundant in several places in Germany; mining is efficient and near-by markets are excellent. Africa, China, and Australia also produce some fluorspar.

Uses:

Fluorspar used in the steel industry must contain not less than 85 percent CaF_2 and not more than 5 percent SiO_2 . The sulphur content must be kept below 0.3 percent. The grade of fluorspar used in metallurgy is known as "gravel," which is not to be confused with the gravel-spar formed by surface weathering. The size of the gravel fragments, although usually from 5/8-inch to dust, actually depends on the nature of the fluorspar deposit and on the milling process.

Fluorspar is of value in the basic open-hearth process because of its low melting point and its fluidity when melted. It has the ability to lower the melting point of the slag by forming eutectics with silica, calcium and barium sulphates, alumina, and other refractory materials, thereby rendering the slag fluid and easy to handle. Furnace temperatures can be lowered and the whole operation is facilitated. Because of the increased fluidity of the slag, the gases from the metal may escape easily; harmful impurities such as sulphur and phosphorus are removed by volatilization and by slagging. The chemistry of the reactions that occur when fluorspar is employed as a flux are not fully understood. The fact remains, however, that fluorspar is more efficient as a flux in this process than limestone, especially when refractory ores are to be smelted, and is more useful than its best substitute, calcium chloride.

An open-hearth furnace has, on the average, a capacity of 50 to 60 tons. First, a quantity of limestone, weighing about one-tenth of the weight of the metal charge, is spread over the bottom. Then the pig iron and scrap are added, and the heating begins. When the melting of the charge is complete, the limestone rises through the charge to the top and floats on the surface. As heating continues, this slag may become a thick mass which prevents the escape of gases from the melted charge. Fluorspar is then added to increase the fluidity of the slag. Operators differ as to the time at which the fluorspar should be introduced; some add it in small quantities throughout the melt but others add it just before tapping. The amount of fluorspar used per ton of steel ranges from 4 lb. to 25 lb., but averages 5 to 8 lb.

Fluorspar has several other uses in the metallurgical industry. It is used in iron foundries as a flux in the production of the finer grades of castings, such as heating and plumbing equipment, and automobile cylinders and blocks. Some electric-furnace plants find a use for fluorspar in making alloy steels in which it performs the same function of a flux as in the basic open-hearth steel process. The quantity used averages 20 lb. per ton of steel. The fluorspar used for making ferro-alloys in electric-furnace plants must be high in CaF_2 and low in SiO_2 , and is usually lump size ranging from 5 to 6 inches in diameter to dust. The production of nickel and monel metal, as well as the smelting of refractory ores, requires small quantities of fluorspar.

The chemical industry requires fluorspar mainly for the manufacture of hydrofluoric acid. Acid-grade fluorspar must contain a minimum of 98 percent CaF_2 and a maximum of 1 percent each of silica and calcium carbonate. Objectionable impurities are lead, zinc, and iron minerals. Acid spar may be ground at the mines, or may be shipped in lump and gravel sizes. The acid is produced by treating ground fluorspar with concentrated sulphuric acid. Hydrofluoric acid is used in etching glass and in making fluorine compounds, the inorganic and organic fluorides and the silico-fluorides. Many fluorine compounds are used industrially in preservatives, insecticides, and dyestuffs. "Freon," dichlorodifluoromethane, a new refrigerating medium, is nonexplosive, noninflammable, and almost nonpoisonous. Fluorspar is also employed in the manufacture of artificial cryolite. The fluorspar is used to produce hydrofluoric acid, which in turn is used to make the synthetic cryolite, a sodium aluminum fluoride. Aluminum is then recovered by electrolytic methods from a combination of natural and artificial cryolite.

Fluorspar is also used in the chemical industry in the extraction of potassium from feldspar and from portland cement flue dust; it is also used in the manufacture of calcium carbide and cyanamid.

In ceramics, fluorspar is valued for its ability to produce cloudy or white opaque glass. It is also employed in the manufacture of enamels, facings for brick, and portland cement. Ceramic spar must contain from 95 to 98 percent CaF_2 and not more than 3 percent SiO_2 . It must be pure white when ground, and free of lead, zinc, and sulphur impurities.

A very small amount of fluorspar is absorbed each year by the optical industry. Optical spar must be as clear as glass, with no inclusions, cracks, incipient cleavage marks, or cloudiness. Colorless crystals are best, although those with faint tinges of yellow or green may also have value. Because of its low index of refraction, its weak color dispersion, and its lack of double refraction fluorspar is used to correct lenses for color and spherical aberration. The lenses are used in spectrosopes, microscopes, and small telescopes. Colored fluorspar crystals, although relatively soft, may be made into jewelry. Optical spar is found in places in Illinois and Kentucky.

The following table, taken from Minerals Yearbook, 1941, gives the tonnages of the fluorspar shipped from mines in the United States in 1940-41, by uses:

Use	1940		1941	
	Percent of total	Short tons	Percent of total	Short tons
Steel	69.68	162,772	66.77	214,120
Foundry	1.21	2,829	.85	2,724
Glass & enamel	8.68	20,269	9.99	32,051
Hydrofluoric acid	14.39	33,608	16.43	52,674
Miscellaneous	2.41	5,640	2.16	6,916
	<hr/> 96.37	<hr/> 225,118	<hr/> 96.20	<hr/> 308,485
Foreign consumption	3.63	8,482	3.80	12,184
	<hr/> 100.00	<hr/> 233,600	<hr/> 100.00	<hr/> 320,669

Prospecting, mining, and milling:

Deposits of fluorspar may be recognized on the surface by the presence of gravel-spar, the result of surface weathering of fluorspar-rich deposits. In an area of known vein deposits, a search for faults may disclose new fluorspar-bearing veins. In the Illinois-Kentucky field, prospecting by geophysical methods has brought to light concealed faults which may prove to contain spar. In the West, the presence of fluorspar sand in anthills, or as a gangue mineral in metalliferous veins may indicate commercial deposits.

The nature of the deposit and the skill of the operator determine the method of mining. Usually, fluorspar is mined underground, as metallic ores are mined. However, where gravel-spar is sufficiently rich it may be mined by open-pit methods. These deposits are now being worked extensively owing to the increased demand of the steel industry for spar.

Industrial Minerals and Rocks (1937) gives these methods of preparation of the ore: selection in the mine, crushing, washing with jets of water or in log washers, hand picking on belts, screening, gravity concentration by jigs and tables, and flotation. The method of milling would depend in part upon the nature and quantity of the impurities. The character of the ore and the use to which it is to be put also affect the milling process. Although some deposits are so pure that a marketable product can be obtained by hand cobbing and sorting, most deposits need a more thorough preparation for market. Some impurities, such as calcite, quartz, clay, and sand, are not actually harmful although they reduce the calcium fluoride content of the finished product. Others, such as barite, galena, sphalerite, and pyrite, are definitely objectionable, and must be removed by one method or another before the spar can be shipped.

Prices:

In the United States in 1941, the average composite selling price of all grades of fluorspar (both domestic and imported), as delivered to the consumer, was \$20.98 per ton. This is only slightly above the 1940 composite price of \$20.40. The average selling price of fluorspar shipped to domestic steel plants, f.o.b. Illinois-Kentucky mines, was \$19.62 a short ton; to manufacturers of hydrofluoric acid, \$26.78; and to makers of glass and enamel, \$27.39. On January 20, 1942, the Office of Price Administration asked producers not to sell fluorspar, or publish or quote prices on the mineral, above the prices in effect on January 2, 1942. However, since that date substantial increases in price have been granted, giving impetus to the previously lagging production.

The War Production Board rates fluorspar in Group I among the materials in insufficient supply to satisfy war plus essential industrial demands. Government purchases of the mineral made through the Metals Reserve Co. are f.o.b. the railroad point nearest the mine at a price based upon "Effective CaF_2 Content." This is determined by deducting $2\frac{1}{2}$ times the silica (SiO_2) content from the total CaF_2 content. For metallurgical grade the maximum price for effective CaF_2 content is the amount listed below plus either (1) railroad freight from producer's shipping point to the producer's plant, or (2) railroad freight from Rosiclare, Illinois, to consumer's plant, whichever is lower:

<u>Effective CaF_2 content</u>	<u>Base Price per short ton</u>
70% or more	\$33.00
65% but less than 70%	32.00
60% " " " 65%	31.00
Less than 60%	30.00

For acid and ceramic grades the base analysis is 95.5% CaF_2 and 1.5% SiO_2 with base price of \$37.00 per ton plus railroad freight as computed for metallurgical grade. Premiums are given and penalties imposed for variations from the base analysis. Specifications may be obtained from Metals Reserve Company.

World production:

About four-fifths of the total annual world production of fluorspar is furnished by the United States, Germany, France, the United Kingdom, and the U.S.S.R. From 1913 through 1926, the United States produced more fluorspar annually than any other country. In 1927 Germany led the world in fluorspar production. Since that time the lead has alternated between Germany and the United States. For years Germany furnished the bulk of the fluorspar imported into the United States, but recently, and with good reason, this supply has been cut off. In 1941 fluorspar was imported from Mexico, Spain, the United Kingdom, and other Allied and non-belligerent nations.

Within the last few years the tonnage of fluorspar shipped within the United States has almost doubled. In 1939, 165,806 tons was shipped; in 1940, 211,917 tons; and in 1941, 290,095 tons. Although production statistics of the Axis nations are lacking, the United States probably leads the world in production, importation, and consumption of fluorspar.

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Joyce B. Priestaf

CHROME MINING ACTIVITY

The Sourdough Chrome mine on Baldface Creek, Curry County, which was formerly owned and operated by Rustless Mining Corporation, has been taken over by Mr. J.K. Remsen and is currently being operated by a crew of four men under the supervision of Ben Baker. Remsen reports that 66 tons of low-iron ore running about 45% Cr_2O_3 has already been delivered to the Metals Reserve depot at Grants Pass and that the prospects for more ore of better grade are good.

The Cyclone Gap property in Siskiyou County, northern California, which has been operated by Remsen for the past three years, will be reopened next week when a crew of three or four men will start a drift to the east from the present ore body to determine if any additional ore can be obtained.

The Grey Eagle Chrome mill, formerly operated by Rustless Mining Corp., 30 miles west of Willows, California, has been sold to a mining company in New Mexico which intends to use it for concentrating manganese ore. The Grey Eagle mill ceased operations this spring after exhausting a large body of low-grade chrome ore.

John Robertson continues to ship good chrome ore from the Illinois Chrome mine on the Illinois River 18 miles west of Selma, Oregon. Production is at the rate of about 700 tons a month, and the ore is trucked to the Metals Reserve Company purchasing depot at Grants Pass.

UNITED STATES MERCURY PRODUCTION, 1943

According to Mineral Market Report No.1191 released by the U.S.Bureau of Mines, June 10, 1944,

"The mercury output in 1943 totaled 51,929 flasks which represented a new peak rate since 1882. This high production was in response to the stimuli provided by historic peak prices, Government buying and other aids and was made despite labor shortages and inefficiency, and other handicaps. The opening of the New Idria-Alaska (Red Devil) mine, Alaska, on a larger scale in 1943, the attainment of peak annual production at the New Idria mine, Calif., after more than 80 years operation, the almost quadrupling of output at the Abbott mine, Calif., the substantial gain at Mt. Jackson mine, Calif., and the almost doubling of large-scale production at the newly opened Hermes mine, Idaho, were the principal factors that erased the losses at many other mines and accounted for the increase already noted.

Mercury Produced in the United States, 1942-43, by States

	1942			1943		
	Producing mines	Flasks (76 pounds)	Value 1/ 1/	Producing mines	Flasks (76 pounds)	Value 1/ 1/
Alaska	(2/)	(2/)	(2/)	3	786	\$ 153,435
Arizona	7	701	\$ 137,641	3	541	105,609
Arkansas	16	2,392	469,669	18	1,532	299,062
California	85	29,906	5,872,043	65	33,812	6,600,440
Idaho	(2/)	(2/)	(2/)	1	4,261	831,790
Nevada	40	5,201	1,021,217	33	4,577	893,476
Oregon	23	6,935	1,361,687	16	4,651	907,922
Texas	(2/)	(2/)	(2/)	7	1,769	345,326
Utah	(2/)	(2/)	(2/)	-	-	-
Washington	(2/)	(2/)	(2/)	-	-	-
Undistributed	13	5,711	1,121,355	-	-	-
	184	50,846	9,983,612	146	51,929	10,137,060

1/ Value calculated at average price at New York. 2/ Included under "Undistributed", Bureau of Mines not at liberty to publish."

* * * * *

"The average grade of ore treated rose in 1943, against the historic trend. In 1943 the grade was 0.31 percent (6.28-pound ore), compared with 0.25 percent in 1942 (5-pound ore), 0.26 (5.2-pound ore) in 1941, 0.31 (6.2-pound ore) in 1940, and 0.37 (7.4-pound ore) in 1939."

COAL SHORTAGE

Addressing the National Association of Purchasing Agents this week Deputy Solid Fuels Administrator Charles J. Potter estimated a bituminous coal shortage of 30 million tons this coming winter (596 million tons production against 626 million requirements), with an 8 million ton shortage in anthracite. Potter stated that recourse can be had to three measures, (1) reduce consumption by domestic consumers, (2) substitute less desirable coal in many services, and (3) cut down on industrial consumption. He stated that the first two measures are being followed out in varying degree and forecast the possibility of either a curtailment in the supply in non-essential industries or a general cut-back affecting all industries.

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