STATE OF ILLINOIS
DEPARTMENT OF REGISTRATION AND EDUCATION

# FLUORSPAR IN ILLINOIS

*The State Mineral of Illinois*

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# FLUORSPAR IN ILLINOIS

*Cover photo: Cluster of cubic crystals of fluorite, approximately one-third actual size, from a cavity in an Illinois fluorspar deposit.*

# FOREWORD

The Seventy-fourth General Assembly of the Illinois State Legislature in July of 1965 passed an act designating a State mineral. According to the Act, "the mineral calcium fluoride, commonly called 'fluorite,' is designated and shall be known as the official State mineral of the State of Illinois." This action was particularly appropriate as the State of Illinois has been the leading domestic producer of fluorspar, the commercial ore of fluorite, since 1942. In recent years, Illinois has accounted for about 60 percent of the total United States production of this commodity.

The fluorspar mining district is located in Hardin and Pope Counties in extreme southern Illinois. Because of the importance of the fluorspar mining industry to the state, the Illinois State Geological Survey has long had an interest in this commodity. Over the years, the Geological Survey has published a number of circulars, reports of investigations, and bulletins concerning various phases of the geology, mining, milling, and economics of the fluorspar industry. This present circular is a complete revision and expansion of the earlier Circular 296 (1960), which is now out of print, and presents the latest information available at this time on the geology, mining, milling, economic aspects, and uses of fluorspar and fluorine chemicals. It is presented in a semi-technical form, as an introduction to the Illinois fluorspar industry, suitable for both the interested layman and technical and commercial people. We hope that it will find wide use among both groups.

February 1968

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# FLUORSPAR IN ILLINOIS

**J. C. Bradbury, G. C. Finger, and R. L. Major**

## ABSTRACT

Fluorspar deposits, found in Hardin and Pope Counties of extreme southeastern Illinois, occur as fissure fillings in faults and as replacement bodies in limestone. Practically all of the production comes from underground mines. The crude fluorspar ore is beneficiated in modern flotation mills to produce a high-quality finished product that is satisfactory for use in the metallurgical, ceramic, and chemical industries. Lead and zinc concentrates are important co-products of these operations.

For many years, Illinois has been the leading producer of fluorspar in the United States, a position due in part to its strategic geographical location with respect to water, rail, and highway transportation, and to consuming industries. However, since the early 1950's, imported fluorspar has been entering the United States market in sizable quantities because of its lower cost. This foreign competition has sharply curtailed the growth of the domestic fluorspar mining industry. The development of fluorspar briquets and pellets, however, has helped the domestic producers to recapture part of their lost markets in the steel industry.

In 1966, 54 percent of the fluorspar consumed in the United States was used by the chemical industry in the manufacture of hydrofluoric acid, a basic material in the production of fluorine chemicals and compounds. The iron and steel industry consumed another 38 percent of the fluorspar as a fluxing agent. Smaller amounts were also used as a flux and opacifying agent in the ceramic industry for the manufacturing of glass and for enamel coatings on sinks, bathroom fixtures, stoves, refrigerators, and signs. In addition, use of acid and ceramic grades of fluorspar concentrate has increased in cement manufacture, zinc smelting, magnesium production, buff- and white-colored face brick manufacture, fiber glass manufacture, and special flux formulation manufacture.

Fluorine chemicals are useful in the production of primary aluminum, in nuclear fuel processing, in fluoridation of water, and in the manufacture of rocket and missile fuels, aerosol propellants, plastics, insecticides, fungicides, and medicinals.

## INTRODUCTION

From the hills of extreme southern Illinois comes the mineral fluorite, commonly called fluorspar, which performs many important and essential functions in modern industry. In the making of steel, enamels, aluminum, special glasses, and a host of chemicals, Illinois fluorspar plays an important role. For many years, Illinois has been the largest producer of this mineral in the United States, and modern mines and mills continue to supply a variety of grades of fluorspar to meet the needs of various industrial consumers.

Part I - "Geology, Mining, and Milling," was written by J. C. Bradbury, geologist; Part II - "Economic Aspects," by R. L. Major, mineral economist; and Part III - "Uses of Fluorspar and Fluorine Chemicals," by G. C. Finger, chemist.

### Acknowledgments

Information on fluorspar and fluorine chemicals was obtained from many sources. The cooperation of the Illinois fluorspar producers and the fluorine chemical manufacturers is gratefully acknowledged. The personnel and the reports of the U. S. Bureau of Mines, U. S. Department of the Interior; Bureau of the Census, U. S. Department of Commerce; and Inorganic Chemicals Branch of the Business and Defense Services Administration, U. S. Department of Commerce, all in Washington, D. C., were of great assistance in preparing this report.

In addition, this publication would not have been possible without the wealth of information available from company literature and brochures, trade magazines, journals, the daily press, newsletters of scientific societies, as well as many other publications. Much of the information in Part III was obtained from Chemical and Engineering News, Oil, Paint, and Drug Reporter, Chemical Age, Science News, and the Wall Street Journal.

Finally, special thanks for critically reviewing Parts I and II of this report are due Mr. Gill Montgomery, Vice President and General Manager of the Fluorspar Mining Division of The Minerva Company, Eldorado, Illinois; and Mr. Harold E. Bailie, General Superintendent of the Ozark-Mahoning Company of Rosiclare, Illinois.

## PART I

## GEOLOGY, MINING, AND MILLING

The following paragraphs contain a brief, semi-technical account of the geology, mining, and milling of Illinois fluorspar. For a more comprehensive and technical treatment of the subject, the reader is referred to Weller, Grogan, and Tippie (1952).

## GEOLOGY

### Mineralogy

Fluorspar, also called fluorite, consists of two chemical elements, calcium (51 percent) and fluorine (49 percent). Its chemical name is calcium fluoride, and its formula is $CaF_2$. It is a glassy mineral with a hardness of 4 and a specific gravity of 3.18. Illinois fluorspar is commonly colorless, white, or grayish, but some of it is purple, pink, blue, green, yellow, or tan. Characteristically, crystals of fluorspar have a cubic shape (cover photograph), and pockets of such crystals are found in the southern Illinois deposits. However, most of the fluorspar is massive-that is, it occurs in a compact body of interlocking crystals.

### Producing Districts

The fluorspar of Illinois occurs in Hardin and Pope Counties, in the extreme southern part of the state, in the Illinois portion of the Illinois-Kentucky fluorspar mining district. Rosiclare, Cave in Rock, and Elizabethtown are headquarters for the mining industry in Illinois. Figure 1 shows the distribution of the mining districts.

In the past, the area's main production has come from the Rosiclare vein system, a belt of mineralized faults near the town of Rosiclare, and from the bedded replacement deposits of the Cave in Rock district, a northeast-trending belt of "blanket" deposits about 3 miles north of the town of Cave in Rock. Today, the bulk of Illinois production comes from the Cave in Rock district, with only minor production from the Rosiclare district. Prominent outlying areas include the Stewart vein system, just south of Eichorn in western Hardin County, and the Empire district, an area of vein deposits in eastern Pope County, about 2 miles northwest of Eichorn.

### Vein Deposits

Vein deposits are steeply inclined, sheetlike deposits that occur as fissure fillings along faults. A fault is a crack in the rocks of the earth's surface along which movement has taken place. The width and continuity of the vein deposits depend upon the width of the fault opening in which they were formed. In the fluorspar area, the faults are usually vertical, or nearly so, and the rocks on one side of the faults have moved downward in relation to the rocks on the other side. At some places, there is also evidence of lateral movement along the faults.

The fault surfaces were never perfectly even, but were wavy and irregular, preventing a good fit of one side of the fault against the other. As a result, the walls of the fault were pushed apart, producing openings in which fluorspar veins were later deposited.

The amount of vertical movement along a fault also had an important bearing on the formation of ore deposits. For example, a small amount of vertical movement, 25 feet or less, probably would not push the fault walls far enough apart to

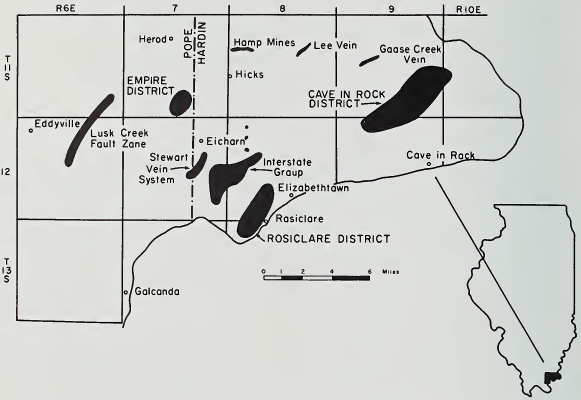


Figure 1 - Principal fluorspar mining districts in the extreme southern Illinois region.

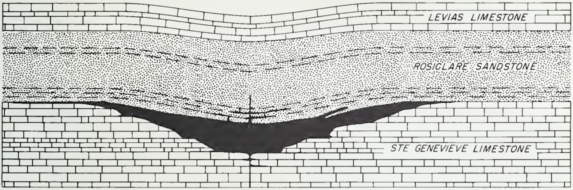
create openings in which the ore could be deposited. Along the very large faults that had 1000 feet or more of vertical movement, the crushing and grinding were so intense that few open spaces of suitable size were left for formation of minable ore deposits. However, faults of moderate displacement commonly had less shattering and, therefore, possessed more favorable characteristics for ore deposition. Within the fluorspar district, faults of 100 to 500 feet of displacement apparently offered the best conditions for vein deposition.

The exact manner in which the fluorspar veins were formed is not known. Presumably, they were deposited by crystallization from hot, rising solutions that originated deep below the surface of the earth.

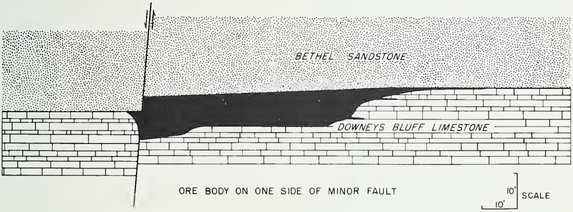
## Bedded Deposits

The bedded replacement deposits (fig. 2) are flat-lying, irregular bodies of ore parallel to the beds of the host limestone. The deposits are elongate and range from 200 to more than 10,000 feet in length and from 50 to 300 feet in width. Thicknesses are commonly from 4 to 15 feet, with the ore wedging out at the margins.

Unlike the vein deposits, in which the fluorspar simply filled open fissures, the bedded deposits were formed by a chemical reaction between the fluoride-bearing solutions and the limestone that changed the calcium carbonate of the limestone to calcium fluoride or fluorite. The chief reason for this difference in behavior of the solutions was probably the character of the fracture zones through which they moved.



ORE BODY SYMMETRICAL ABOUT CENTRAL FISSURE



ORE BODY ON ONE SIDE OF MINOR FAULT

Figure 2 - Schematic cross sections of two general types of bedding-replacement fluorspar deposits (adapted from Grogan, 1949).

The vein deposits, it will be recalled, are found in faults of considerable displacement, along which open spaces as much as 30 feet wide were formed. The bedded deposits, on the other hand, follow groups of jointlike fractures or minor faults of a few inches to 20 feet of displacement where the amount of movement was not enough to create large openings. Along the larger faults, then, ample space was provided for the mineralizing solutions to deposit their load, but the lack of open space in the joints and minor faults caused the solutions to move out laterally along bedding planes, or, possibly, even through the pores of the less dense layers of rock. The resulting intimate contact between solutions and rock led to chemical reaction between the two and the resulting replacement of limestone by fluorite.

## Mixed Deposits

A few other deposits, combining features of the bedded and vein deposits, occur in faults of small displacement (approximately 25 feet). The deposits are characterized by a rather narrow vein (2 to 3 feet) with one or more small replacement ore body extending laterally from the vein where it intersects limestone beds favorable for replacement. Such replacement deposits have been relatively common along veins in the Empire district.

## Relation of Deposits to Kind of Rock

Just as the character of the faults influences the size or type of deposit, the various kinds of rock also have their effects on the deposits, both vein and bedded. Figure 3 shows the succession of rock formations present in the fluorspar district. In the veins, the best deposits occur where the fault walls are composed of the stronger, or more competent, rocks such as limestone and well cemented sandstones. The weaker, or less competent, formations, such as shale and shaly limestone or sandstone, were easily crushed by movement along the fault and filled rather than created openings.

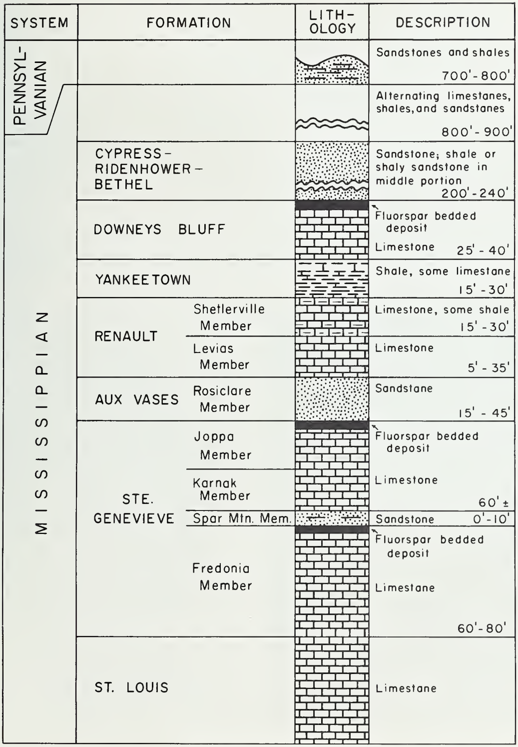
Because they are strong and competent, the Ste. Genevieve and St. Louis Limestones are the most favorable strata for vein deposits. Good vein deposits may be found in higher formations, but because many higher rocks are shaly, the deposits are likely to be of limited size. Some competent rock units exist in these higher beds, but the accompanying incompetent beds tend to plug the fault, causing numerous barren or lean portions along the vein.

The bedded replacement deposits occur chiefly in a relatively small vertical thickness of rock from the base of the Bethel Sandstone downward to the top of the Fredonia Limestone Member (fig. 3). The principal deposits are found at three favored positions within this 190-foot interval—in the top part of the Downeys Bluff Limestone, in the top part of the Ste. Genevieve Limestone, and near the level of the Spar Mountain Sandstone Member, 45 to 60 feet below the top of the Ste. Genevieve—possibly because these limestone beds are purer, more porous, or more fractured than other beds. A fourth favored position, in the Shetlerville and Levias Limestone Members of the Renault Formation, is not as productive as the other three but is reported to contain substantial amounts of fluorspar in parts of the Cave in Rock district. Other levels in the Ste. Genevieve Limestone between the Rosiclare and Spar Mountain Sandstones may be mineralized locally.

## Minerals Comprising the Ore Deposits

The valuable minerals of the fluorspar deposits are fluorite (calcium fluoride, $CaF_2$), sphalerite (zinc sulfide, ZnS), and galena (lead sulfide, PbS). Sphalerite and galena are the common ore minerals of zinc and lead, respectively. The mineral calcite (calcium carbonate, $CaCO_3$) is common in the deposits but is of little commercial value at present. Barite (barium sulfate, $BaSO_4$) is also a relatively common mineral, but production of it has been minor, chiefly because of its erratic distribution.

In the veins, fluorite and calcite are the chief minerals. Sphalerite and galena are abundant in a few deposits, but in most deposits are present only in small amounts, usually at the margins of the veins, and represent only a minor product of vein mining in the district as a whole. Barite has been found at various places but noteworthy concentrations are known in only a few areas. Apparently the last mineral to be deposited during the ore-forming period, it occupies the central parts of fluorspar veins or occurs in narrow fissures next to the veins.



| SYSTEM | FORMATION | | LITHOLOGY | DESCRIPTION |
|---|---|---|---|---|
| PENNSYLVANIAN | | | | Sandstones and shales 700'-800' |
| | | | | Alternating limestones, shales, and sandstones 800'-900' |
| MISSISSIPPIAN | CYPRESS-RIDENHOWER-BETHEL | | | Sandstone; shale or shaly sandstone in middle portion 200'-240' |
| | DOWNEYS BLUFF | | | Fluorspar bedded deposit<br>Limestone 25'-40' |
| | YANKEETOWN | | | Shale, some limestone 15'-30' |
| | RENAULT | Shetlerville Member | | Limestone, some shale 15'-30' |
| | | Levias Member | | Limestone 5'-35' |
| | AUX VASES | Rosiclare Member | | Sandstone 15'-45' |
| | STE. GENEVIEVE | Joppa Member | | Fluorspar bedded deposit<br>Limestone 60' ± |
| | | Karnak Member | | |
| | | Spar Mtn. Mem. | | Sandstone 0'-10' |
| | | Fredonia Member | | Fluorspar bedded deposit<br>Limestone 60'-80' |
| | ST. LOUIS | | | Limestone |

Figure 3 - Principal fluorspar-bearing portion of stratigraphic column of the southeastern Illinois fluorspar district. Black bands represent horizons most favorable for the occurrence of bedded deposits. The most productive parts of veins generally occur below the Rosiclare Sandstone.

In the bedded deposits, as in the vein deposits, fluorite is the chief valuable mineral, but sphalerite and galena are important ore minerals in some places. Calcite is less common than in the vein deposits but is abundant locally. Barite is almost entirely absent in some deposits but is abundant in parts of others, particularly around the margins.

The fluorite commonly occurs as alternating coarse- and fine-grained layers in banded ore (fig. 4A) and as massive bodies of various shapes within the ore bodies. Where abundant, sphalerite takes the place of the fine-grained fluorite layers in banded ore (fig. 4B). Galena occurs in the coarse-grained layers of banded ore as separate masses, one-fourth to three inches in diameter. Barite occurs as alternating layers with fluorite in banded ore and also as massive bodies that have filled cavities or replaced limestone or fluorite.

## Percentages of Valuable Constituents in the Ore

The amounts of the valuable constituents—fluorite, zinc, and lead—in ore that is mined in the fluorspar district vary considerably from one ore body to an-

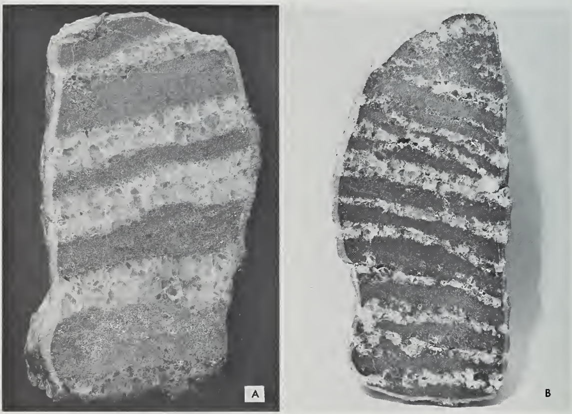


Figure 4 - A. Polished specimen of banded fluorspar. Light bands are coarse-grained, darker bands are fine-grained fluorspar. About half actual size.
B. Polished specimen of banded fluorspar-zinc ore. Light bands are fluorspar, darker bands are sphalerite (zinc sulfide). About half actual size.

other. Anderson (1953) reported that ore being fed to the mill at Minerva Mine No. 1 in the Cave in Rock district averaged 29.6 percent fluorite, 3.8 percent zinc, and no lead. Weller, Grogan, and Tippie (1952) stated that ore from the Davis-Deardorff Mine of Ozark-Mahoning Company, also in the Cave in Rock district, "for a number of years. . .assayed approximately 50 to 60 percent fluorspar, 12 to 14 percent zinc, and 3 to 5 percent lead." According to Schaefer, Harrison, and Myslinski (1961), crude ore from vein deposits in the Rosiclare district entering the mill of Aluminum Company of America averaged 49.7 percent fluorite, 1.3 percent lead, and 0.3 percent zinc.

Cadmium and germanium are valuable minor constituents that are contained in the zinc mineral, sphalerite, in some of the ore bodies in the Cave in Rock district. The zinc concentrates from these ores, consisting of nearly pure sphalerite, contain up to 1.0 percent cadmium and 0.03 percent germanium (Anderson, 1953; Bailie, 1954). However, not all the sphalerite from the Cave in Rock district is cadmium-bearing, and no cadmium or germanium have been reported in the zinc concentrates produced from ores of the Rosiclare district.

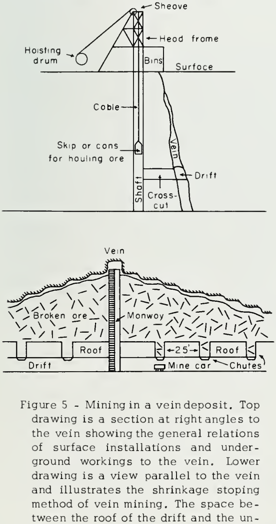


Figure 5 - Mining in a vein deposit. Top drawing is a section at right angles to the vein showing the general relations of surface installations and underground workings to the vein. Lower drawing is a view parallel to the vein and illustrates the shrinkage stoping method of vein mining. The space between the roof of the drift and the undisturbed vein material is called the stope.

## MINING

Most of the fluorspar produced in southern Illinois comes from underground mines, although minor tonnages are produced from open pits in shallow, weathered deposits where the common types of earth-moving machinery, such as bulldozers, power shovels, and drag lines, are used. Underground mining methods must be suited to the particular type of deposit being worked and, usually, are shrinkage stoping in the vein deposits and room-and-pillar methods in the bedded deposits.

### Vein Mining

In vein mining (fig. 5), a vertical shaft is first excavated in the rock adjacent to the vein. From this shaft, a tunnel-like opening, called a crosscut, is driven horizontally into the vein at a selected depth below the ground surface. Upon reaching the vein, a drift (horizontal tunnel following the vein) is driven and serves as a haulage level and starting point for shrinkage stoping. The stope (open space created as ore is removed from the vein) is excavated upward from the drift by drilling and blasting.

In wide veins, the roof, or back, of the drift is commonly an arch of vein material left in place (fig. 5); in narrow veins, however, timbers are used to form a roof. The broken ore is drawn down from the stope into mine cars through chutes and hauled to the shaft for hoisting to the surface. Only enough ore is removed during the stoping operation to give working room for the miners (fig. 5).

Other haulage levels may be driven above or below the initial level, usually at vertical intervals of 100 feet. Stoping progresses upward from one level to the next. If the overlying drift is to be preserved, pillars of unbroken vein material are left in place.

### Mining of Bedded Ore

Bedded fluorspar deposits are mined underground by a modified form of the room-and-pillar method in which the ore is excavated from rooms, with pillars left between the rooms to support the mine roof. Technically, the method is called open stoping (Montgomery, Daly, and Myslinski, 1960; Bailie, Powell, Melcher, and Myslinski, 1960). Bedded deposits that are exposed on steep hill slopes can be mined by driving a tunnel, called an adit, directly into the ore body. Vertical shafts are sunk to those ore bodies that are not easily accessible by such direct means. In either case, a main haulage drift is usually driven along the center of the ore body, and rooms are mined out from it at intervals throughout the workable deposit. The ore is drilled and blasted, loaded by machines into cars or trucks, and hauled to the mine shaft, or, if an adit mine, to bins or stockpiles on the surface (figs. 6, 7). The larger mines are highly mechanized.

## MILLING

As it comes from the mines, the fluorspar ore commonly is a mixture of fluorspar, calcite, sphalerite, and galena, plus various amounts of limestone and other waste rock that are unavoidably mined with it. Much of the sphalerite contains cadmium and germanium that are later extracted as by-products during the smelting process. Milling is the general term for the processes involved in separating the ore from the waste material and in separating the valuable minerals from each other (fluorspar from the metallic sulfides, for example).

### Hand-picking and Washing

A few small mines use hand-picking to separate lumps of fluorspar from the crude ore in order to get a premium product, but most ore goes through one or more mechanical processes to beneficiate it. The most simple process, washing, is useful in separating spar from contaminating clay. This usually is satisfactory only for the weathered ores and involves the use of a mechanical washing device, known as a log washer, or washing on a vibrating screen or on a trommel.

### Jigging

Jigging, another relatively simple method for beneficiating fluorspar, uses water as the separating medium. Fluorspar is heavier than most of the waste materials found with it, and thus the unwanted material is floated over the sides of the jig cell, by an up-and-down pulsating action, while the heavier fluorspar remains behind. However, because the specific gravity of fluorspar is not greatly different from that of the waste materials (fluorspar = 3.1, calcite = 2.7, quartz = 2.7, and limestone = 2.6 to 2.7), jigging does not effect a high degree of separation. Although now largely replaced by heavy-media separation (described below), jigging has been used chiefly for producing the lower commercial grades of fluorspar and as a primary separation process to eliminate a portion of the waste materials before putting the ore through subsequent milling operations. Jigging has also been used to separate galena (specific gravity = 7.5) from mixed fluorspar-galena ores, but this part of the processing is now done by other, more effective methods.

### Heavy-media Separation

A newer and more efficient process, based on differences in specific gravities, is heavy-media separation (HMS) in which the ore minerals are separated from waste in a cone or a drum containing a suspension of finely ground ferrosil-

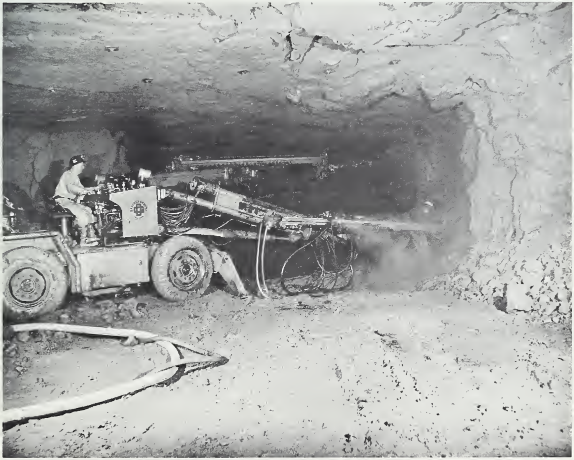


Figure 6 - Underground mining operations at The Minerva Company's No. 1 Mine, showing rubber-tired, mechanized jumbo drill in operation.

icon in water. The specific gravity of the suspension, or heavy medium, is maintained between 2.55 and 2.62 at the top of the cone and 2.85 and 3.1 at the bottom.

Crude ore is introduced at the top of the cone, and particles having specfic gravities greater than that of the medium near the bottom (such as fluorite and the metallic sulfides) sink and are recovered at the bottom. Particles of lesser gravity (such as quartz and calcite) are buoyed up and carried away with the overflow from the cone. Ferrosilicon is washed from the ore and waste materials, is recovered magnetically, and is returned to the cone. The product of heavy-media separation may be marketed directly or further processed by flotation.

### Flotation

Most of the higher grades of fluorspar shipped from Illinois mines are in the form of concentrates produced by the flotation process (fig. 8). Flotation is valuable to the Illinois fluorspar industry because it allows the use of lower grade ores and also permits the selective separation and economic collection of the val-

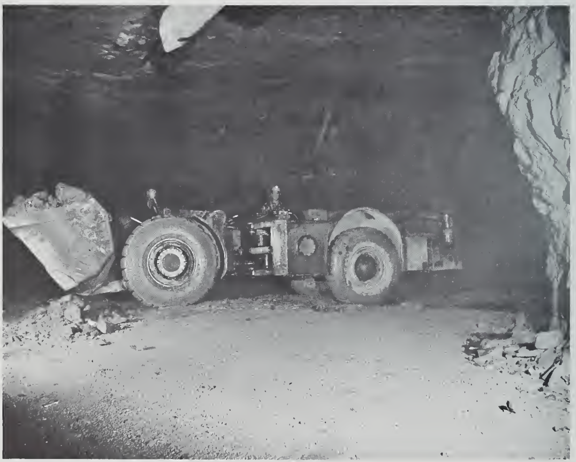


Figure 7 - Underground mining operations at The Minerva Company's No. 1 Mine, showing an articulated underground diesel front-end loader.

uable lead and zinc minerals, galena and sphalerite, that occur with the fluorspar in some of the deposits.

Because of the intermixture of fluorite with waste rock in lower grade ore and of sphalerite and galena with both these materials in the mixed ores, it is necessary to mill the ore to a very fine size in order to liberate the various components. In turn, however, this creates the problem of accumulating exceedingly small particles into concentrates of fluorite, zinc, and lead.

It has been found that if specific chemical reagents are mixed with water in which particles of galena, sphalerite, and fluorite are present, and if the mixture is agitated to produce a froth, the particles of galena will adhere to the froth bubbles and be carried to the surface while the other materials remain in the suspension. The froth is then collected and dewatered by vacuum filters, producing a lead concentrate. Other reagents are added to the remaining mixture of sphalerite, fluorite, and waste rock, and a zinc concentrate is produced next. In the third stage of this flotation recovery, the fluorite is separated from the waste rock to produce an acid-grade fluorspar concentrate. Published descriptions of the various

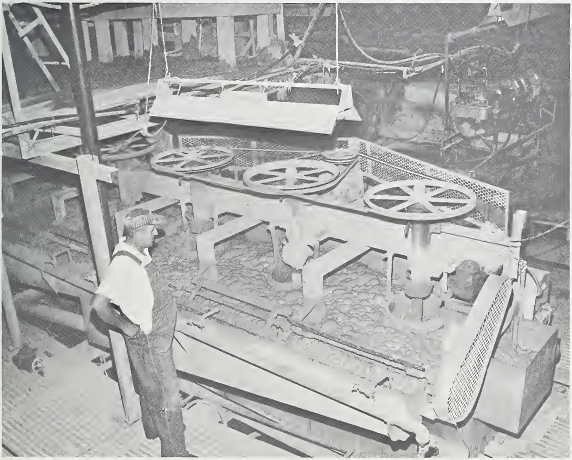


Figure 8 - Bank of flotation cells in Ozark-Mahoning Company' s mill at Rosiclare, Illinois.

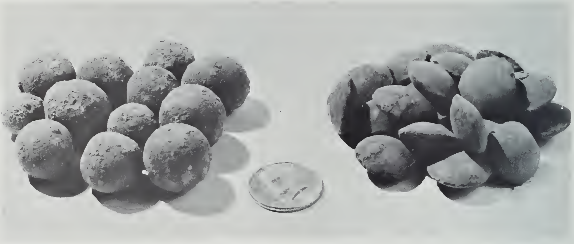


Figure 9 - View showing comparison of size and shape of fluorspar briquets and pellets. Half-dollar is included for scale.

milling operations in the fluorspar district by Anderson (1953), Bailie (1954), and Schaefer, Harrison, and Myslinski (1961) indicate that the flotation process recovers over 90 percent of the valuable constituents in the ores.

### Commercial Grades and Specifications

Fluorspar is marketed in three general grades—metallurgical, ceramic, and acid. Metallurgical grades, used chiefly in steel making, specify a certain number of effective units of $CaF_2$, usually expressed as "effective percent of $CaF_2$." This figure is obtained by subtracting $2\frac{1}{2}$ times the percentage of silica ($SiO_2$) from the percentage of $CaF_2$ in the fluorspar concentrate. For example, a concentrate assaying 85 percent $CaF_2$ and 5 percent $SiO_2$ will contain $72\frac{1}{2}$ percent effective $CaF_2$. The grades most commonly listed in market quotations are 60, 70, and $72\frac{1}{2}$ percent effective $CaF_2$.

Ceramic and acid grades of fluorspar are of higher purity than metallurgical grades, and specifications are expressed in percentage of $CaF_2$. Ceramic grades range from 85 to 96 percent $CaF_2$. Acid grade, used chiefly in the aluminum and chemical industries, must contain 97 percent or more $CaF_2$.

### Pelletizing and Briquetting

In order to convert the fine, powdery fluorspar flotation concentrates into a form that can be used in steel furnaces, one Illinois producer presses the concentrates into briquets and another rolls the powder into pellets (fig. 9).

The briquets are made by combining the fluorspar powder with an organic binder and passing the mixture through a press. The briquets are then dried in an oil-fired furnace. The resulting product is a "peach-seed"-shaped object about 1 inch in diameter (fig. 9).

The pelletizing process, in contrast, used by another Illinois fluorspar producer, utilizes a shallow, tilted, rotating pan. Fluorspar flotation concentrate (or filter cake) and a binder solution are fed continuously into the pan. As the pan rotates, the powdered fluorspar mixes with the binder and rolls up into small balls that spill over the lip of the pan when they reach the desired size. The balls, or pellets (fig. 9), are then carried by conveyor belts to an oven where the excess water is driven off and the pellets are hardened. Size of the pellets can be controlled by the angle of tilt of the pan, the speed of rotation, and the moisture content. These fluorspar pellets and briquets are superior to natural gravel spar because their composition is more uniform and they are easier to handle.

## Exploration for Additional Deposits

The ability of the Illinois fluorspar industry to continue to supply a vitally needed raw material to the nation's industries depends upon forward-looking exploration programs to discover new deposits. In the early days of fluorspar mining in Illinois, a miner had only to sink a shaft or drive an adit into an outcrop of ore. As the mining industry grew, the good surface exposures of ore were used up and prospecting of less promising deposits by means of shafts and other excavations became too costly. Drills that could penetrate and sample buried rock units came into general use.

Today, systematic core drilling programs are directed by geologists who are trained to evaluate the information gained by the study of the surface rock exposures and drilling samples (cores). However, in the future, even more subtle ore-finding methods will be needed. To this end, mining company exploration staffs and Illinois State Geological Survey geologists are constantly on the alert for new ideas on ore occurrence or new methods of exploration.

Geochemical exploration, involving the application of chemical analytical methods to field geology, has been tried with varying degrees of success in recent years by the mining companies and by the Geological Survey. One company has claimed good results in tracing a vein by analysis of soil samples for fluorine.

Various geophysical methods also have been investigated both by government agencies and private companies. The U. S. Geological Survey, in cooperation with the Illinois State Geological Survey, demonstrated that some faults can be discovered and accurately located by an electrical method called earth resistivity (Currier and Hubbert, 1944). The seismic method, consisting of measurement of the velocity of artificial earthquake waves generated by a small charge of dynamite, has been tried by the Illinois State Geological Survey in a limited way and also appears to be capable of detecting and tracing faults (Johnson, 1957 and 1964).

Photogeologic techniques, used in the Illinois fluorspar district for several years, involve the inspection of pairs of aerial photographs with the aid of a stereoscopic viewer. The three-dimensional effect thus produced helps to emphasize minor differences in topography and vegetative cover, aiding in the mapping of such rock structures as faults. This procedure is reported to be a useful tool in the search for new mineralized belts and is credited by one company with several important discoveries.

Standard field geology methods were employed by the Illinois State Geological Survey in the recent revision of the 1920 geologic map of the fluorspar mining district. The availability of new and more accurate topographic base maps and the existence of a wealth of data accumulated by the mining companies through exploration drilling over the past 40 years have made it possible to produce a more detailed and accurate map. The new map has been issued in three parts, with accompanying text, as Circular 342 (Baxter, Potter, and Doyle, 1963), Circular 385 (Baxter and Desborough, 1965), and Circular 413 (Baxter, Desborough, and Shaw, 1967). This is expected to be an important aid in the discovery of new deposits because of the more accurate location of faults and better definition of formation boundaries.

## PART II

## ECONOMIC ASPECTS

The first recorded fluorspar mining in Illinois was in 1842 when a small operation was begun in Hardin County near the site of the present Rosiclare Mine (Hatmaker and Davis, 1938, p. 16). Since that year, production has been more or less continual.

Illinois has long been a major source of production in the United States and for many years has been the principal domestic producer. To date, it has provided more than half of the total fluorspar produced within the United States.

The prominent position of Illinois as a fluorspar producer stems primarily from the accessibility and strategic geographic location of its relatively shallow-depth deposits, which are easily exploited. Surrounding the fluorspar deposits, and closely linked to them by railway, highway, and waterway networks, are major centers of industrial, chemical, and steel production. Nowhere else within the United States are fluorspar deposits so favorably situated.

### PRODUCTION TRENDS

United States production of fluorspar rose from 96,000 tons in 1930 to the record high of 413,000 tons in 1944 and then declined sharply in the postwar period. Since the more recent peak years of 1951 (347,000 tons) and 1956 (330,000 tons), domestic production has declined, and after 1959 has averaged only 210,000 tons annually. The growth in fluorspar production has not paralleled the increase in domestic consumption because of the increased use of imported ores, principally from Mexico. The effect of the imports has been only partially offset by the protection offered by United States tariffs and by the increased demand for fluorspar resulting from the Federal Government's stockpiling program.

The extent of the United States fluorspar reserves has been the subject of much disagreement over the years, with consumers and importers understandably more pessimistic than independent domestic producers. Because of the nature of fluorspar deposits in the major mining districts, much time and money would be required to accurately determine the total tonnage, the accessibility, and the quality of fluorspar available (U. S. Tariff Commission, 1962, p. 40). The major independent producers contend that the discovery of reserves is largely determined by the prosperity of the industry, and that when profits are sufficient to support active exploration programs, more ore will be found. This statement is corroborated to some degree by the fact that between 1945 and 1956, a period of prosperity in the domestic industry, the Department of Interior's estimates of domestic fluorspar reserves increased from 14.5 to 22.6 million tons (containing 35 percent or more calcium fluoride, or the equivalent thereof in calcium fluoride plus metallic sulfide values). Reserves in the Illinois-Kentucky fluorspar district were estimated in 1956 at 8.1 million tons of measured ore and 4.0 million tons of inferred ore (U. S. Geological Survey, 1956).

Of the total fluorspar produced annually within the United States, Illinois accounts for over half. In 1965, Illinois led in production (shipments) with 159,140 tons, followed by Kentucky with 31,992 tons. Other states producing during 1965 were Utah, Colorado, Montana, and Nevada, with a total production of 49,800 tons. Table 1 gives data on annual shipments from Illinois fluorspar mines for the period from 1940 through 1965.

In the past, Illinois fluorspar output has come from numerous mines ranging in size from those whose production is only a few hundred tons per year to those producing tens of thousands of tons annually (Appendix). In general, the output of the small mines is sold to larger operators who have facilities for upgrading the raw

TABLE 1 - FLUORSPAR SHIPMENTS, CONSUMPTION, AND PRICES, 1940-1965[a]

| Year | U.S. fluorspar shipments (tons) | Illinois fluorspar shipments | | | Fluorspar consumed in U.S. (tons)[c] | Illinois shipments as percent of U.S. consumption |
|---|---|---|---|---|---|---|
| | | Tons | Illinois, as percent of U.S. shipments | Average value per ton[b] ($) | | |
| 1940 | 233,600 | 104,698 | 44.8 | 22.10 | 218,500 | 47.9 |
| 1941 | 320,669 | 133,333 | 41.6 | 22.85 | 303,600 | 43.9 |
| 1942 | 360,316 | 161,949 | 44.9 | 26.59 | 360,800 | 44.9 |
| 1943 | 406,016 | 198,789 | 49.0 | 31.66 | 388,885 | 51.1 |
| 1944 | 413,781 | 176,259 | 42.6 | 33.79 | 410,170 | 43.0 |
| 1945 | 323,961 | 147,251 | 45.5 | 34.06 | 356,090 | 41.4 |
| 1946 | 277,940 | 154,525 | 55.6 | 35.55 | 303,190 | 51.0 |
| 1947 | 329,484 | 167,157 | 50.7 | 36.78 | 376,138 | 44.4 |
| 1948 | 331,749 | 172,561 | 52.0 | 36.64 | 406,269 | 42.5 |
| 1949 | 236,704 | 120,881 | 51.1 | 38.23 | 345,221 | 35.0 |
| 1950 | 301,510 | 154,623 | 51.3 | 39.52 | 426,121 | 36.3 |
| 1951 | 347,024 | 204,328 | 58.9 | 45.49 | 497,012 | 41.1 |
| 1952 | 331,273 | 188,293 | 56.8 | 50.35 | 520,197 | 36.2 |
| 1953 | 318,036 | 163,303 | 51.3 | 52.46 | 586,798 | 27.8 |
| 1954 | 245,628 | 107,830 | 43.9 | 55.54 | 480,374 | 22.4 |
| 1955 | 279,540 | 166,337 | 59.5 | 47.12 | 570,261 | 29.2 |
| 1956 | 329,719 | 178,254 | 54.1 | 47.51 | 621,354 | 28.7 |
| 1957 | 328,872 | 169,939 | 51.7 | 51.94 | 644,688 | 26.4 |
| 1958 | 319,513 | 152,087 | 47.6 | 52.15 | 494,227 | 30.8 |
| 1959 | 185,091 | 112,469 | 60.8 | 52.53 | 589,979 | 19.1 |
| 1960 | 229,782 | 134,529 | 58.5 | 51.55 | 643,759 | 20.9 |
| 1961 | 197,354 | 116,908 | 59.2 | 50.95 | 687,940 | 17.0 |
| 1962 | 206,026 | 132,830 | 64.5 | 48.12 | 652,888 | 20.3 |
| 1963 | 199,948 | 132,060 | 66.1 | 49.58 | 736,350 | 17.9 |
| 1964 | 217,137 | 127,454 | 58.7 | 50.62 | 831,561 | 15.3 |
| 1965 | 240,932 | 159,140 | 66.1 | 49.40 | 930,127 | 17.1 |

[a] U.S. Bureau of Mines tonnage figures.

[b] Numerical average derived by dividing the total f.o.b. plant value by the total Illinois fluorspar shipments.

[c] Fluorspar consumed includes domestic and foreign material.

mine product, but in some instances, the small mines sell directly to consumers that can use fluorspar in the sizes and purity that can be obtained through hand sorting. The larger producers operate mills where the run-of-mine material is crushed, ground, and processed either by gravity or flotation processes to remove impurities.

The extremely competitive conditions in the domestic fluorspar industry have forced most of the small, higher cost producers out of business. In 1958, 35 companies and individuals reported fluorspar production in Illinois, but the top four, each producing in excess of 20,000 tons, accounted for 89 percent of Illinois production. By 1965, only five producers were reported to be active, and the top two, each producing more than 200,000 tons of crude ore, accounted for 90 percent of the state's production.

More than 90 percent of the finished fluorspar produced in Illinois is shipped in the form of flotation concentrates; the remainder is shipped in the form of "gravel," pellets, and briquets. In 1965, 42.9 percent of the fluorspar shipped from Illinois mines went into the manufacture of hydrofluoric acid; 21.4 percent for ceramic uses; 14.0 percent in steel manufacture; and the remainder, 21.7 percent, served miscellaneous uses.

## CO-PRODUCTS AND BY-PRODUCTS

All of the major domestic producers of acid-grade fluorspar in the Illinois-Kentucky district also produce lead and zinc concentrates. Galena (lead sulfide) or sphalerite (zinc sulfide), and often both of these minerals, are widely disseminated throughout the fluorspar deposits. Because these sulfides are deleterious in many fluorspar uses, they must be removed before the fluorspar is sold. Sometimes the sphalerite contains small, but valuable, amounts of cadmium and germanium that later can be extracted profitably as by-products. Zinc smelters will pay the fluorspar producers a bonus for the cadmium that is present in the zinc concentrate.

The income derived from the sale of lead and zinc concentrates is essential to the profitability of the larger fluorspar operations in Illinois. Although the value of these co-products varies with the markets for lead, zinc, cadmium, and germanium, their combined value still is sizable. In 1965, the income from the sale of lead and zinc concentrates amounted to about 40 percent of the combined value of the sales of fluorspar, lead, and zinc. From this it can be seen that these base metal concentrate co-products contribute greatly to keeping Illinois fluorspar producers competitive.

## MARKETING

Shipments of fluorspar from Illinois mines usually enter the market through one of three principal channels. Some mines are captive operations whose entire output normally goes directly to the consuming plants of the parent organization. Since the closing of the Aluminum Company of America's (Alcoa) mine at Rosiclare, Illinois, all of the remaining captive fluorspar mines in the United States are operated by chemical companies. Producers having no affiliations with consumers usually sell the major portion of their product on a commission basis through a sales agency or mineral broker who maintains contact between the producers and the potential consumers. A third way in which fluorspar may be marketed is by direct contract between the producing firm and the purchaser. The output of small mines is usually sold to the larger producers who either sell it as direct-shipping ore or process it into a beneficiated product before it enters the market.

Because of its varied uses, fluorspar is consumed in many places throughout the United States. At least 37 states reported consumption during 1964 and 1965, as shown in table 2.

Figure 10 shows the location of major steel plants and hydrofluoric acid plants in the United States. A concentration of these plants along the Great Lakes and inland waterways is apparent. Of the total fluorspar used in the United States during 1965, the top five states—Texas, Louisiana, Pennsylvania, Ohio, and Arkansas—accounted for over 50 percent of the consumption. The recent emergence of Texas and Louisiana as prime consuming states is due to great expansion in hydrofluoric acid plants located there (fig. 10). The proximity of the Illinois fluorspar deposits to the major inland consuming areas shown on the figure places them in a favorable position to serve the entire midwest region.

Fluorspar may move from mine to market in several ways. Shipments of the larger metallurgical-grade sizes of fluorspar commonly are made in open-type railroad cars or open barges; bulk shipments of the finer sizes are transported in boxcars, covered hoppers, or in covered barges. Pellets move in both covered railroad hoppers and in covered barges. Finely ground fluorspar also is shipped in paper bags that usually hold 100 pounds. Truck shipments are either in bulk or in bag. Loading docks on the Ohio River, a short distance from the fluorspar operations, are used to transfer fluorspar to barges for shipment up or down stream. Barges of several hundred ton capacity are used for such shipments.

## TRENDS IN FLUORSPAR CONSUMPTION

Prior to 1888, United States consumption of fluorspar was very small and, according to existing records, probably never exceeded 5000 tons per year. The material was used principally in the production of glass, enamel, and hydrofluoric acid, although smaller amounts were used in smelting nonferrous and precious metals. That year, the introduction of commercial open-hearth steel production into the United States opened up a new market whose importance quickly overshadowed all former uses.

Following the introduction of the open-hearth process, United States consumption of fluorspar increased rapidly from about 5000 tons per year in 1888 to 930,127 tons in 1965. For more than 60 years, the steel industry was the leading consumer of fluorspar, and, until World War II, accounted for 75 to 80 percent of the total quantity consumed. With such a large portion of the total consumption going into steel manufacturing, the fluorspar industry was vitally affected by the frequent ups and downs of steel production.

Between 1921 and 1965, steel production in the United States rose from 20 to 131 million tons per year, an increase of 555 percent. During this period, however, fluorspar consumed in steel manufacturing increased from 138,000 to 354,896 tons, or an increase of only 157 percent. Despite a marked increase in the use of fluorspar in steel production over the years, the consumption for this purpose has failed to keep pace with growth in steel output.

TABLE 2 - FLUORSPAR (DOMESTIC AND FOREIGN) CONSUMED IN THE UNITED STATES, BY STATE, 1964-1965, IN SHORT TONS[a]

| State | 1964 | Rank | 1965 | Rank |
|---|---|---|---|---|
| Alabama, Georgia, and North Carolina | 11,605 | 14 | 10,336 | 14 |
| Arkansas, Kansas, Louisiana, Mississippi, and Oklahoma | 111,983 | 2 | 132,674 | 2 |
| California and Hawaii[b] | 32,618 | 9 | 39,844 | 10 |
| Colorado and Utah | 23,606 | 12 | 26,463 | 12 |
| Connecticut | 1,385 | 20 | 1,680 | 20 |
| Delaware and New Jersey | 102,134 | 3 | 77,047 | 5 |
| Florida, Rhode Island, and Virginia | 1,371 | 21 | 1,331 | 21 |
| Illinois | 54,972 | 6 | 56,697 | 7 |
| Indiana | 26,720 | 11 | 28,855 | 11 |
| Iowa, Minnesota, Nebraska, and Wisconsin | 5,041 | 16 | 4,576 | 16 |
| Kentucky | 41,535 | 8 | 49,122 | 8 |
| Maryland | 9,505 | 15 | 8,742 | 15 |
| Massachusetts | 242 | 22 | 254 | 22 |
| Michigan | 50,813 | 7 | 57,816 | 6 |
| Missouri | 3,000 | 17 | 3,599 | 17 |
| New York | 16,623 | 13 | 19,041 | 13 |
| Ohio | 76,911 | 5 | 83,960 | 4 |
| Oregon and Washington | 1,616 | 19 | 1,859 | 19 |
| Pennsylvania | 83,195 | 4 | 103,140 | 3 |
| Tennessee | 2,666 | 18 | 1,960 | 18 |
| Texas | 144,488 | 1 | 179,489 | 1 |
| West Virginia | 29,532 | 10 | 41,642 | 9 |
| Total | 831,561 | | 930,127 | |

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[a] Source: U.S. Bureau of Mines (1966, p. 418).
[b] 1964 only.

The failure of fluorspar consumption to parallel steel production increases is the result of improved methods and efficiency that reduced spar usage from 8.2 pounds per ton of open-hearth steel in 1921 to 3.4 pounds per ton in 1965. Even with this reduction in per ton usage, steel still remains a major consumer of fluorspar, as can be seen from the severe slump in 1958 and 1959 when the economy suffered a recession and a long steel strike (fig. 11).

One encouraging development—the perfection and growing use of the basic oxygen furnace (BOF) for the making of steel—should be noted. Prior to 1960, the basic oxygen furnace accounted for less than 1 percent of the total steel tonnage produced in the United States. Although total steel production only increased by 32 percent between 1960 and 1965, BOF steel production increased by 584 percent. This has important implications for the fluorspar industry, as the basic oxygen furnace uses considerably more fluorspar per ton than does the open-hearth furnace (which accounted for 73 percent of the steel production in 1965). In 1965, basic oxygen furnaces used an average of 12.6 pounds of fluorspar per ton of steel for a total of 139,240 tons. This means that although the basic oxygen furnaces accounted for only 17.4 percent of the total steel production in 1965, they consumed 39.2 percent of the fluorspar used for metallurgical purposes. Further growth in BOF steel production should stimulate an increased use of metallurgical spar.

The lag in consumption of fluorspar in steel manufacture, coupled with a tremendous increase in hydrofluoric acid production during recent years, has caused

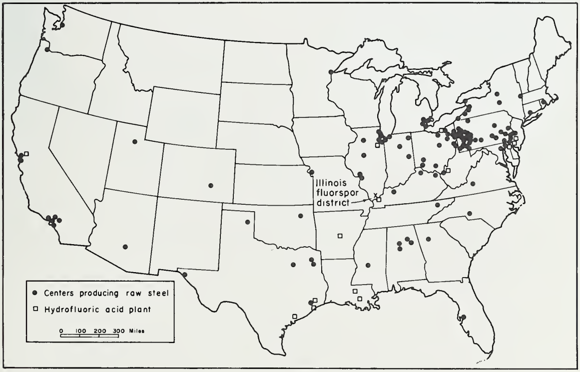

Figure 10 - Location of steel and hydrofluoric acid plants in the United States. (Source: American Iron and Steel Institute, 1966; Oil, Paint, and Drug Reporter, 1967)

steel to drop into second place among fluorspar consumer groups over the past 25 years.

The hydrofluoric acid industry has long been an important consumer of fluorspar, and with the phenomenal growth of this industry in recent years, the quantity of fluorspar used for this purpose has rapidly increased. Between 1957 and 1966, consumption of fluorspar in acid manufacture increased 73 percent. In 1966, acid manufacture accounted for about 54 percent of the total fluorspar consumed. Much of the growth of the hydrofluoric acid industry stems from the increasing use of fluorine chemicals. Fluorine compounds are used for insecticides, wood preservatives, welding fluxes, antiseptics, concrete hardeners, tooth decay preventives, synthetic optical crystals, plastics, and many other purposes.

Another reason for the marked expansion in hydrofluoric acid production is the important role that this acid plays in the production of aluminum. The aluminum industry uses hydrofluoric acid to manufacture aluminum fluoride and synthetic cryolite; about 40 to 60 pounds of both aluminum fluoride and synthetic cryolite, having a combined equivalent of 100 to 150 pounds of fluorspar, are used for each ton of aluminum. An increase in aluminum output from 495,000 tons in 1945 to 2,970,000 tons in 1966 had a pronounced effect on the demand for hydrofluoric acid.

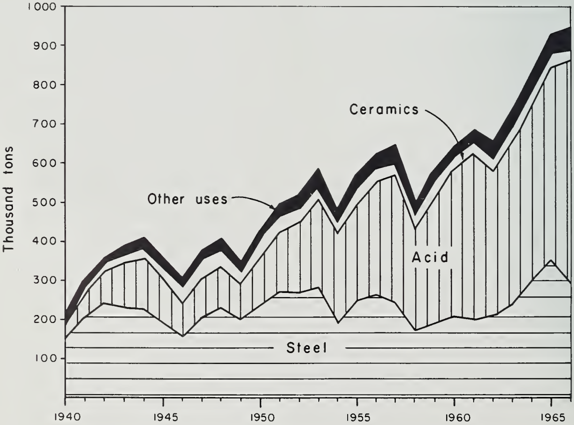

Figure 11 - Fluorspar consumption in the United States by uses, 1940-1966. (Based on U. S. Bureau of Mines data)

The use of fluorspar in ceramics and for other purposes has not varied much in recent years. In ceramics, fluorspar is used principally in the manufacture of opal, opaque, and colored glass, and to make various colored enamels for coating metal and metalware and ceramic tiles. Fluorspar is also used as an artificial abrasive and as an additive in portland cement, rock wool, basic refractory cements, and buff-colored face bricks. Ceramic and miscellaneous uses have averaged 9.8 percent of total annual consumption over the past 5 years.

As mentioned, the specifications for the three grades in which fluorspar is marketed—acid, ceramic, and metallurgical—depend upon effective calcium fluoride content, the presence of certain mineral impurities (silica being the most important), and, to some degree, particle size. Table 3, showing the various uses for each of the grades of fluorspar, reveals considerable overlapping of grades in some uses. For example, in glass and enamel manufacture, all three grades find some use. Conversely, for making steel or hydrofluoric acid, only one grade is used. Traditionally, it was thought that metallurgical grade fluorspar used in the steel furnaces had to be "gravel" or "lump" spar to perform satisfactorily as a flux and that consumers of acid-grade fluorspar required a finely ground, high-purity product. However, recent successes with pelletized and briquetted fluorspar for metallurgical and foundry use have created a market for the fluorspar fines produced during processing.

## FOREIGN TRADE AND COMPETITION

Prior to World War II, imports of fluorspar into the United States were small, averaging only 24,000 tons annually in the 1937-1939 period (U. S. Tariff Commission, 1962, p. 43). After reaching a wartime peak of 104,925 tons in 1945, imports declined sharply. However, by 1952, imports supplied 68 percent of United States consumption for that year. Between 1956 and 1965, imports of fluorspar averaged 576,000 tons annually, or the equivalent of 75 to 98 percent of annual consumption during the same period (fig. 12). The apparent surpluses shown in figure 12 can be accounted for by the sizable tonnages of fluorspar that were being stockpiled then.

It is evident that imports have become an important factor in the domestic market. Part of the growth in the use of imported fluorspar has been at the expense of the domestic industry. Shipments from United States mines have declined from their record peaks of 413,781 tons in 1944 and 347,024 tons in 1951 to an annual average of approximately 200,000 tons for the past 5 years. From table 1 it can be seen that although Illinois has increased its share as a domestic supplier from 45 to 66 percent of the total United States shipments between 1940 and 1965, these shipments represented a smaller percentage of total United States consumption (47.9 percent versus 17.1 percent).

An examination of the import statistics for the past 15 years reveals that foreign competition has come mainly from five countries: Canada, West Germany, Mexico, Spain, and Italy. Although both Canada and West Germany exported sizable tonnages of fluorspar to the United States in the mid-1950's, both countries have since become net importers.

During the 1950's, Italy and Spain battled for second place behind Mexico as a supplier of imported fluorspar for the United States market. However, since 1960, Italy has been consistently in third place behind Mexico and Spain. Labor costs for producing Italian fluorspar increased about 25 percent with the approval

TABLE 3 – FLUORSPAR (DOMESTIC AND FOREIGN) CONSUMED IN THE UNITED STATES BY GRADES AND INDUSTRIES, 1964–1965, IN SHORT TONS[a]

| Grade and industry | 1964 | | 1965 | |
|---|---|---|---|---|
| | Tonnage | Percent | Tonnage | Percent |
| Acid grade: | | | | |
| Hydrofluoric acid | 447,719 | 97.7 | 490,345 | 97.6 |
| Glass | 6,614 | 1.4 | 6,053 | 1.2 |
| Enamel | 325 | 0.1 | 226 | 0.1 |
| Welding rod coatings | 1,298 | 0.3 | 2,946 | 0.6 |
| Special flux<br>Ferroalloys<br>Primary aluminum | 2,253 | 0.5 | 2,719 | 0.5 |
| Total | 458,209 | | 502,289 | |
| Ceramic grade: | | | | |
| Glass | 23,462 | 62.5 | 23,230 | 60.7 |
| Enamel | 4,746 | 12.6 | 4,749 | 12.4 |
| Welding rod coatings[b] | 3,003 | 8.0 | 3,481 | 9.1 |
| Nonferrous | 297 | 0.8 | 299 | 0.8 |
| Special flux<br>Ferroalloys | 6,034 | 16.1 | 6,540 | 17.0 |
| Total | 37,542 | | 38,299 | |
| Metallurgical grade: | | | | |
| Glass | 439 | 0.1 | 608 | 0.2 |
| Enamel | — | — | — | — |
| Nonferrous[c] | 10,952 | 3.3 | 11,684 | 3.0 |
| Special flux<br>Ferroalloys<br>Primary magnesium | 1,469 | 0.4 | 1,687 | 0.5 |
| Iron foundry | 18,066 | 5.4 | 20,664 | 5.3 |
| Open–hearth steel | 160,770 | 47.9 | 162,200 | 41.6 |
| Basic oxygen furnace steel | 95,720 | 28.5 | 139,240 | 35.7 |
| Electric–furnace steel | 48,394 | 14.4 | 53,456 | 13.7 |
| Total | 335,810 | | 389,539 | |
| All grades: | | | | |
| Hydrofluoric acid | 447,719 | 53.8 | 490,345 | 52.7 |
| Glass | 30,515 | 3.7 | 29,891 | 3.2 |
| Enamel | 5,071 | 0.6 | 4,975 | 0.5 |
| Welding rod coatings | 4,301 | 0.5 | 6,427 | 0.7 |
| Nonferrous | 11,249 | 1.4 | 11,983 | 1.3 |
| Special flux | 4,680 | 0.6 | 4,949 | 0.5 |
| Ferroalloys | 2,041 | 0.2 | 2,202 | 0.3 |
| Primary aluminum<br>Primary magnesium | 3,035 | 0.4 | 3,795 | 0.4 |
| Iron foundry | 18,066 | 2.2 | 20,664 | 2.2 |
| Open–hearth steel | 160,770 | 19.3 | 162,200 | 17.4 |
| Basic oxygen furnace steel | 95,720 | 11.5 | 139,240 | 15.0 |
| Electric–furnace steel | 48,394 | 5.8 | 53,456 | 5.8 |
| Total | 831,561 | | 930,127 | |

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[a] Source: U.S. Bureau of Mines (1966, p. 417).

[b] Includes metallurgical grade to avoid disclosing individual company confidential data.

[c] Includes a small amount of acid grade to avoid disclosing individual company operations.

of a new mining labor contract in November 1962. Transportation and port handling charges also increased. The higher costs, combined with increased western European consumption and the depletion of high-grade Italian fluorspar deposits, have resulted in a decreasing role for Italy as a supplier to the United States market (U. S. Bureau of Mines, 1964, p. 531).

Since 1960, Spain has been the second largest supplier of fluorspar imported into the United States. Between 1947 and 1965, imports of Spanish fluorspar grew from 12,000 to 110,000 tons. During the same period, United States imports of Mexican fluorspar have grown even more rapidly from 52,000 to 632,000 tons. Between 1956 and 1965, on the average, Mexico has accounted for 80 percent of the annual United States imports of fluorspar. Figure 13 graphically demonstrates the growth and present dominance of Mexico as a supplier of fluorspar to the United States market. With this in mind, it is advantageous to discuss briefly the economics of the Mexican fluorspar industry.

## The Mexican Fluorspar Industry

In 1962, 38 fluorspar mines were operating in Mexico, 18 of which produced primarily metallurgical-grade fluorspar and the remaining 20 produced pri-

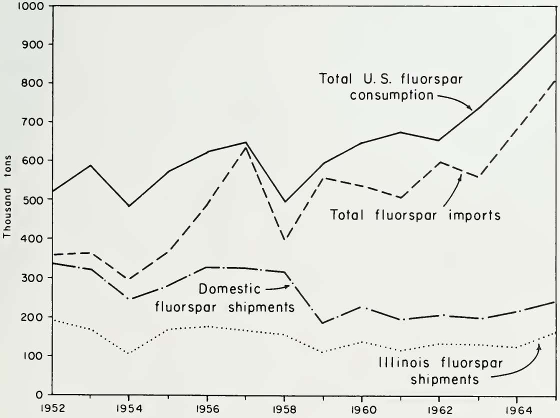

Figure 12 - Trends in the fluorspar industry, 1952-1965. (Based on U. S. Bureau of Mines data)

marily acid grade. Eight flotation plants produced acid-grade filter cake, and three heavy-media plants produced metallurgical-grade fluorspar (Gomez-Ruiz, 1962, p. 17-18). In 1961, 85 percent of the Mexican fluorspar was produced by nine foreign concerns, and the remaining 15 percent was produced by small, independent Mexican miners. Three American chemical companies (Pennsalt Chemicals, Allied Chemical Corp., and Dow Chemical) and one American aluminum producer (Reynolds Metals) maintained captive operations that accounted for 37 percent of the production (Gomez-Ruiz, 1962, p. 20).

Seven of the nine foreign companies supplement their mill feed by purchases of ore produced by smaller, nonintegrated mines. These small mines are nonunionized and use primitive, labor-intensive methods, including hand cobbing (hand sorting). As a result, their mining costs are quite low and they are able to ship ore directly without further beneficiation.

The larger mines, including all of the foreign-owned mines, are unionized. Even so, the prevailing union wage in Mexico in 1967 was quite low by United

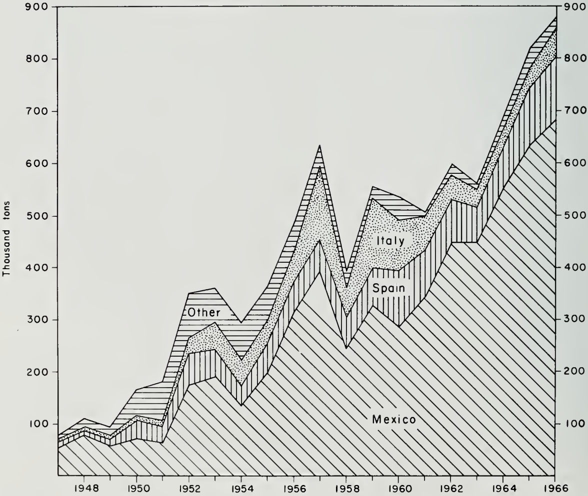

Figure 13 - Sources of fluorspar imported into the United States, 1947-1966, by countries. (Based on U. S. Bureau of Mines data)

States standards, averaging between 30 and 60 cents per hour, depending upon job classification (H. P. Ehrlinger, 1967, personal communication). However, the lower productivity of the relatively unskilled Mexican labor and the small amount of mechanization due to the low labor costs tend to minimize the apparent cost advantage. More men are required to operate a plant in Mexico than a comparable one in the United States, and, therefore, the labor cost per ton produced is probably about the same for plants in both countries.

The nature of the deposits is the biggest advantage that the Mexican producers have in their favor. These deposits are quite rich and pure, and, because they are surface deposits, they may be mined by relatively low-cost open pit methods. It has been reported that Mexico possesses large reserves of direct-shipping ore (requiring little or no processing or treatment) of metallurgical grade ("gravel" type). In addition, the Mexican deposits are located in areas of low rainfall, and, therefore, these mines do not have the water problems that plague some of the southern Illinois mines.

As a result of these conditions, the Mexican producers often have a distinct cost advantage over domestic producers, except for local markets near domestic mines. This is especially profitable for customers whose plants are located on the Gulf and Atlantic coasts and are equipped to handle water-borne shipments. These low prices have been achieved despite Mexican production and export taxes and United States tariffs.

## GOVERNMENT PROGRAMS AND LEGISLATION

The United States Government, through its many programs and regulations, profoundly affects the domestic fluorspar mining industry. Of most direct influence are the tariffs and duties and the stockpiling programs.

The Tariff Act of 1922 provided for one rate of duty, $5.60 per ton, applicable to all grades of fluorspar. Subsequent changes in the rates and classification were made in 1928, 1930, 1939, 1943, 1948, and 1951 (U. S. Tariff Commission, 1962, p. 13). The existing rates, as of 1967, were $8.40 per long ton for metallurgical-grade fluorspar (containing 97 percent or less by weight of calcium fluoride) and $2.10 per long ton for acid-grade fluorspar (containing more than 97 percent by weight of calcium fluoride).

As foreign imports of fluorspar increased during the mid-1950's, domestic producers sought relief from the Federal Government. "Escape-clause" investigations by the Tariff Commission were requested by domestic producers in 1953, 1955, and 1958. Legislation was introduced in 1958 and 1959 to place quotas on fluorspar imports. Another bill considered in 1958 would have provided subsidies for domestic producers of five minerals, including acid-grade fluorspar. However, none of these measures was ever acted upon. The general attitude of the United States Government has been that fluorspar imports are not a threat to national security and that additional import restrictions on either or both classes of fluorspar would not contribute to the soundness and stability of the domestic fluorspar mining operations.

The crux of this matter revolves around the problem of defining the true strategic position or value of fluorspar. Both acid-grade and metallurgical-grade fluorspar are defined as strategic minerals. The curtailment of domestic production as the result of foreign competition has changed the supply picture of the United States and has provoked arguments as to what course of action should be taken. On the

TABLE 4 - FLUORSPAR IN GOVERNMENT INVENTORIES AS OF DECEMBER 31, 1965, IN TONS[a]

| Grade | Objective | National stockpile[b] | DPA inventory[c] | CCC and supplemental stockpiles[d] | Total | Surplus or (deficiency) |
|---|---|---|---|---|---|---|
| Acid | 540,000 | 463,049[e] | 19,700[f] | 323,232[g] | 805,981 | 265,981 |
| Metal-lurgical | 850,000 | 369,443[h] | —— | 42,800 | 412,243 | (437,757) |

[a] Source: U.S. Bureau of Mines (1966, p. 414).

[b] National (Strategic) Stockpile Program—supervised by the Office of Emergency Planning.

[c] Defense Production Act (DPA)—supervised by the Office of Emergency Planning.

[d] Commodity Credit Corporation (CCC)—the so-called "barter program"; surplus agricultural goods are traded for strategic mineral materials available in countries needing the commodities (for example, U.S. cotton for Indian manganese).

[e] Includes 10,193 tons of non-stockpile grade.

[f] Includes 2383 tons of non-stockpile grade.

[g] Includes 4548 tons of non-stockpile grade.

[h] Does not include 350,000 tons of acid-grade fluorspar credited to metallurgical-grade fluorspar as 438,000 tons.

one hand, it has been argued that domestic production (producing capacity) should be maintained at all costs to keep mines in operation for emergency; on the other hand, others claim that the availability of nearby supplies in contiguous Mexico and Canada is practically equivalent to the domestic supply. The final solution to this dilemma has not yet been found.

Stockpiling of strategic raw materials began in 1939 with the enactment of Public Law 117. At that time, the major objective was "protection against the geographic hazards of dependence on foreign sources of supply resulting from the vulnerability of lines of communication to enemy attack" (A.I.M.E., 1959, p. 538). The stockpiling program has since been revised and added to several times. As of December 31, 1965, 805,981 tons of acid-grade fluorspar and 412,243 tons of metallurgical-grade fluorspar were in various government stockpiles. Table 4 gives a breakdown on these various stockpiles. The actual buying and selling of materials in the stockpiles is carried out by the General Services Administration (GSA).

In recent years, the Federal Government has been reviewing its stockpiling program in the light of modern warfare needs and strategies. As a result, it has been decided that the stockpile objectives for many commodities can and should be reduced. In 1966, the GSA was authorized to dispose of approximately 32,000 tons of acid-lump fluorspar for metallurgical purposes.

## TRENDS IN THE DOMESTIC FLUORSPAR INDUSTRY

Several trends indicate a possible improvement in market conditions for domestic fluorspar producers. Rapidly growing consumer demand in Europe will tend to absorb production from Italy, France, and West Germany, and thus divert them from competing in the United States market.

TABLE 5 - COMPARISON OF COSTS PER UNIT OF $CaF_2$, BY GRADES

| Grade of fluorspar (% $CaF_2$) | Price[a] ($/short ton) | Cost (¢/lb of $CaF_2$) |
|---|---|---|
| Metallurgical (60%) | 32 to 34 | 2.67 to 2.83 |
| Metallurgical (72½%) | 37 to 39[b] | 2.55 to 2.69 |
| Acid (97%) | 47 | 2.42 |
| Ceramic (93 to 94%) | 44 | 2.37 to 2.34 |

[a] Source: Engineering and Mining Journal, 1966, p. 24.
Prices given for short tons, f.o.b.
[b] Dry basis, bulk rate; wet filter cake, dry content—less $2.50/ton.

From recent reports, it appears that severe competition and low prices are having their effects on Mexican producers. In 1963, the Government of Mexico announced plans for "a quota system to allocate production and exports of fluorspar among existing producers in proportion to their records as producers and exporters" during the previous 5-year period. These export controls were instituted to prevent some of the older fluorspar producers from being forced out of business by price cutting by new producers and to assure that price levels would be maintained (U.S. Bureau of Mines, 1964, p. 528).

Another trend favoring fluorspar producers in Illinois is the development and commercial production of fluorspar pellets and briquets. This has enabled domestic operators to market a product made from flotation concentrate that is acceptable for metallurgical use. However, the competitive position of these producers might be improved even more if the richer, acid-grade pellets were to be used in the manufacture of steel instead of the usual metallurgical grade. Although the acid-grade pellets would be more expensive on a per ton basis, they would contain more effective units of $CaF_2$ per dollar of cost and less inert material to end up in the slag (table 5 compares these costs). In addition, even though the higher grade acid pellets might carry a somewhat higher freight charge, the tonnages required for a comparable job might be sufficiently reduced to effect a delivered cost saving to the consumer.

# PART III

# USES OF FLUORSPAR AND FLUORINE CHEMICALS

## DIRECT USES OF FLUORSPAR

### Hydrofluoric Acid Manufacture

In 1966, the chemical industry, the largest consumer of fluorspar, used 572,727 tons of acid spar or about 54 percent of the total fluorspar consumed (Ambrose, 1967, p. 4). For the same year, U. S. Bureau of the Census data show that the production of hydrofluoric acid was 246,786 tons, a 300 percent increase in a decade. In 1967, the hydrofluoric acid production capacity of 14 plants was estimated at 286,000 tons. Several other chemical firms are rumored to be in the process of watchful waiting for possible expansion into hydrofluoric acid manufacture. The future of hydrofluoric acid as a key chemical in a rapidly growing fluorine chemical industry is most promising. A recent report predicts that the demand for HF in 1971 will be 315,000 tons (Oil, Paint, and Drug Reporter, 1967).

Two types of hydrofluoric acids are commercially available, "aqueous" and "anhydrous." The "aqueous" acid is a water solution of hydrogen fluoride, whereas the "anhydrous" type has a very low moisture content, usually less than 5 percent. The anhydrous product is known in trade language as HF or anhydrous HF (also AHF), or by the misnomer of anhydrous hydrofluoric acid. From a chemical standpoint, these two products exhibit marked differences in properties and may be considered as two different chemicals. Both are made by the same basic reaction— that of acid spar with sulfuric acid in heated kilns or retorts:

$$CaF_2 + H_2SO_4 \longrightarrow 2\ HF + CaSO_4.$$

For many years, aqueous hydrofluoric acid has been prepared by absorbing the hydrogen fluoride gas from a retort in water in suitable lead cooling and absorbing towers. By recycling or redistilling the absorption liquors, various strengths of acid, up to 60 percent, were prepared. Acids below 60 percent are shipped in lead, rubber, and polyethylene containers; for acids of 60 percent and higher, steel containers are used. In modern practice, aqueous acid is prepared by dilution of the anhydrous product to the desired strength, usually at the time a purchase order is received. This has simplified the storage problem, because the anhydrous product can be stored in steel.

Anhydrous acid is made by the same general chemical reaction, but under more rigidly controlled conditions. The generator is ordinarily a horizontal revolving steel kiln that is heated externally, usually by direct fire (fig. 14). Finely ground acid spar is mixed with a slight excess of strong sulfuric acid in a hopper or a special mixer and is fed continuously into one end of the generator. A large vent pipe serves as a collector for the HF and other gaseous products. At the opposite end of the generator, waste calcium sulfate is usually expelled by a screw drive into water. By special treatment, the calcium sulfate may also be recovered as a high-grade gypsum.

The composition of the hot gaseous mixture from the generator is about 95 percent HF, 4 percent air, and 1 percent impurities such as $H_2SO_4$, $SiF_4$, $H_2O$, $CO_2$, and $SO_2$. Aluminum fluoride, synthetic cryolite, and some other fluorides can be prepared directly from this gas. A partially purified anhydrous hydrofluoric acid can be obtained by passing the generator gas through special condensers. For a higher quality anhydrous acid, the gas is put through a purification process. The gaseous mixture is cooled and absorbed countercurrently in a tower with a weak cycle sulfuric acid to a 70 percent HF concentration. Upon distillation of the concentrated acid, the water remains with the sulfuric acid residue, and the HF is collected as a distillate. Redistillation in a suitable column separates the low-boiling $SiF_4$, $CO_2$, and $SO_2$ from the higher boiling HF (boiling point 19°C). To avoid contamination of the atmosphere, the exit gases may be passed into water absorption towers where the $SiF_4$ is converted into fluosilicic acid ($H_2SiF_6$). This same acid is recovered on a tonnage basis as a low-cost by-product in the phosphate fertilizer industry.

The anhydrous HF is stored in steel containers and is available in a purity as high as 99.95 percent HF. The current price is 19 to 20 cents per pound in carload lots. It must always be remembered that hydrofluoric acid is a highly corrosive and hazardous chemical; however, in view of the tremendous tonnages that are being produced, it is obvious that the handling of it has been perfected to a routine operation. An Olin Mathieson plant, having an annual capacity of 12,000 tons of HF, is located at Joliet, Illinois (fig. 14).

In the manufacture of 1 ton of HF, about 5 tons of fluorspar and acid are required and about 4 tons of calcium sulfate is formed as waste product. About 2.4 tons of acid spar is required to produce a ton of HF, according to the U.S. Bureau of Mines; however, it is suspected that some plants may use approximately 2.2 tons, and recent technological advances may lower the figure still further. Theoretically, 1.95 tons of pure calcium fluoride will yield one ton of HF. The sulfuric acid is usually a commercial 96 to 98 percent grade, and a 5 to 10 percent excess is used.

Figure 14 - View of Olin Mathieson Chemical Corporation' s hydrofluoric acid plant at Joliet, Illinois. Note the six rotary kilns in lower foreground. (Photograph courtesy of Olin Mathieson Chemical Corp.)

Because the quality of the acid fluorspar is very important, the specifications for it are rigid. A typical specification is not less than 97 percent $CaF_2$, not more than 1 percent $SiO_2$, 0.05 percent S, 1 percent moisture, and a minimum of calcium carbonate. The relation of $CaF_2$ content to HF yield is obvious. Reasons for the other items are that each part of $SiO_2$ causes a loss of 1 1/3 parts of HF as $SiF_4$, sulfur causes process difficulties, moisture affects efficiency, calcium carbonate wastes sulfuric acid, and $CO_2$ liberated causes foaming. It is essential also that the spar be finely ground, because the particle size influences the rate of reaction with sulfuric acid.

## Metallurgy

### Steel

Agricola, in 1556, mentioned the use of fluorspar as a flux in metallurgy (Hoover and Hoover, 1950). As a result of this early use, the name fluorspar was coined from the Latin, literally meaning the rock that flows.

In 1966, the steel industry was the second largest user of fluorspar, consuming about 38 percent, mostly in the form of metallurgical spar (Ambrose, 1967, p. 4). Some steel plants are beginning to use a low-grade acid spar in preference to the gravel spar formerly used, because of its higher effective calcium fluoride content. The spar functions as a fluxing agent and may assist also in the refining process; it is used in the basic open-hearth, electric, and Bessemer steel furnaces. The Bessemer furnace is a minor consumer of fluorspar. Within the last decade, the productivity of the various furnaces has been increased 30 percent or more by direct injection of oxygen into the molten metal. A new basic oxygen process, developed in Austria, gives even greater productivity. It is important to note that the transition of the steel industry to oxygen furnaces is occurring at a very rapid rate. It is estimated that by the early 1970's, over 50 percent of the steel production will be from these basic oxygen furnaces. These new furnaces with a "milk bottle" shape combine the high output per unit of time of the Bessemer converter with the high quality of the open-hearth furnace. The heat cycle for the basic oxygen furnace is about 45 minutes as compared to 8 to 10 hours for the conventional open-hearth furnace.

Prior to the introduction of the basic oxygen furnace, the open-hearth steel process consumed about 80 percent of the metallurgical fluorspar. Operation of the open-hearth furnace first involves spreading spar in granular or pellet form on the furnace floor. After the smelting operation is under way, additional spar is shoveled into the furnace so that it is uniformly spread over the slag. For better slag control and more efficient operation, especially in the case of furnaces with oxygen injection, it is becoming increasingly popular to charge the furnaces with plastic bags containing weighed amounts of fluorspar pellets or briquets. Depending upon economic conditions and type of furnace, as much as 40 pounds of fluorspar per ton of steel may be used, but the average for all furnace types in 1965 was only 5.4 pounds per ton (U. S. Bureau of Mines, 1966, p. 417). For a number of years, the average amount of fluorspar used per ton of steel produced was decreasing, but recently, a reversal in the trend has been observed as the new oxygen furnaces are put into operation. In other words, the basic oxygen furnaces are being operated with a higher ratio of fluorspar to steel, a situation favorable to increased spar consumption. The spar gives fluidity to the slag, thus resulting in a better steel recovery and lower fuel cost. It also causes the solid lime lumps to dissolve more rapidly in the slag so that a maximum amount of lime is available for the most effective removal of sulfur and phosphorus from the metal.

The furnace gases, as in most metallurgical and foundry processes using fluorspar, may contain considerable quantities of $SiF_4$ formed by the reaction of the spar with silica ($SiO_2$). Severe cases of air pollution by such fluoride fumes are known, causing damage to crops and animals, thus necessitating an expensive fume catching system. A process for the recovery of the fluorine for reuse would have considerable merit.

The manufacture of steel in the electric furnace requires between 14 and 40 pounds of spar per ton of steel. Only about 10 percent of the metallurgical spar is consumed in this process. As the demand for special steels is increasing, it is expected that the demand for spar also will increase. A higher grade metallurgical spar or even the acid grade is preferred for this process.

Typical metallurgical-grade specifications demand a minimum of 60 percent effective $CaF_2$, not more than 0.30 percent sulfur, nor more than 0.25 to 0.50 percent lead. Silica is objectionable because one part requires 2.5 parts of $CaF_2$ to flux it; therefore, the silica percentage is multiplied by 2.5 and deducted from the actual $CaF_2$ content to get the effective $CaF_2$. More than 5 percent silica is usually not accepted. Barite ($BaSO_4$) is objectionable because it decreases fluidity of the slag.

In general, steel producers have been purchasing the spar in a gravel size—that is, a size that passes through a 1- to $1\frac{1}{2}$-inch mesh screen and that contains not more than 15 percent fines. Recently, there has been a trend toward the purchase of spar in the form of pellets and briquets made from flotation concentrates. In many instances, spar producers are now in a position to custom-prepare pellets of special sizes and composition not only for metallurgical purposes but for many other uses.

### Foundries

In 1965, about 20,000 tons of metallurgical-grade spar was used as a flux by iron foundries, primarily in the production of fine-grained castings, such as automobile engines. The spar causes the charge to melt more rapidly, aids in removal of sulfur and phosphorus, gives a more liquid slag, minimizes lime accumulation at air inlets, and gives a cleaner drop at the end of the pouring period. Cleaner, more malleable, and higher tensile strength castings are reported.

An average of 15 to 20 pounds of spar per ton of metal is added to the cupola as lumps (nut size and up); about 3 percent of ground spar per ton of metal may be added to the ladle. The basic open-hearth steel specifications on spar apply to foundry practice.

Domestic mills provide 1- by $1\frac{1}{2}$-inch foundry lump in 60 percent effective grade. Most of the larger size lump is hand sorted.

### Ferroalloys

A ferroalloy is a special alloy of iron with a high proportion of another element such as chromium, manganese, molybdenum, silicon, titanium, tungsten, vanadium, or other metal. These alloys are commercially designated as ferrochromium, ferromanganese, and so on. For the most part, they are added in limited amounts to iron and steel melts to function as scavengers and deoxidizers and for imparting special properties (such as toughness, hardness, and corrosion resistance) to a finished steel. Most of them are produced in an electric furnace, and fluorspar is added as a fluxing agent.

The amount and grade of fluorspar added varies widely from plant to plant and depends upon the type of steel produced and upon economic considerations. The consumption will vary from 1 to more than 200 pounds per ton of ferroalloy. A fine size is desired for uniform distribution in the furnace. All grades of spar are used, although the higher grades are preferred.

### Special Fluxes

Special fluxes include a variety of fluxes used in the refractory, aircraft, and welding industries, and in some chemical processes. All grades of fluorspar are used, and a ground material is desired. In 1963, about 5000 tons was utilized for these purposes.

### Welding Rod Coatings

Fluorspar, along with many other fluorides, is used extensively in welding fluxes and welding rod coatings. The function of a flux in welding is to act as a surface cleansing agent and to protect the surface from oxidation or burning. The flux is usually prepared by melting the components to form a homogeneous mixture, after which it is cooled and then ground. For coating welding rods, a binder is added. When fluorspar is used, it comprises from 2 to 50 percent of the mixture.

Most of the fluorspar used in coatings is ceramic grade, 35 percent is acid spar, and the remainder is metallurgical grade. A finely ground material is specified. An estimated 5000 tons of spar was used in 1963 for this purpose.

### Primary Aluminum

Fluorspar is added to the cryolite bath of the aluminum reduction cell as a flux to lower the melting point. In normal operation, the molten electrolyte contains 6 to 10 percent $CaF_2$ and the temperature is held at 950 to 980° C. After a cell is operating, only very little fluorspar is added to balance the slight mechanical losses. About 600 tons of spar was used in this manner in 1957.

A ground acid-grade spar is preferred because it contains fewer of the impurities that affect the quality of the aluminum metal and the efficiency of the cell. Iron and silicon contaminate the metal; they also form volatile fluorides. Lead and zinc remain in the aluminum, and sulfur reduces cell efficiency and forms sulfur gases.

### Smelting: Magnesium, Zinc, and Other Metals

A small amount of ground metallurgical spar is used as a flux in magnesium reduction. It is likely that some spar also is used in resmelting and casting of the metal.

Zinc smelting by the horizontal retort process benefits by the addition of fluorspar. The furnaces are charged with a mixture of about 16 pounds of powdered ceramic spar per ton of sintered zinc ore. The spar serves as a flux and increases the yield of the metal. For this purpose, a spar containing 88 to 90 percent $CaF_2$ and not more than 1 to $1\frac{1}{2}$ percent moisture is satisfactory.

Minor amounts of fluorspar are reportedly used as a flux in the smelting and refining of antimony, copper, chromium, gold, lead, silver, tin, nickel, and other metals.

Excluding magnesium, consumption of fluorspar by the preceding nonferrous metals was about 10,000 tons in 1963. Metallurgical spar is usually specified, although some of the acid and ceramic grades also are used.

## Ceramics

### Glass

The glass industry is a stable consumer of fluorspar, demanding about 30,000 tons per year. The spar is used as a flux and opacifier. Clear glass requires the least spar in its formulation, whereas opal and colored glass demand a larger quantity to obtain opacity. Depending upon the glass desired, 50 to 500 pounds of ground spar are used for each 1000 pounds of sand in the glass batch. Examples of opal glass are lamp bulbs, globes, shades, cosmetic and medicinal containers, and many other items. Fluorspar is also used in the manufacture of fiber glass. Frequently, other fluorides are added along with spar in glass formulations.

About 85 percent of the spar used by the glass industry is ceramic grade; the remainder is almost entirely acid spar. Ground fluorspar is required and is classified as coarse, fine, or extra fine.

A typical specification for No. 1 ceramic-grade fluorspar is not less than 95 percent $CaF_2$, not more than 3 percent $SiO_2$, 1 percent $CaCO_3$, and 0.12 percent $Fe_2O_3$. Only traces of lead, zinc, barium, and sulfur are permitted. Iron gives a green or yellow tint to the glass. The calcite is converted to lime in the glass furnace, and an excess will cause brittleness of the glass and difficulty in formula control. Most fluorspar producers can meet the demands of the customer even if specifications differ from the above.

### Enamel

Enamels and glazes are low-melting glasses used for coating cast iron, steel, and other metals. Fluorspar and other fluorides serve as fluxes in lowering the melting point of the glass melt and give opacity to the finished coatings. About 5000 tons of fluorspar per year are used in this manner. Examples of enameled products are prefabricated metal buildings and store fronts, bathtubs, lavatories, sinks, refrigerators, stoves, signs, and artware.

The fluorspar or fluoride content of enamels ranges from 0 to 15 percent. A small amount will lower the melting point, but opacity requires more, usually 6 percent. The ceramic grades are usually specified, although small amounts of the other grades are purchased.

Specifications on the spar for enamel or glazing purposes are much the same as for glass, and for the same reasons. However, there is a tendency to specify a higher quality ceramic spar and a finer screen size.

## Water Fluoridation

One part per million of fluorine in drinking water is considered desirable for the prevention of dental caries. Various fluorine chemicals are being used for the fluoridation of municipal water supplies, but not until recently was it possible to use fluorspar, the lowest priced fluoride available. The very low solubility of fluorspar in water was the deterrent. In the late 1950' s, Maier and Bellack (1957) of the Division of Dental Public Health, United States Public Health Service, Washington, D. C., developed a controlled fluoridation process, based on the reaction of alum (aluminum sulfate) with fluorspar to form soluble fluoride. Since 1956, the demonstration plant at Bel Air, Maryland, has been proving the practicability of the process. In 1958, a similar plant was installed at Rosiclare, Illinois, with equal success.

A finely ground spar with a high $CaF_2$ content is required. It is estimated that 18 pounds of ceramic-grade spar (95 percent $CaF_2$) will fluoridate one million gallons of water.

The approximate cost per pound of fluorine from various commercial fluorides, based on September 1966 prices, is as follows: $CaF_2$, \$0.048; $Na_2SiF_6$, \$0.123; $(NH_4)_2SiF_6$, \$0.218; $H_2SiF_6$ (25 percent solution), \$0.303; and NaF, \$0.331.

## Miscellaneous

### Portland Cement

It is common practice in Germany for manufacturers of portland cement to add 1 to 5 percent of low-grade fluorspar to the raw cement mix. The fluorspar lowers the sintering temperature and acts as a mineralizer. In the United States, the quantity of spar reported used in the cement industry is very small. However, domestic cement manufacturers may benefit from a new process for the use of fluorspar as a mineralizer in promoting formation of tricalcium silicate at lower clinkering temperatures. The success of this results in lower fuel costs, increased kiln capacity, longer life for the kiln liner, and more ready availability of white portland cement.

Some western cement firms are adding fluorspar to their raw material as an aid in the volatilization of potassium and sodium salts during the clinkering process. Low-grade crude ore is used for this purpose.

### Calcium Cyanamide

Calcium cyanamide ($CaCN_2$) is produced by reacting nitrogen with calcium carbide. In the Frank-Caro electrothermal process, about 2 to 3 percent of finely ground fluorspar is added to the calcium carbide to lower the fusion point and increase the velocity of the reaction. The fluorspar must have less than 0.1 percent moisture and must contain a minimum of 90 percent $CaF_2$. Calcium cyanamide is used as a fertilizer, cotton defoliant, and in the manufacture of melamine resins, sulfa drugs, explosive propellants, and other synthetic organic nitrogen chemicals.

### Mineral Wool

The presence of 1 to 2 percent of acid- or ceramic-grade spar in certain rock-wool melts will give greater fluidity at a given temperature and a smaller fiber diameter to the final product.

### Brick Stain Inhibitor

The principal contributor to yellow, green, or brown efflorescent stain on light-colored face brick is vanadium. A small percentage of fluorspar added to the clay mix will inhibit this efflorescence to varying degrees, depending on the clay.

### Binding Material

A small amount of fluorspar is used as a binder in abrasives and high-temperature brick.

### Optical Lenses

Because clear fluorspar has a low index of refraction, high ultraviolet transmission, and low dispersion, it is used in optical lenses for some scientific instruments. As clear, colorless natural crystals are very rare, large artificial crystals are now produced by controlled cooling of a melt of semioptical-grade spar (see p. 59 for other optical grade fluorides).

To reduce reflection on optical lenses and prisms, a very thin film of LiF, $MgF_2$, $CaF_2$, or other fluorides can be used.

### Dental Cements

Some dental cements contain 10 to 15 percent fluorine in the form of $CaF_2$ and NaF.

### Jewelry

Colored spar finds some use as a gemstone in jewelry and stone ornaments. Wealthy Romans 2000 years ago treasured their goblets of fluorspar from Parthia (Persia). The Mound Builder aborigines in America carved crude figures from fluorspar. Many beautiful goblets, urns, and vases of native spar were cut and polished in the 1700' s and 1800' s in England. A small amount of attractive fluorspar jewelry is still produced near Castleton in the Derbyshire district of central England.

## FLUORINE CHEMICALS AND THEIR USES

### Hydrofluoric Acid

Hydrofluoric acid (HF), the fluorine chemical produced in largest quantities, is an important chemical for two reasons: (1) it is used in nonfluorinating processes as a catalyst, reaction medium, metal pickling agent, and in many other ways, and (2) it is a key chemical in almost all fluorine chemical manufacturing processes.

Aqueous hydrofluoric acid is used in the manufacture of many inorganic fluorides and acid fluorides—in frosting, etching, and polishing of glass; as an antiseptic in breweries and distilleries; in electroplating; in cleaning of copper and brass; in pickling and galvanizing metals; in removal of efflorescence from stone and brick; in extraction of tantalum and columbium; in the making of filter paper and carbon electrodes; in removal of silica from graphite; and in acidizing oil wells to increase oil production.

Anhydrous HF is a versatile and useful chemical. It can advantageously replace aqueous acid in many instances, and it has many special applications where it is used in large tonnages. It is especially useful in organic chemistry for fluorination, hydrofluorination, polymerization, esterification, catalysis, alkylation, nitration, sulfonation, and many other processes, and is used as a reaction medium.

TABLE 6 - CONSUMPTION OF HF IN 1957 AND 1966

| Use | 1957[a] |  | 1966[b] |  |
|---|---|---|---|---|
|  | HF (short tons) | % of total | HF (short tons) | % of total |
| Aluminum | 53,000 | 39 | 98,400 | 40 |
| Fluorocarbons | 38,500 | 29 | 108,200 | 44 |
| Uranium production (AEC) | 16,000 | 12 | 7,400 | 3 |
| Petroleum alkylation | 6,000 | 4 | 12,300 | 5 |
| Stainless steel pickling | 7,000 | 5 | 12,300 | 5 |
| Salts, glass etching and frosting, special metals, and others | 14,500 | 11 | 7,400 | 3 |
| Total | 135,000 | 100 | 246,000 | 100 |

[a] Source: Stuewe (1958).
[b] Source: Oil, Paint, and Drug Reporter (1967).

The uses and consumption of HF in 1957 and 1966 are given in table 6. Recent estimates on HF consumption indicate that about 85 percent of the HF now consumed is being used in the manufacture of two commodities, aluminum and fluorocarbons. Therefore, it can be said that most of the growth in HF consumption since 1957 has been due to the rapid expansion of the aluminum and fluorocarbon industries. The major HF consuming industries usually produce their own HF with the result that only about 25 percent of the consuming market is open to merchant producers. For the past several years, HF demand has declined in the uranium industry, but a reversal in this trend is expected with the increased number of atomic power plants being planned. Some expansion in HF use is expected in petroleum alkylation and in stainless steel pickling. Consumption of HF in the manufacture of fluoride salts (other than aluminum fluoride and synthetic cryolite), for glass polishing and etching, and for other miscellaneous uses is rather static, or somewhat on the downward trend.

## Aluminum Fluoride and Synthetic Cryolite

Practically all of the aluminum fluoride ($AlF_3$) and most of the synthetic cryolite ($Na_3AlF_6$) are used as fluxes and electrolytes in the production of primary aluminum. Some of the more recently installed electrolytic aluminum reduction cells are 12 to 15 percent more efficient due to the addition of 2 to 8 percent of lithium fluoride by weight to the molten electrolyte. The U. S. Bureau of Mines (1965, p. 31) reported that 40 to 60 pounds of aluminum fluoride and 40 to 60 pounds of cryolite are used per ton of primary aluminum. These data, when related to the production of 2.97 million tons of primary aluminum in 1966, are impressive evidence of the importance of fluorspar, as the source of these fluorine compounds, to the aluminum industry. In the electrolytic refining of primary aluminum to super-pure

TABLE 7 - CONSUMPTION OF FLUOROCARBONS[a]

| Use | 1965 |  | 1970[b] |  |
|---|---|---|---|---|
|  | Million lbs | % of total | Million lbs | % of total |
| Aerosols | 215 | 46.2 | 150 | 27.1 |
| Refrigerants | 135 | 29.0 | 175 | 31.5 |
| Plastics | 50 | 10.8 | 90 | 16.2 |
| Solvents | 25 | 5.4 | 75 | 13.5 |
| Blowing agents | 20 | 4.3 | 45 | 8.1 |
| Exports | 10 | 2.1 | 5 | 0.9 |
| Miscellaneous | 10 | 2.2 | 15 | 2.7 |
| Total | 465 | 100.0 | 555 | 100.0 |

[a] Source: Oil, Paint, and Drug Reporter, 1966.
[b] Predicted consumption.

aluminum, some barium fluoride may be added to the cryolite-aluminum fluoride mixture.

Aluminum fluoride usually is prepared by the reaction of HF with alumina:

$$6\ HF + Al_2O_3 \longrightarrow 2\ AlF_3 + 3\ H_2O.$$

If synthetic cryolite is desired, an alkaline solution of alumina is reacted with HF:

$$6\ HF + Al(OH)_3 + 3\ NaOH \longrightarrow Na_3AlF_6 + 6\ H_2O.$$

An alternate source of these fluorides, especially synthetic cryolite, is the silicofluoride route. This will become increasingly important as the phosphate fertilizer industry produces larger tonnages of low-cost silicofluoride by-product.

A small amount of aluminum fluoride and appreciable quantities of synthetic cryolite are used as metallurgical and welding fluxes and as opacifiers in ceramics. Cryolite also is used as an insecticide.

## Fluorocarbon Manufacture

The terms fluorocarbons and fluorochemicals have been coined to define carbon compounds containing fluorine. A number of authors have conveniently abbreviated the term fluorocarbon to FC. These materials are used as refrigerants, aerosols, plastics, solvents, blowing agents, degreasing agents, dielectrics, lubricants, coolants, wetting agents, fire extinguishers, and for many other purposes.

Production of these useful products is a major industry, and its future growth is most promising, as indicated in table 7. The table also indicates the thinking of some market analysts regarding changes in consumption for various uses, which might occur by 1970. Total consumption estimates for 1970 range from 555 to 600 million pounds. In addition to the expected growth in refrigerant uses, it is especially interesting to note that a phenomenal growth is forecast in the solvent, blowing agent, and plastic categories. The over-all dollar value of fluorocarbon sales is difficult to estimate. In 1965, fluorocarbon sales to the air conditioning and refrigeration industry totaled about 60 million dollars, and as shown in table 7, 135 million pounds of fluorocarbons were sold as refrigerants for the same year. Anticipating future growth, fluorocarbon production capacity is currently rated at 725 million pounds, involving 13 plants; this is well ahead of the market demand at the present time.

## Principal Fluorocarbon Syntheses

Almost all of the fluorocarbons with one or two carbon atoms are produced by the same general reaction or by some variation of it, to achieve the same end result. The basic reaction was discovered in 1892 by Swarts, a Belgian chemist, and was developed commercially in 1930 in the United States by Midgley and Henne for the manufacture of the Freon refrigerants. The reaction, expressed in its simplest terms, involves the replacement of chlorine in a suitable organic chloride with fluorine by means of a metallic fluoride or anhydrous HF. This is illustrated by the preparation of dichlorodifluoromethane (FC-12), $CCl_2F_2$. In practice, carbon tetrachloride and anhydrous HF in a definite ratio are fed continuously to a heated reactor containing antimony trifluoride and a catalyst. The volatile reaction products pass into a distillation column where the fluorocarbon is separated. By varying reactor conditions and by using other chlorinated methanes and ethanes, a large group of fluorocarbons can be produced. Approximately 1 ton of HF will produce 3 tons of fluorocarbon. The two fluorocarbon "work horses," or those being produced in the largest amounts and accounting for 80 percent of the market, are $CCl_3F$ (FC-11) and $CCl_2F_2$ (FC-12). An additional 15 percent of the market is represented by $CHClF_2$ (FC-22), $CCl_2FCClF_2$ (FC-113), and $CClF_2CClF_2$ (FC-114). A fluorocarbon plant (Allied Chemical Corp.) is located at Danville, Illinois (fig. 15).

$$3\ CCl_4 + 2\ SbF_3 \xrightarrow{\text{catalyst}} 3\ CCl_2F_2 + 2\ SbCl_3$$

Small amounts of fluorocarbons and derivatives are prepared also by the Simons electrochemical process. This unique process achieves fluorination without the use of free fluorine by the electrolysis of a suitable organic compound in anhydrous HF. Various fluorocarbons are used as "building blocks" for a host of new compounds by cracking or pyrolysis; for example, $CHCl_2F$ and $CHF_3$ yield tetrafluoroethylene for teflon plastic manufacture, octafluorocyclobutane (FC-C318), and other fluorocarbons.

As the chemical names of the fluorocarbons are rather cumbersome for everyday usage, industry has developed general trade names and code symbols. The first commercial fluorocarbons were produced by the duPont Company and were trade named Freon. The "F" in these duPont names is equivalent to FC used above (i.e. duPont's F-11 = FC-11 = $CCl_3F$). Examples are F-11, $CCl_3F$; F-12, $CCl_2F_2$; F-13, $CClF_3$; F-13B1, $CBrF_3$; F-14, $CF_4$; F-21, $CHCl_2F$; F-22, $CHClF_2$; F-23, $CHF_3$; F-C318, cyclo-$C_4F_8$; F-112, $CCl_2FCCl_2F$; F-113, $CCl_2FCClF_2$; F-114, $CClF_2CClF_2$; F-114B2, $CBrF_2CBrF_2$; F-115, $CClF_2CF_3$; and F-116, $CF_3CF_3$. Other companies retained the same code numbers but prefixed their trade names such as Genetron (General Chemical Co.), Isotron (Pennsalt Manufacturing Co.), Ucon (Union Carbide Chemicals), and Kaiser (Kaiser Chemicals). Presumably, Racon, Inc., and subsequent fluorocarbon producers will also use the standard code with suitable trade names. All fluorocarbon producers offer FC-11 and FC-12, whereas the other fluorocarbons are available generally only from the large capacity operators.

### Syntheses of Fluorinated Aromatic and Heterocyclic Compounds

Although still of minor importance among fluorochemicals, the fluorinated aromatic, alicyclic, and heterocyclic compounds and their derivatives are receiving increased attention in academic and industrial laboratories. Because of their limited application thus far, no production or dollar value data are available. Their relatively high cost limits them to specialized applications where their unusual properties make them uniquely useful. Areas of future possible applications include agricultural chemicals, dyestuffs, solvents, medicinals, lubricant and hydraulic liquids, dielectric and antiradiation fluids, rubber additives, coolants, surfactants, and polymers.

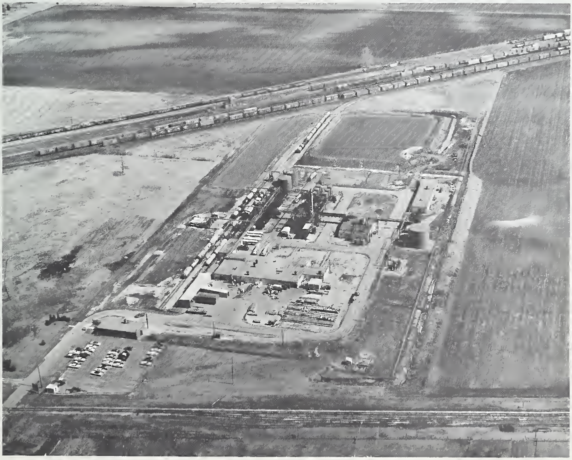

Figure 15 - Aerial view of the Genetron fluorocarbon plant of General Chemical Co.— Division of Allied Chemical Corporation near Danville, Illinois. (Photograph courtesy of Allied Chemical Corp.)

Fluorinated aromatic and heterocyclic compounds are being synthesized by four general methods: (1) pyrolysis of a variety of fluorocarbons of one or two carbon atoms, (2) fluorination and subsequent dehalogenation of a suitable aromatic hydrocarbon, (3) application of the diazotization reaction, such as the Schiemann synthesis starting with aromatic amines, and (4) exchange fluorination starting with halogenated aromatics.

Pyrolysis of $CFBr_3$, $CHCl_2F$, or $CHClF_2$ yields a complex mixture from which $C_6F_6$ can be isolated.

The best known fluorination-dehalogenation process involves complete fluorination of an aromatic hydrocarbon or a chloroaromatic compound with cobalt trifluoride ($CoF_3$) or chlorine trifluoride ($ClF_3$) to a fluoro or chlorofluoro saturated cyclic system followed by a final dehalogenation or dehydrohalogenation for the restoration of the aromatic or heterocyclic ring system. A company in England is offering a series of polyfluoroaromatic compounds prepared by the cobalt trifluoride procedure.

Diazotization of an aromatic amine in anhydrous HF has met with some success in the synthesis of fluorobenzene and a few other fluoroaromatics. A very versatile laboratory and semicommercial process for the preparation of simple but not highly fluorinated aromatics is the thermal decomposition of an aryl diazonium fluoborate salt prepared from an aryl amine. This procedure is known as the Schiemann synthesis and was discovered in 1927 by the German scientist whose name it bears. A Schiemann synthesis of fluorobenzene ($C_6H_5F$) from aniline is depicted in the following reaction sequence:

$$C_6H_5NH_2 \longrightarrow C_6H_5N_2BF_4 \longrightarrow C_6H_5F.$$

The Pierce Chemical Co. of Rockford, Illinois, basing its development of the fluoborate process on laboratory studies made by the Illinois State Geological Survey, utilized the procedure so effectively that it became one of the world's outstanding producers of aromatic fluorine compounds for research.

Exchange fluorination, as applied to aromatic fluorides, is a form of the Swarts reaction with certain modifications. Benzotrifluoride ($C_6H_5CF_3$) and some of its chloro derivatives are prepared commercially from the corresponding benzotrichlorides by exchange fluorination with HF. In 1956, investigations at the Geo-

$$C_6H_5CCl_3 + 3\ HF \longrightarrow C_6H_5CF_3 + 3\ HCl$$

logical Survey showed that various activated chlorine atoms in chloroaromatic compounds could be replaced by fluorine if treated with potassium fluoride (KF). This served as a stimulus for further KF exchange fluorination research, not only in the United States but also in Germany, England, and Russia. Reliable sources indicate that the KF process is linked to new market sources of 4-fluoroaniline, hexafluorobenzene ($C_6F_6$), chloropentafluorobenzene ($C_6ClF_5$), and other compounds.

## Fluorocarbon Uses

### Refrigerants

The fluorocarbon gases are ideal as refrigerants because they are nontoxic, odorless, stable, noncorrosive, and have a low fire hazard. They are available in a wide range of boiling points, thus enabling refrigeration engineers more efficiently to match the machine to the application. For instance, demands differ widely between air conditioners (home, automobile, and commercial), industrial process cooling systems, refrigerators, and freezers. The average home refrigerator and air conditioner is charged with 1 to 2 pounds of refrigerant.

Fluorocarbons 11 and 12 are the giants in the refrigerant industry with FC-12 in first position. In addition, fluorocarbons 22, 114, 115 (p. 46), and azeotropic fluorocarbon mixtures are used in some compressors for certain specialized applications.

Some market analysts expect a growth rate of about 5 percent per year in the refrigeration industry for some years ahead. Fluorocarbon consumption in this category is expected to reach 175 million pounds or more in 1970, as compared to 135 million pounds in 1965. Air conditioning of automobiles is growing at a rapid pace; about 2,108,000 of the 1965 model cars contained factory-installed air conditioning, as compared with 1,428,000 for the 1964 models. Home and large industrial cooling also has a promising future. The world' s largest room air conditioner, with a cooling capacity equivalent to 6600 tons of melting ice daily, maintains the comfort of 45,000 sports fans in the mammoth domed stadium (Astrodome) at Houston, Texas.

## Aerosols

Fluorocarbons were first used as inert aerosol propellants in the "bug bombs" for rapid fumigation purposes in World War II for the Armed Forces. Their properties of high stability, nontoxicity, noncorrosiveness, and good volatility suited them well for this purpose. Out of this development came the rapidly growing aerosol industry, which in 1966, in the United States and Canada, produced 1.83 billion spray dispenser units. Some surveys expect the market to expand to 3.4 billion units by 1974.

Although the fluorocarbons quickly gained the forefront among propellants, they are now experiencing increased competition from lower cost gases. The hydrocarbon gases, such as propane, isobutane, and butane, already hold a strong position in some categories and are expected to show further gains. Other competing gases are nitrous oxide (a favorite in food aerosol units), carbon dioxide, vinyl chloride, and nitrogen. Also, exploratory studies have been reported on dimethyl ether. It has been estimated that more than 300 items have appeared on the market charged with an aerosol, and no shopper has escaped the enchantment of pressing the button on an aerosol unit.

The most important fluorocarbon propellants are FC-12 ($CCl_2F_2$) and FC-11 ($CCl_3F$). Occasionally, a nonfluorocarbon-fluorocarbon mixture finds a special application. To solubilize certain ingredients, some use is made of fluorocarbons FC-22 ($CHClF_2$) and FC-114 ($CClF_2CClF_2$).

The aerosol market of 1.83 billion units in 1966 was divided into 1765 million nonfood and 69 million food units. A wide range of food aerosols has been market tested, but consumer acceptance of many items has been disappointing. It appears that the whipped cream, milk flavoring, cheese spread, and cake decoration products have achieved commercial significance. FC-C318 (octafluorocyclobutane) and FC-115 (chloropentafluoroethane) have been approved as food additives by the Federal Food and Drug Administration and are now trying to get a foothold in the food aerosol market against strong competition. A mixture of FC-C318 and nitrous oxide is also used as a food aerosol.

A market breakdown of nonfood aerosol production for 1966 in terms of million units is as follows: 890 for personal products, 531 for household products, 161 for spray paints and coatings, 91 for insect sprays, 23 for automotive specialties (deicers, engine starters, tire inflators, polishes and waxes, etc.), 20 for industrial aerosols, and 8 for aerosols used on animals. The personal products category is a heavy consumer of fluorocarbons and includes hair sprays (the largest single item), shaving lathers, colognes and perfumes, and pharmaceuticals. Household products, such as room deodorants and disinfectants, cleaners, waxes, polishes, laundry products, starches, and certain other categories, are promising sales targets for hydrocarbon gases. Special aerosol containers have also been designed for dry powder ejection. An interesting use of propellants is in outer space, where astronauts, when "walking" in space, have propelled themselves by a gun charged with a fluorocarbon propellant; likewise, the space capsules and vehicles are equipped with nozzles for maneuvering by bursts of gas from them. In spite of some weak spots in the market, fluorocarbon aerosol sales will continue to face a promising future.

## Plastics

The development of the atomic bomb during World War II stimulated a search for materials with unusual stability that resulted in the development of the fluorocarbon plastics and resin industry. The first products to appear were two polymers, polytetrafluoroethylene $(CF_2 = CF_2)_x$ and polychlorotrifluoroethylene $(CF_2 = CClF)_x$, now commonly known under the trade names of Teflon (duPont) and Kel-F (Minnesota Mining), respectively. Although many fluorinated plastics have appeared on the market since the 1940's, it is believed that about 80 percent of the market is held by the polytetrafluoroethylene (PTFE) product.

In 1965, 20 million pounds of fluorocarbon polymers were produced from 50 million pounds of fluorocarbons, mostly FC-22 $(CHClF_2)$. These plastics can be characterized as nonflammable, insoluble in organic solvents, very stable to chemical agents, and highly stable toward heat. They possess good physical strength and toughness, exhibit low surface friction, and are excellent dielectric materials. They are fabricated and machined into special gaskets, O-rings, packings, diaphragms, pump lines, tubing, pipe, wire and cable coating, filter cloths, and many other items where their high cost is justified by the application.

Teflon has a waxy surface with a low friction factor; it is molded into bearings having the property of natural lubrication and is an excellent antisticking coating for rollers, conveyor belts, pans, and cooking utensils. Modern automobiles, aircraft, and other equipment are heavy users of the so-called self-lubricating bearings; the Boeing jet airplane 727 has approximately 1000 bearings lined with Teflon fibre. Since the invention of the Teflon-coated frying pan in France in 1956, kitchen utensils with this coating have become commonplace. About 60 million, or one-third, of the cooking and baking utensils produced in 1965 were Teflon coated, and 55 percent of the families now have one to eight pieces of coated ware.

Kel-F is quite transparent and is thermoplastic. As both plastics are excellent electrical insulators, they are used for wire and cable jacketing and for coatings on electrical and electronic equipment. It is estimated that a ton of Teflon is involved in the launching of an Atlas space vehicle.

If the conversion or polymerization process of the fluorocarbon monomer is stopped at the proper stage—that is, before the rigid plastic stage is reached—any of a range of liquids, oils, lubricants, greases, and waxes can be obtained; these have many of the previously mentioned intrinsic properties. Many of these liquids are being used as hydraulic fluids, coolants, transformer oils, inert reaction media, antiradiation and gyroscope fluids, lubricants, and hydrocarbon grease and water repellants.

A number of other fluorocarbon polymers and co-polymers have appeared on the market. Polymeric materials are being produced from such monomers as vinyl fluoride ($CH_2{=}CHF$), vinylidene fluoride ($CH_2{=}CF_2$), and hexafluoropropylene ($CF_3CF{=}CF_2$). Industry is also producing a wide range of co-polymers from various combinations of mixed fluorocarbon and fluorocarbon-nonfluorocarbon monomers. Some of these polymers and co-polymers are being processed into nonsticky, moisture-resistant, pliable film finishes and food packaging materials, protective coatings for the chemical industry, seamless, inert lining for steel pipe, and exterior coatings for commercial buildings and homes with a weather resistance of about 25 years. Some market analysts believe that films and coatings have exceptional opportunities for commercial growth; fluoropolymer coating resins are expected to expand from today's half-million pounds per year to four million pounds by 1970. Fluorocarbon puttylike materials are being used as sealants for fuel tanks, hydraulic systems, and chemical process equipment. Teflon has been used by heart surgeons to repair intra-cardiac defects, such as holes between heart chambers. Also, porous discs molded of a fluorocarbon plastic are being used as blood filters in cardiac surgery. Attempts are being made to use fluorocarbon plastic membranes for special separation processes; for example, the Teflon type of membranes are more permeable to carbon dioxide and helium, thus permitting the separation of these gases from carbon dioxide-oxygen, helium-nitrogen, and helium-methane mixtures.

Among the less common polymeric materials are the fluorosilicone fluids, plasticizers, and rubbers pioneered by the Dow-Corning Corporation under the Silastic trade name. Silastic LS-53 is a polytrifluoropropylmethylsiloxane rubber $[(CF_3CH_2CH_2)(CH_3)SiO{-}]_x$ with properties comparable to most silicone rubbers; it has good resistance to most organic solvents, and it retains its rubbery nature to 100° F.

Research laboratories are trying to develop some special fluorocarbon polymers for military agencies for use under severe conditions. For instance, plastics are needed for prolonged resistance to such missile and rocket fuels as nitrogen tetroxide ($N_2O_4$), various hydrazines, and other high energy fuels. Considerable research effort is being made to introduce various atoms such as sulfur, oxygen, phosphorous, and nitrogen into basic fluorocarbon structures in order to obtain heterofluoropolymers with unusual properties.

The future market for fluorocarbon resins and plastics appears to be promising. It is expected that 90 million pounds of fluorocarbons will be used in 1970 to produce an estimated 30 million pounds of fluorocarbon plastics. Fluorinated polymers are expensive, but because of their superior properties, they are admirably suited to space age technology.

## Cleaning and Degreasing Solvents

Modern technology, with its increasingly complex precision machines, electrical instruments, electronic controls, military equipment, and aerospace systems, is demanding an almost incredible degree of super-cleaning. A microscopic speck of dirt or a minute grease film in precision equipment may be the cause of a multimillion dollar failure or the loss of human life. The use of ultrasonic equipment with a superior solvent such as fluorocarbon FC-113 ($CCl_2FCClF_2$) (boiling point 117.6° F) in a dust-free shop are the best answers to modern cleaning problems. FC-112 ($CCl_2FCCl_2F$) (boiling point 199° F) also has some use as a solvent.

Although FC-113 is expensive, it has many physical properties that approach the ideal for a super-cleaning solvent. It is nontoxic, nonflammable, nonexplosive, odorless, and will not harm plastics, paints, dyes, fabrics, electrical insulation, or corrode metals. Other attractive features are selective solvent action on oil, grease, and dirt, immiscibility with water, low surface tension (good spreading power) and viscosity, electrical nonconductivity, and high chemical and thermal stability. Its volatility is such that rapid drying of cleaned equipment and easy recovery of solvent are possible.

FC-113 is used in cleaning of electrical or electronic instruments and controls, motors, motion picture and television film, magnetic tape, printed circuit boards, gyroscopes, bearings, vending machine components, coin chutes in pay telephones, small pipes and components of oxygen assemblies, and air and missile tube systems of submarines. About 50 percent of the FC-113 solvent produced is used in the aerospace industry.

A special coin-operated dry cleaning machine is reported to be using FC-113, and it is claimed that it has a shorter dry cleaning cycle—15 rather than 45 minutes—because of time saved during the drying stage.

An excellent future for fluorocarbon solvents is predicted. In 1965, the total market for FC-113 was 30 million pounds, of which 80 percent was used for solvent purposes. By 1970, the market demand could increase to about 75 million pounds. It is also anticipated that other specialized fluorinated solvents will be introduced to the trade in the near future.

## Blowing Agents

Urethane foam is a type of plastic produced by submitting a resin, such as a reactive polyfunctional isocyanate mixture, to a final frothing or blowing operation to develop a cellular structure. In 1958, it was discovered that fluorocarbon blowing doubled the thermal insulation efficiency of urethane foam and aided in lowering the foam density. Various types of foam are produced: (1) a flexible or resilient cushioning product for automobiles, furniture, and bedding, (2) a semirigid material such as crash padding, and (3) a rigid board or foamed-in-place insulation for appliances, industrial refrigeration, construction, small boats, and other items.

Although the Frost patent (U. S. 3,072,582) listed a number of fluorocarbons for foam blowing, low-cost FC-11 ($CCl_3F$) (boiling point 74.8° F) has a high preference rating for rigid urethane foams. The rigid foams contain about 15 percent by weight of fluorocarbon. Some FC-11 is used in flexible foams, but methylene chloride ($CH_2Cl_2$) has become a strong competitor. Consumption of rigid foams of all kinds is expected to increase from 80 million pounds in 1965 to about 200 million pounds in 1970. It is also predicted that in 1970, about 90 million pounds of fluorocarbons will be used as blowing agents.

## Stain Repellants

A number of fluorinated derivatives are being used as stain-resistant textile finishes. These finishes are oil-, grease-, and water-repellent and act as a protective barrier to such soiling agents. A familiar advertising demonstration is the spilling of catsup on a stain-repellent suit and removing the spot without leaving a stain. This also points up the fact that the repellants withstand washing and dry cleaning. Perhaps the best known fluorocarbon stain repellants are "Scotchgard" (Minnesota Mining Co.) and "Zepel" (duPont). This fluorochemical is being applied as a sizing to cotton, wool, rayon, pile fabrics, and other materials for use in rainwear, clothing, draperies, slipcovers, and upholstery goods. A stain repellant is available in an aerosol dispenser for home use. A new market development is fluorochemically sized paper that is stain-resistant to grease and grime for menus, repair manuals, disposable sacks, and multi-ply wrapping. Upon approval of the Federal Food and Drug Administration, fluorochemically treated paper is expected to find increased use in food wrapping.

The fluorochemical repellant market in 1965 was estimated at 10 million dollars; in 1970, sales are expected to reach 15 million dollars.

## Surfactants and Fire Extinguishing Agents

Surface active agents (surfactants) possess high spreading power because of their low surface energy. They are useful where efficient surface wetting is necessary, as in making dispersions and in electroplating. Various fluorochemical derivatives, such as the carboxylic acids and alkyl sulfonates, are powerful surfactants and have exceptional chemical, thermal, and electrical stability. They are used in electroplating to reduce metal losses caused by foaming of the baths. Because they lower interfacial tensions, the fluorochemical surfactants are used as anti-foaming additives and as leveling agents in polishes, oil-water mixtures, and coating materials. On the other hand, some derivatives are useful in forming stable foams and emulsions.

A fluorocarbon surfactant has been added to a foam-dry potassium carbonate fire extinguisher mixture for fighting fires involving gasoline, oil, and similar fuels. The surfactant brings about rapid spreading of a water and foam blanket on the surface of the fuel.

Several bromine-fluorine compounds have been developed as fire extinguishing agents for fighting fuel, grease, and electrical fires in jet airplanes, industrial plants, boat cabins, home appliances, and especially gasoline powered equipment. Chemists have combined the fire fighting properties of bromine compounds and the high stability, low corrosive effect, and low toxicity of fluorine compounds into single compounds. Bromotrifluoromethane ($CBrF_3$), trade named "Freon" FE-1301 (duPont), is used in fire protection systems for engines in modern airliners and in some hand extinguishers. Also reported to be good fire extinguishers are dibromodifluoromethane ($CBr_2F_2$) and bromochlorodifluoromethane ($CBrClF_2$). These agents blanket a fire as a dense gas that will not support combustion and will not leave a residue.

## Pharmaceuticals and Medical Applications

The development of new general anesthetics based on fluorochemicals has brought about dramatic changes in surgical practice, such as lower explosion and fire hazards in operating rooms, easier control of anesthesia, better muscular relaxation of the patient, less nausea, and more rapid recovery.

Halothane ($CF_3CHBrCl$), also known as Fluothane, appeared on the market as the first fluorocarbon general anesthetic, and today is the leader. It was discovered in 1951 in England (Imperial Chemical Industries) and was introduced into the United States in about 1958. By 1963, it was reportedly being given to 2.5 million patients annually. It was recently given "a clean bill of health" after an exhaustive study by the National Academy of Sciences—National Research Council.

Methoxyfluorane ($CH_3OCF_2CHCl_2$), another new anesthetic, was developed jointly by the Abbott and Dow companies and approved by the Federal Food and Drug Administration in 1962 for use as a general anesthetic for human beings. It was also discovered in England, but the manufacture and purification of it were perfected by the Dow Chemical Corporation in the United States. It is known on the market under the trade names Penthrane (Abbott) for human use and Metofane (Dow) for animal use.

Other fluorine-containing anesthetics are reported to be in the testing stage. A vinyl ether ($CF_3CH_2OCH{=}CH_2$) has been mentioned as a possible anesthetic; it was named "Fluoromar" by its discoverer, in honor of Maryland.

An unusual fluorinated ether, $CF_3CH_2OCH_2CF_3$, discovered in 1957 and called Indoklon, is being used as a pharmacoconvulsive agent in mental therapy. It is reported to be as good as or better than the electric shock treatments.

Modern tranquilizers and diuretic drugs are among our most powerful medical tools for mental therapy and for control of body liquids, respectively. Fluorinated derivatives of these complex organic compounds are also available to the physician for special situations. A discussion of these fluorinated products and their chemistry is beyond the scope of this review.

Fluorinated cortisone and steroid derivatives are being used in the treatment of arthritic, rheumatic, and inflammatory diseases. Some ointments or salves of the above products are also being used for the treatment of chronic eczema and other skin conditions. A number of fluorinated nonsteroid types of compounds that do not have the undesirable side effects of the cortico-steroids are being studied for arthritis therapy.

Organic fluorine compounds are being investigated in the search for materials that posses anti-cancer activity. Some beneficial effects have been observed with the use of 5-fluorouracil for certain tumors, skin cancers, and keratinous tissue.

For weight reduction, an appetite depressant that is a type of benzotrifluoride derivative is being sold in France under the name Ponderal. It has not been approved for the American market.

### Additional Uses

A good gaseous dielectric for dry-type transformers and electronic equipment in pressured capsules must be nonflammable, inert, dense, thermally stable, chemically noncorrosive, and have high specific heat for cooling. Octafluorocyclobutane (FC-C318) and octafluoropropane ($C_3F_8$) are rated highly as gaseous dielectrics.

A high-density liquid (specific gravity 2.4) derived from the controlled polymerization of bromotrifluoroethylene ($CBrF{=}CF_2$) is used as a fluid to balance or "float" rotor assemblies in guidance systems of aircraft and missiles. Liquids used for this purpose must be very stable toward oxidation, radiation, and higher temperatures.

Fluorinated alcohols, ketones, and acids are being offered commercially and are being investigated extensively for new uses. They offer many excellent opportunities in such areas as organic synthesis and specialty organic solvents. For example, trifluoroacetic acid has acidic properties equal to those of strong mineral acids. It is an excellent catalyst, has unusual solvent properties, and can function as a reaction medium.

It would be a mistake to give the impression that all fluorocarbon chemicals are nontoxic. Among the most poisonous agents known is a nerve gas, isopropyl methyl fluorophosphonate, called GB nerve gas by the Army and also known as the German Sarin gas. It was discovered in both Germany and England during World War II, but because of its simultaneous discovery in both countries, it provided no strategic advantage to either side. Another very potent poison, used mostly to kill rodents, is monofluoroacetic acid ($FCH_2COOH$) and its derivatives. In its natural form, it is the toxic constituent of a common plant growing in South Africa. Other examples of toxic fluorocarbon chemicals are known to the research chemist.

An effective killer of the lamprey eel, for example, is 3-trifluoromethyl-4-nitrophenol (TFM). This was found by the Great Lakes Fishery Commission, a joint agency of the United States and Canada, after screening thousands of chemical compounds. Invasion of the Great Lakes by the lamprey eel had virtually wiped out the commercial fishing industry in these waters by the 1950's. The adult lamprey kills fish by attaching itself to the fish with its mouth, rasping a hole in the body, and sucking the body fluids. The concentration required for lamprey control does not affect the trout or other fish, and, thus, since 1959, the Fishery Commission, beginning with Lake Superior, has been treating lamprey spawning areas in the Great Lakes system with TFM. In Lake Superior, 90 percent of the lamprey eels have been eliminated and the trout population is up ten-fold.

Another effective fluorocarbon chemical is trifluralin (Lilly), a benzotrifluoride derivative, and an effective weed killer for crab grass and other weeds. It is nontoxic to many productive crops. Fluorosalan (Stecker Chemicals) (3,5-dibromo-3'-trifluoromethylsalicylanilide) is a germicidal agent for use in cosmetics, soaps, textiles, rubber, and plastics.

Some coal tar dyes of the benzotrifluoride type find limited application as bright colors for cotton. Interest has been revived in an $\alpha, \beta, \beta$-trifluorostyrene polymer, or co-polymers, with a variety of vinyl compounds.

No doubt there are many other uses for fluorinated compounds. Chemists are taking advantage of the reactivity of fluorine in certain organic fluorides to synthesize new compounds with chemical structures not readily available by other means.

## Petroleum Alkylation

During World War II, the HF process for producing high-octane blending components for gasoline was developed. The HF functions as a catalyst for the conversion of olefins and isoparaffins into an alkylate that consists of a mixture of isomers of heptane, octane, etc. As the process is catalytic, very little HF is needed to maintain the reactors at their capacity. Unconfirmed reports indicate that some reactors use an initial charge of 50 tons of anhydrous HF. Although the sulfuric acid process is the major producer of alkylate, the HF process is expected to continue to show a small, steady increase.

## Atomic Energy

Uranium 235, a key nuclear fuel component, is found in very small amounts along with larger quantities of uranium 238 in naturally occurring uranium ore. The separation and concentration of the $U^{235}$ isotope posed the problem of finding a thermally stable uranium compound with a high vapor pressure at room temperature. Uranium hexafluoride ($UF_6$), with a sublimation point of 56° C, met these specifications. The isotopes are conveniently separated by submitting the $UF_6$ vapor to a diffusion process. A gas centrifuge system of separation is also being studied.

The $UF_6$ feed material for diffusion is produced by a two-step process. Uranium dioxide is treated with anhydrous HF to form the so-called "green" salt, $UF_4$:

$$UO_2 + 4\ HF \longrightarrow UF_4 + 2\ H_2O.$$

The green salt is then fluorinated with fluorine gas to form uranium hexafluoride:

$$UF_4 + F_2 \longrightarrow UF_6.$$

As enriched uranium metal is used as the reactor fuel, it is necessary to reduce the $U^{235}F_6$ to the metal. Part of the fluorine is recovered and returned as 70 percent aqueous hydrofluoric acid to the HF merchant for other purposes.

Atomic or nuclear power for industrial purposes has been increasing at a rapid rate, and in some geographical areas, it already is competitive with coal. Since the advent of nuclear power, coal, oil, and natural gas have been referred to as the "fossil fuels." In March 1967, the status of commercial nuclear power plants in the United States was as follows:

| Status | Number of plants | Capacity (kilowatts) |
|---|---|---|
| In operation | 14 | 1,881,200 |
| Under construction | 13 | 7,359,200 |
| Planned | 32 | 22,906,600 |
| | | 32,147,000 |

The Dresden (Morris No. 1) Nuclear Power Plant of the Commonwealth Edison Company, completed in 1959, was the first such plant in Illinois. Since that time, plans to build five more plants within the state have been announced (Wainerdi, 1967).

Nuclear-powered submarines of various types and surface ships, such as the 85,000-ton aircraft carrier, Enterprise, can carry a fuel load sufficient for 2 to 3 years, or about 100,000 miles of travel. As an example of the fuel load needed for such a performance, the 22,000-ton nuclear cargo-passenger ship, Savannah, is said to require 692 pounds of uranium fuel.

With the rapid increase in the number of operating and proposed nuclear power plants, uranium mining and processing has upsurged to meet the increasing nuclear fuel requirements. This will also mean a greater demand for hydrofluoric acid, offsetting the current reduced demands by the Atomic Energy Commission and the Defense Department.

## Elemental Fluorine

Although Moissan in 1886 succeeded in preparing fluorine as a free element by the electrolysis of potassium acid fluoride, it was not until World War II that a large-scale production process was perfected. The development of an industrial fluorine cell was a necessity in the production of an atom bomb.

Commercial fluorine cells still use potassium acid fluoride as an electrolyte. However, by feeding HF to the cells to maintain the proper composition, continuous fluorine generation is achieved. Two large Government-owned fluorine plants are operated by the Atomic Energy Commission to supply its own needs. The largest privately owned plant (Allied Chemical Co.) is located at Metropolis, Illinois (fig. 16). It is believed that the Metropolis plant, also a producer of uranium hexafluoride, has a capacity of over 1000 tons of fluorine per year. A number of other firms also own commercial fluorine-producing cells.

Fluorine gas is available in cylinders. Liquid fluorine, available in 25,000 pound lots, is transported in liquid nitrogen-cooled Monel metal tanks mounted on trailer trucks. Rocket and missile research centers have been receiving liquid fluorine by tank trailer for a number of years.

Besides its use in making $UF_6$, liquid fluorine is being seriously considered for use as an oxidizer in rocket engines. Rocket velocity and range are determined

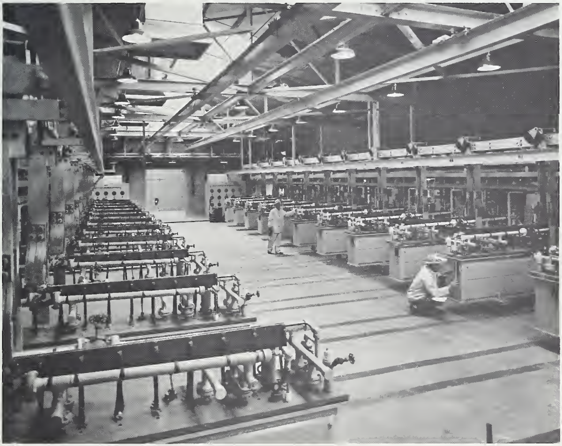

Figure 16 - World's largest privately owned fluorine gas plant, operated by Allied Chemical Corp., in Metropolis, Illinois. Gas is produced from HF made in Louisiana for use in treating uranium ore and converting it into nuclear fuel. Major consumer is the Atomic Energy Commission plant, in Paducah, Kentucky, just across the Ohio River from Metropolis. (Photograph courtesy of Allied Chemical Corp.)

by the specific impulse or thrust of a fuel and oxidizer. When it reacts with existing fuels, liquid fluorine gives the highest specific impulse of the bipropellant systems. Fluorine, the most reactive element and most powerful oxidizer known, is hypergolic—that is, it ignites spontaneously with fuels without an ignition system. Some rocket power engineers believe that fluorine would be especially useful in the upper-stage engines. A liquid oxidizer called "flox" (a mixture of 30 percent fluorine and 70 percent oxygen), used with kerosene as a fuel, is of considerable interest to the National Aeronautics and Space Administration (NASA). It is claimed that flox can increase the pay load capacity of an Atlas booster engine by at least 30 percent. An oxidizer-fuel system of fluorine and hydrogen would give a blast of huge proportions compared to the current nitrogen tetroxide ($N_2O_4$)-hydrazine ($H_2N$-$NH_2$ and derivatives) systems. Chlorine trifluoride ($ClF_3$), oxygen difluoride ($OF_2$), tetrafluorohydrazine ($F_2N$-$NF_2$), and perchloryl fluoride ($ClO_3F$) are commercially available oxidizers also capable of providing a greater impulse than $N_2O_4$. Because of the extreme reactivity of fluorine and related fluorine-based oxidizers, many problems related to their handling still have to be solved. In the event of the adoption of fluorine in one form or another as a standard fuel in space vehicles, it has been estimated that 2 to 3 million pounds of fluorine will be needed annually.

A small amount of fluorine is used for other purposes. Sulfur hexafluoride is prepared by direct combination of sulfur and fluorine. Higher metallic fluorides ($CoF_3$, $AgF_2$, $MnF_3$, etc.) and interhalogen compounds ($ClF_3$, $BrF_3$, $BrF_5$, $IF_5$) are prepared by direct fluorination. Nitrogen trifluoride ($NF_3$) is prepared by the electrolysis of ammonium bifluoride, and $NF_3$ is converted by a catalytic process to $F_2N$-$NF_2$.

A small, dependable laboratory fluorine generator is available and recommended for studies with elemental fluorine in research laboratories. By using the generator in a good fume disposal system, research quantities of fluorine are easily handled. This avoids the hazard of storing and handling fluorine gas under pressure.

## Other Inorganic Fluorides

Besides the fluorides mentioned previously, there are a variety of other useful, common inorganic compounds. In 1958, a market analyst estimated their total production to be about 14,500 tons per year; the sodium, ammonium, and boron fluorides totaled about 12,500 tons, and the remainder included fluoboric acid and its salts, potassium bifluoride, and miscellaneous compounds. On the basis of the fragmentary information that is available, it is reasonable to assume that the total production of these fluorides today is greater than in 1958. Some that were formerly laboratory curiosities have advanced to the production stage.

Most of the common inorganic fluorides are prepared by reacting aqueous hydrofluoric acid with the corresponding carbonates, oxides, or hydroxides. The bifluorides or acid fluorides are formed with an excess of acid. Anhydrous HF is used to prepare the water-sensitive fluorides such as boron trifluoride and others.

Sodium fluoride is used in water fluoridation and in manufacture of rimmed steel ingots, opaque glass, tooth paste, wood preservatives, and insecticides. About 7000 tons was produced in 1964, as compared with 6000 tons in 1958. Some sodium fluoride is obtained also from silicofluorides. Only very small amounts of ammonium and potassium fluorides are used, the potassium salt being used in organic syntheses and in solder fluxes.

Synthetic optical crystals of sodium, potassium, lithium, rubidium, calcium, barium, and magnesium fluorides are available for scientific instruments where high transmission of certain wave lengths of light is desired, especially in the infrared and ultraviolet regions. Some of the crystals are being coated or "doped" with special elements for laser research.

The ammonium, potassium, and sodium bifluorides have many diverse uses. They all can be used in the frosting and etching of glass. Both the ammonium and sodium salts are used as laundry sours and iron stain removers. Sodium bifluoride is used in the acid treatment of steel prior to electrotinning for tin cans. The ammonium salt is utilized also in the treatment of oil wells, as an antiseptic and preservative, for the removal of scale in boilers and auto radiators, and in the extraction of beryllium. Potassium bifluoride is used in the production of fluorine gas and in solder composition.

In 1958, boron trifluoride ($BF_3$) production was estimated to be about 2000 tons and probably has increased since then. It is available in cylinders or in combination with certain organic solvents and is very corrosive in the presence of moisture. Its chief use is in the manufacture of coumarone-indene resins, petroleum resins, lubricating oil additives, and as a catalyst in organic syntheses. An interesting application is its use as a catalyst in the manufacture of a new and more powerful propellant, a nitroalkane derivative, that is being used in the long-range Polaris submarine missiles.

Annual production of fluoboric acid ($HBF_4$) and its salts, usually prepared from boric acid or borax with hydrofluoric acid, is probably about 1000 tons. The acid is used in the cleaning and pickling of metals, electropolishing of aluminum, and in organic syntheses. Because of high anode and cathode efficiency and the formation of a fine-grained deposit, the acid and certain salts are used in baths for specialty electroplating, such as cadmium, chromium, copper, indium, iron, lead, lead-tin, nickel, silver, tin, and zinc. Ammonium fluoborate is added to the molds used in magnesium casting to prevent oxidation. The sodium salt is used in the heat treatment of aluminum alloys to prevent blistering and crack formation and as a flux in nonferrous metallurgy. The use of potassium fluoborate in the manufacture of brazing and soldering fluxes and in grinding wheels has been reported.

Silicon tetrafluoride ($SiF_4$) gas has been useful in sealing off downhole water zones during drilling of oil and gas wells. The $SiF_4$, upon injection into a well, penetrates into the permeable water zone where it hydrolyzes to a fluosilicic acid gel that plugs the pore passages.

Tungsten metal is being produced by the reduction of tungsten hexafluoride ($WF_6$) with hydrogen.

A variety of fluorinated sulfur compounds is now commercially available. Sulfuryl fluoride ($SO_2F_2$) is used in organic synthesis and as a fumigant gas called "Vikane" (Dow) for the control of termites, ants, spiders, and other insect pests. Sulfuryl chlorofluoride ($SO_2ClF$) is used in organic syntheses. Sulfur tetrafluoride ($SF_4$), a very toxic gas, is available in cylinders and is used in special fluorination procedures. The very inert and nonpoisonous sulfur hexafluoride ($SF_6$) is used as a gaseous dielectric in transformers, X-ray tubes, and electronic equipment.

Stannous fluoride ($SnF_2$) and sodium fluoride (NaF) are being added to tooth pastes as decay preventives. Both sodium fluophosphate ($Na_2PO_3F$) and zirconium fluoride ($ZrF_4$) can be used as anti-cavity additives.

Atomic and rocket age demands for new materials have stimulated fluorine chemical producers to offer many fluorides, some of which were considered rarities 20 years ago. Sales advertisements have been noted on the fluorides of antimony, barium, bismuth, cadmium, caesium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, rare earths, rubidium, selenium, silver, strontium, tin, titanium, tellurium, tungsten, zinc, zirconium, and many double fluorides of chromium, iron, tantalum, titanium, zinc, and zirconium in the form of ammonium, potassium, and sodium complexes. Difluorodiazine (FN=NF) is being suggested as a polymerization catalyst and an intermediate for organic syntheses. Perchloryl fluoride ($ClO_3F$), besides being a potent oxidizer, can also be used as a fluorinating agent on organic compounds.

An interesting group of compounds, at present only of theoretical interest, are the rare gas fluorides. The first of these compounds synthesized was xenon tetrafluoride ($XeF_4$) in 1962. The discovery that the rare gases, previously thought to be inert, could be fluorinated is considered to be one of the great achievements of modern chemistry.

## Fluosilicic Acid and Salts

No discussion on the uses of fluorine compounds is complete without mention of fluosilicic acid and its salts, called fluosilicates or silicofluorides. They can be prepared from low-grade fluorspar and sulfuric acid. However, they are available at low cost either as by-products of phosphate rock acidulation in domestic fertilizer plants or as imports from Europe and Japan. Under these circumstances, it is not economically feasible to produce them from fluorspar.

Fluosilicic acid ($H_2SiF_6$) is most extensively used in water fluoridation; consumption for this purpose is believed to be more than 21 million pounds per year. According to a 1965 report, New York City is expected to use more than 2400 tons of fluosilicic acid annually for its water supply. Fluosilicic acid is used also for electroplating and concrete hardening, as a wood preservative, and in the manufacture of metallic fluosilicates and fluorides.

The production of sodium fluosilicate ($Na_2SiF_6$) in 1964 was 39,000 tons. In 1965, about 15,000 tons was added to drinking water. Other uses are as a laundry sour, in synthetic cryolite manufacture, in enamel and opal glass, in insecticides, in foam rubber, and as a preservative in glue and leather. The potassium salt ($K_2SiF_6$) is used in enamels, light metal fluxes, synthetic mica, and as a sand inhibitor in magnesium metal casting.

Zinc fluosilicate is used as a wood preservative, as a mothproofing agent for textiles, and, like the magnesium salt, as a laundry sour and concrete surface hardener. The chief uses for ammonium fluosilicate are in water fluoridation, electroplating of copper on zinc and iron, mothproofing, and as a laundry sour. The barium and calcium salts are used as insecticides and in ceramics as opacifying agents. Lead fluosilicate is used in electrolytic lead refining and plating. Occasionally salts of aluminum, iron, nickel, and silver are mentioned for special uses.

# APPENDIX

## DIRECTORY OF ILLINOIS FLUORSPAR MINES AND MILLS

The fluorspar mining industry in Illinois traditionally has been divided into two main categories: the major companies and the independent miners. The former group is made up of the larger companies that operate mines in conjunction with processing mills; these account for the bulk of the state's production. The latter group is made up of a large number of individuals, partnerships, and corporations that have operated mines independent of processing mills. Some of the companies have been in business on a continual basis, while the others have operated on a more irregular basis in response to varying market conditions. During the past decade, the number of producers has sharply declined, as the competitive position of the domestic industry has deteriorated under pressure from foreign competition.

As of July 1967, the following major companies were operating:

Aluminum Company of America, Rosiclare:
  Mill: 400-ton flotation and heavy-media plant, Rosiclare

The Minerva Company, Div. of Minerva Oil Company, Eldorado:
  Mills: 1000-ton flotation and heavy-media plant, Mine No. 1, Cave in Rock
    325-ton flotation and heavy-media plant, Crystal Mine, Route 1, Elizabethtown

  Mines: Mine No. 1, Cave in Rock
    Jefferson Mine, Route 4, Golconda
    Fairbairn Mine, Route 4, Golconda
    "Gaskins" lease, 2 miles north of Eichorn (Empire District)—under development; production expected in early 1968

Ozark-Mahoning Company, Mining Division, Rosiclare:
  Mills: 675-ton flotation mill, Rosiclare
    800-ton heavy-media separation plant (capacity rated on two-shift basis)

  Mines: North Green Mine, near Cave in Rock
    East Green Mine, near Cave in Rock
    West Green Mine, near Cave in Rock
    Hill-Ledford Mine, near Cave in Rock
    Oxford Mine No. 7, near Cave in Rock
    Oxford Mine No. 11, near Cave in Rock
    Shaft No. 2, near Cave in Rock
    Shaft No. 3, near Cave in Rock
    Shaft No. 4, near Cave in Rock
    Shaft No. 5, near Cave in Rock
    Shaft No. 10, near Cave in Rock
    Parkinson Mine, near Shetlerville
    Barnett Mine, near Shetlerville

In addition, the U. S. Bureau of Mines reported that the following independent miners produced fluorspar during 1966:

Hastie Mining Company, Cave in Rock: adit on Spar Mountain

J. W. Patton and Sons, Elizabethtown: a mine near Eichorn in Pope County

Ridge Mining Company (Harold Patton), Karbers Ridge: Ridge Mine

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