

Mines Branch Information Circular IC 127

FLUORSPAR

by

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SYNOPSIS

Fluorspar, a non-metallic mineral hitherto used largely as a flux, has become the basic source material for an active and growing chemical industry producing chemicals and materials with unique characteristics of great value to industry. These materials are finding such large-scale, diverse and essential applications that marked increases in demand are foreseen. Such demands will be difficult or impossible to satisfy from known fluorspar resources.

Present trends in production, consumption and trade indicate that shortages may be expected, particularly in the highly industrialized countries where consumption is currently large and growing rapidly. For these reasons known fluorspar resources should be evaluated and their development encouraged. Efforts should be made to find new deposits and to develop methods of recovering fluorine from other ores in which it may be present.

This Information Circular provides data on the properties and uses of fluorspar, on the world production and consumption trends, and on Canadian deposits and occurrences.

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Direction des mines

Circulaire d'information IC 127

LE SPATH FLUOR

par

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RÉSUMÉ

Le spath fluor, minéral non métallique utilisé surtout comme fondant, est devenu une matière première. Dans l'industrie active et progressive de la chimie, il sert maintenant à l'élaboration de produits chimiques et de matériaux dotés de caractéristiques particulières qui ont une grande valeur dans le domaine industriel. Ces matériaux trouvent des applications tellement étendues, diverses et essentielles qu'on entrevoit une augmentation considérable de demandes. Les ressources connues de spath fluor pourront difficilement alimenter un tel marché.

Les tendances actuelles de la production, de la consommation et du commerce indiquent la possibilité de pénuries, particulièrement dans les pays hautement industrialisés où la consommation présente est forte et croissante. Il importe donc d'inventorier les ressources connues de spath fluor et d'encourager la mise en valeur. On devrait s'efforcer d'en découvrir de nouveaux gîtes et de mettre au point des procédés de récupération de la fluorine à partir d'autres minerais susceptibles d'en contenir.

La présente Circulaire d'information fournit des données sur les propriétés et les utilisations du spath fluor, sur les tendances de la production et de la consommation dans le monde, ainsi que sur les gîtes et les venues au Canada.

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INTRODUCTION

Fluorspar, a chemically stable non-metallic mineral, has been known in the form of crude jewellery since early times but is today more familiar as a useful flux in the pyrometallurgical industries. Its physical characteristics are distinctive but not unusual. The chemical properties, however, are unique and these fundamental characteristics, which determine the number, rate and nature of the chemical compounds which fluorine will form with other elements, are the basis of an important and growing fluorine chemical industry.

The mineral as found in natural occurrences is physically weak and often disintegrates to inconspicuous particles. Chemically, however, the mineral is very stable and is changed into other compounds only with difficulty. This wide variation in characteristics is inherited by the compounds formed from fluorspar. Some, like the mineral, are remarkably stable and inert to all physical or chemical action. Examples are the unusually stable fluorocarbon plastics such as Teflon and the inert refrigerant and propellant gases such as the Freons. Other compounds of fluorine have violent chemical activity and react with almost all other elements. Examples of these are fluorine gas and hydrofluoric acid. These compounds are highly toxic and corrosive and are therefore very difficult to manufacture, transport and use with safety. At the same time their chemical activity makes them extremely valuable and important for some manufacturing processes. Their toxicity and corrosiveness made commercial

development slow, and many years passed before safe methods of manufacturing and using these compounds were developed. Satisfactory procedures are now in use and rapid development of the fluorine chemical industry can be expected.

Fluorspar, which is the source of compounds with such a wide range of characteristics and such a diversity of applications, has significance greater than its present economic value would indicate. Fluorine chemicals and compounds in several instances are at the leading edge of research in high-energy missile fuels, non-corrosive plastics, and chemical metallurgy. In addition to increasing demands for fluorspar as the steel and aluminum industries expand, even larger demands are being forecast by industry to satisfy fluorine chemical needs. In many instances fluorine chemicals, and products made from them, are finding uses for which no other materials are adequate and for which no satisfactory substitutes are known. Growing demands for these compounds indicate that larger amounts of fluorspar will be needed for their production.

It is of interest to point out similarities between sulphur and fluorspar. Both are naturally occurring minerals that can be used for some purpose in their natural forms but which are much more valuable as a source of strong acids and unique chemical compounds. In the past fifty years sulphur, in the form of sulphuric acid, has become such an essential material for industrial growth and production that the industrial stature of a nation can be measured by its

consumption. It is suggested that a similar development is taking place in fluorine chemistry. While the volume of fluorspar required may never equal present sulphur production, the unique characteristics of fluorine appear to assure it of a position in industry fully equal in importance to that occupied by sulphuric acid today.

Consumption of fluorspar for metallurgical purposes is increasing steadily as the production of steel and aluminum rises. At the same time, demands for fluorine chemicals are increasing and larger amounts of acid-grade fluorspar are required to produce them. Because the fluorine chemical industry is relatively new, its importance is not generally recognized and its future size is still difficult to predict. However, the variety and versatility of its products, and the fact that many have unique characteristics for which no adequate substitutes are known, assure fluorspar an important place among industrial minerals. This is particularly true since new products and applications are continually being announced.

At the present time, fluorspar is produced in fully adequate amounts in many countries and supplies are readily available for all consumers, although some of the major consumers must import substantial amounts. In recent years, increased production in Mexico, Spain and Italy has competed for markets in Europe and the United States and prices have been depressed until many producers in the United States and Canada find profitable operation difficult. The two largest consumers, the United States and the Union of Soviet Socialist

Republics, have imported more than half their annual requirements in recent years. Japan, also, depends very largely on imports. United States companies are active in exploring for and developing fluorspar deposits in Mexico.

It is expected that fluorspar requirements, for fluorine chemicals in particular, will increase markedly. From information now available it appears likely that these demands will exert continuous pressure on present sources of supply, that as a result fluorspar prices will rise, and that considerable effort will be made to find and develop new reserves. For these reasons a review of the mineral fluorspar, covering its properties, occurrences, uses and sources, is timely.

PHYSICAL AND CHEMICAL PROPERTIES

Fluorspar is a non-metallic mineral usually found in coarsely crystalline veins or bodies but sometimes in massive or granular forms. (The terms "fluorspar" and "fluorite" are often used synonymously, but more accurate usage restricts "fluorite" to a mineralogical term referring to crystals, whereas "fluorspar" is a general name for the mineral and ores.) Its composition is calcium fluoride, CaF_2 , in the proportion of 51.1 percent calcium and 48.9 percent fluorine. It crystallizes in the isometric system and its habit is normally cubic, although octohedral, dodecahedral and other forms occur. Cleavage is perfect on (111), fracture is flat-conchoidal, and some forms break into splinters while others disintegrate into granular

fragments. The mineral is brittle, with a hardness of 4 (Mohs scale), and its specific gravity ranges from 3.01 to 3.25. The lustre is vitreous. The colour is often white, but may range from pale shades of yellow and red through green to blue and deep purple. The colour may be concentrated on certain planes in crystals, and all colours disappear on heating. Many varieties are fluorescent, and some are phosphorescent when heated.

Fluorspar decrepitates at approximately 1000°C. It fuses readily at about 1360°C and industry uses this property to aid in the melting of metallic minerals and to make clean slag separations. When heated with sulphuric acid, fluorspar forms hydrofluoric acid according to the equation: $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}$.

In weathered exposures, fluorspar is a difficult mineral to find and identify. Because it is soft and friable, some crystalline forms tend to disintegrate rapidly when exposed and a fluorspar vein at the surface is usually marked by a depression or shallow trench in which the fluorspar is hidden by a cover of rubble and soil. In association with other minerals such as fine-grained quartz or barite, it may be difficult to identify and evaluate in the field. Considerable experience is necessary before reliable evaluations can be made of fluorspar in weathered exposures. It should be noted that these identification difficulties result directly from the physical properties of the mineral.

Fluorine, the active and valuable ingredient in fluorspar,

is difficult to isolate from the mineral as a gas. It was discovered in 1771 but, because of the stability of the mineral and the violent activity of the gas, commercial production methods were not developed until 1886. It is only in recent years that efficient methods of transporting and handling this dangerous material have been developed to the point where large-scale use by industry has been possible. These problems illustrate both the chemical stability of the mineral fluorspar and the violent activity of some of the compounds formed from it.

Fluorine, a gas at normal temperatures and pressures, is the most active element known and combines with almost all other elements, sometimes very violently. This chemical activity makes fluorine valuable since large numbers of useful compounds can be formed, some with unusual and very interesting properties.

USES

To clearly understand the nature and variety of the uses of fluorspar it is helpful to consider them under two headings, "Metallurgical" and "Chemical".

Metallurgical Uses^{(1)*}

Fluorspar is used in pyrometallurgical processes as a flux and as an electrolyte. These applications comprise steel and aluminum smelting, metal welding, porcelain enamelling and glazing, and minor uses of a similar nature. It may be noted that for metallurgical uses fluorspar is mostly consumed in its natural form,

* References are listed at the end of the report in the order in which they are numbered in the text.

with only mechanical preparation such as grinding and concentration by elimination of impurities. In other words, although requirements vary as to grain size and purity, metallurgical consumption is in the form of calcium fluoride.

Steel Industry

The metallurgical uses of fluorspar depend on its low melting point (1270° to 1387°C); on its ability to flux or form eutectics with silica, or calcium and barium sulphates, or alumina and other refractory materials, thus making it easier to melt the furnace charge and form a fluid slag; and on its ability to volatilize or slag off sulphur, phosphorus and other impurities in the iron.

In the basic open hearth process, fluorspar in lump or gravel form is added to keep the slag fluid and eliminate impurities. The addition of fluorspar makes the separation of the valuable and waste materials in the charge faster and more efficient. Lump or gravel "spar" having only a small amount of fines is necessary for metallurgical purposes, because fine material would be sucked out by the furnace draft or would float on the surface rather than sink into the melt. Modern practice requires 4 to 5 pounds of fluorspar per ton of steel, depending on variations in the ore charge and individual preference.

In addition to its use in open hearth furnaces, fluorspar is also used in basic electric steel furnaces, in Bessemer furnaces, in furnaces for smelting refractory non-ferrous ores, and in foundries.

Aluminum Industry (2)

Aluminum is produced by the electrolytic reduction of pure alumina in a bath of dissolved cryolite, Na_3AlF_6 , to which some fluorspar is added to lower the melting point. Cryolite is a rather uncommon fluorine mineral. The only commercial deposit found to date is in Greenland and the ore has been used almost entirely in the aluminum industry. Because natural cryolite supplies are limited, the industry has gradually turned to artificial cryolite, manufactured by the action of hydrofluoric acid (made from fluorspar) on aluminum hydroxide in the presence of soda.

Molten aluminum is produced in a carbon lined steel cell in which a bath of molten cryolite is prepared and to which are added pure alumina and some fluorspar. The approximate composition of the bath is $2\text{AlF}_3 \cdot 6\text{NaF} \cdot \text{CaF}_2$. As the alumina goes into solution under the influence of the electric current and the cryolite and fluorspar, more alumina is added to maintain a content of 3 to 6 percent, and molten aluminum is tapped off at the base of the cell. An 8 x 4 x 4 foot cell produces about 120 pounds of aluminum per day, and ten pounds of metallic aluminum require one pound of cryolite and some fluorspar. The controlling factor in the production of aluminum is the availability of low-cost electric energy, because the process consumes about 10 kwh per pound of aluminum produced.

Ceramics

Fluorspar is added to glass and enamel melts as a flux,

to assist complete melting and to increase fluidity of the charge. Its use gives low porosity and greater strength. For use in ceramics, fluorspar must be in powdered form and, besides having a 95 percent content of calcium fluoride, must be free of iron and other elements that would colour the end products.

Chemical Uses (1) (2)

Fluorspar is consumed by the chemical industry to produce chemicals and compounds of two types. One group is the intermediate materials, such as hydrofluoric acid, which are used in large volume in the chemical processing of other products such as gasoline and uranium. The other group comprises fluorine compound end products, such as refrigerants, propellants and plastics. The significance of the volume and variety of the fluorine chemical end products is not generally appreciated. There are two reasons for this. In some cases, research and development have been for military purposes and security considerations have delayed the growth of commercial applications. In other cases, both the processes and the products are recent developments and are just now beginning to find large-scale applications and markets.

As a raw material for the chemical industry, fluorspar has strict specifications both as to physical size and as to chemical purity. This does not mean that the raw ore is necessarily the highest grade obtainable, because, strangely enough, the mills producing acid-grade fluorspar concentrate often operate on ores that would not be

suitable as sources of metallurgical-grade fluorspar.

Acid-grade fluorspar, although it must contain more than 97 percent CaF_2 , is marketed and used as a fine powder (flotation concentrate), and because the product is fine-grained it can be produced from lower-grade and disseminated ores. Some fluorspar producers are able to market both grades, by first removing the coarse, pure lumps for metallurgical purposes and then collecting the fines, together with additional fluorspar recovered by the further processing of low-grade and disseminated ores, to make acid-grade. The additional grinding and flotation required to make these recoveries add to the cost, but acid-grade commands a higher price than metallurgical-grade.

Consumption of chemical fluorspar, small before 1940, has grown rapidly, particularly in the past ten years. This is illustrated by the United States consumption figures shown in Table 1. Between 1950 and 1957, fluorspar consumption by the steel industry remained about constant (steel production increased but the amount of fluorspar used per ton of steel decreased slightly), while consumption by the aluminum industry is reported to have doubled and consumption by the fluorine chemical industry to have increased by 200 percent. Continued expansion of the fluorine chemical industry is expected, because the market for its products is growing and new products are continually being developed. Comparative consumption figures for Canada are shown in Table 2.

TABLE 1

Consumption of Fluorspar in the United States
(Short Tons)

| Grade | 1940 | 1950 | 1955 | 1956 | 1957 | 1958 ^{2/} | 1959 |
|----------------------|---------|---------|---------|---------|---------|--------------------|---------|
| Acid ^{1/} | 37,000 | 124,400 | 265,600 | 308,100 | 343,400 | 265,800 | 331,935 |
| Metallurgical | 160,100 | 250,500 | 276,400 | 288,400 | 268,900 | 191,700 | 218,709 |
| Ceramic and Other | 21,400 | 51,100 | 29,200 | 25,100 | 33,100 | 36,500 | 39,335 |
| Totals | 218,500 | 426,100 | 571,200 | 621,600 | 645,400 | 494,100 | 589,979 |

Notes: ^{1/}Acid-grade consumption includes fluorspar used to produce aluminum and fluorine chemicals. Consumption for aluminum production has increased but at a lower rate than total acid consumption.

^{2/}Lower consumption in 1958 was due to general business recession. Upward trend appears in 1959.

TABLE 2

Consumption of Fluorspar in Canada
(Short Tons)

| Grade | 1940 | 1950 | 1955 | 1956 | 1957 ^{1/} | 1958 | 1959 |
|----------------------|--------|--------|--------|--------|--------------------|--------|--------|
| Acid ^{2/} | 3,400 | 29,600 | 68,628 | 76,478 | 53,198 | 74,939 | 72,148 |
| Metallurgical | 21,200 | 21,800 | 18,600 | 19,000 | 16,935 | 14,539 | 20,988 |
| Ceramic and Other | 447 | 713 | 689 | 669 | 628 | 455 | 3,116 |
| Totals | 25,095 | 52,137 | 87,927 | 96,126 | 70,761 | 89,933 | 96,252 |

Notes: ^{1/}Consumption lower in 1957, due to general business recession.

^{2/}Consumption of acid fluorspar in Canada is almost entirely in manufacture of aluminum.

For chemical uses, fluorspar is first made into hydrofluoric acid by reacting the fine-ground concentrate with sulphuric acid in heated kilns. The kilns are 4 to 8 feet in diameter and 40 to 60 feet in length, and may be either rotary or stationary. Each yields about 5 tons of anhydrous hydrofluoric acid per day. The HF gas evolved is washed with sulphuric acid in scrubbing towers, to strip it of any water content, and is then condensed in refrigerating coils as anhydrous hydrofluoric acid. The anhydrous acid can be shipped in steel tanks but aqueous acid containing less than 65 percent HF requires containers with non-corrosive linings.

Elemental fluorine is made from anhydrous HF by electrolysis. It is a gas at normal temperatures and pressures but is compressed to a liquid for shipment. Fluorine, as gas or liquid, is difficult to handle because it reacts with almost all other materials. One manufacturer has developed a method of shipping it in multiwall tanks mounted on trucks. Fluorine in the central tank is surrounded by an inner compartment containing liquid nitrogen and by an outer vacuum compartment.

The fluorine chemical products now being produced and the many more under development are too numerous to be listed in detail, and no list could be complete since new applications are being discovered and developed continually. However, to show the versatility and potential volume of fluorine products the more important end products are grouped below, under the fluorine source material from which they are derived.

Aqueous Hydrofluoric Acid

Aqueous HF is used in pickling steel, in galvanizing, in glass etching and polishing, and in enamel stripping. It is also used as the starting point in manufacturing insecticides, wood preservatives, ceramic additions, and ingredients for dyes. The acid fluorides NaHF_2 and KHF_2 are derived from aqueous HF and are used as laundry sours, metal fluxes, stone cleaners, and in the brewing industry.

Anhydrous Hydrofluoric Acid ⁽³⁾

Anhydrous hydrofluoric acid is the starting point for the organic fluorides, which at present appear to have the greatest volume of products and the most important future. These fluorocarbons and fluorinated hydrocarbons are made by reacting anhydrous HF with carbon tetrachloride (CCl_4) and chloroform (CHCl_3). The fluorocarbons include the "Freon"-type refrigerants and aerosol propellants, and the fluorinated hydrocarbons are the basis for the "Teflon", "Kel-F" and other polymers. At present, the aerosols and refrigerants probably have larger-volume markets, but fluorocarbons, resins or polymers appear to have a very large market potential as textile, clothing and leather protective coatings, as dielectric materials in electronic equipment, as greaseless bearings, ⁽⁴⁾ and as gaskets, tubing and fittings where resistance to acid corrosion is required. Other products of this group are fire extinguishants, anesthetics, lubricants, and materials for special plastics.

Inorganic Fluorides⁽¹⁾

The inorganic fluorides include boron trifluoride, a specialized catalyst in polymerization, and sulphur hexafluoride, which has a very high dielectric strength and is used as a gaseous insulator in high-voltage electrical equipment. Sodium fluoride is used to fluorinate drinking water and some 16,000 tons are consumed annually for this purpose in the United States. Most of this amount has been derived from sources other than fluorspar (fluorine recovered in the processing of phosphate rock), but methods have been developed to use fluorspar for fluorination at a cost lower than for sodium fluoride.

There are many other inorganic fluorides but most are used in small amounts in highly specialized operations. Their uses are in insecticides, special fluxes, and wood preservatives, and in the rubber, dyeing and other industries.

Fluorine Gas

Some processes require highly active agents in gaseous form. Fluorine gas was found to be the essential ingredient in the diffusion separation of U^{235} and U^{238} in uranium processing. It is also being used as an oxidizer for fuels in rocket-powered missiles.

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Many new applications for fluorine chemical products are now under development or being tested, and on these little information is available. It has been suggested that the demand for inorganic

fluorides may increase in proportion to population growth, and that the use of fluoro-organic compounds may double by 1965. While these are only estimates, the projected trend, in terms of hydrofluoric acid, by application, is indicated in Table 3.

TABLE 3*

United States Hydrofluoric Acid Consumption, 1957 and 1963 (Estimated)
(Short Tons)

| | 1957 | | 1963 | |
|----------------------|----------|------------------|----------|------------------|
| | HF | Percent of Total | HF | Percent of Total |
| Aluminum fluoride | 40,000 | 29.6 | 65,000 | 30.2 |
| Fluorocarbons | 38,500 | 28.5 | 67,000 | 31.2 |
| Uranium production | 16,000** | 11.8 | 21,000** | 9.8 |
| Synthetic cryolite | 13,000 | 9.6 | 25,000 | 11.6 |
| Conversion to salts | 7,500 | 5.6 | 8,400 | 3.9 |
| Stainless steel | 7,000 | 5.2 | 8,100 | 3.8 |
| Petroleum alkylation | 6,000 | 4.5 | 9,000 | 4.2 |
| Special metals | 3,000 | 2.2 | 6,000 | 2.8 |
| Etching and frosting | 2,000 | 1.5 | 2,200 | 1.0 |
| Others | 2,000 | 1.5 | 3,300 | 1.5 |
| Total | 135,000 | 100.0 | 215,000 | 100.0 |

* This table is from an article by A.H. Stuewe, Stauffer Chemical Co., New York, printed in Chemical and Engineering News, December 22, 1958.

** Net consumption.

SPECIFICATIONS AND PREPARATION FOR MARKET

Fluorspar is marketed in three grades that have different physical and chemical specifications, require different processing, and command variable prices. The richest natural deposits do not always provide the highest-grade concentrates for industry. More often the physical nature of the occurrences, rather than their chemical purity,

is the deciding factor in determining their end use and, paradoxically, the highest-grade natural occurrences often reach market with the lowest physical and chemical specifications, and vice versa. The explanation of this anomaly lies both in the nature of the occurrences and in the requirements of the consuming industries.

Metallurgical fluorspar, also referred to as "standard fluxing gravel", or "lump grade", may be sold under definite specifications such as a minimum of 85 percent CaF_2 , a maximum of 5 percent CaCO_3 and 5 percent SiO_2 , and low-to-trace amounts of sulphur and metallics. In recent years, however, most metallurgical fluorspar has been sold under "effective units" specifications. This requires that each one percent unit of silica shall be cancelled by a two and a half percent unit of calcium fluoride and the remaining calcium fluoride be considered the "effective units" of CaF_2 . While this system provides some flexibility, there are definite limits, both for minimum calcium fluoride and for maximum silica, calcium carbonate, sulphates, sulphur and metallics. In addition to these chemical specifications, metallurgical fluorspar must be in coarse sizes. Particles should range from $3/8$ inch to $1\ 1/2$ inches and fines must not exceed 15 percent.

The requirement of coarse size for metallurgical uses means that only high-grade coarsely crystalline deposits are satisfactory sources. For these reasons it is quite usual to see the highest-grade natural deposits providing the lowest-grade end product, while

low-grade disseminated fluorspar occurrences often provide mill feed for acid- and ceramic-grade concentrates. Because these products are marketed as fine powders, disseminated lower-grade ores can be used to produce them.

At the present time, most metallurgical-grade fluorspar is being produced in low-wage countries by simple and often primitive mining and milling methods. The ore is brought to surface and crushed, associated waste is removed by hand picking, and fine material is removed by screening.

Ceramic- and acid-grade fluorspar concentrates have more rigid specifications but are most often produced from deposits that are not satisfactory, either physically or chemically, for metallurgical grade. As an example, it can be pointed out that many of the largest individual fluorspar bodies are found in association with granitic rocks. Such bodies are usually of a uniform character and normally contain more silica than metallurgical fluorspar specifications permit. However, for acid or ceramic uses, where a finely ground product is necessary, the silica can be eliminated by fine grinding and flotation. Such sources are thus chemically adequate and have the advantages of uniform and relatively large tonnage as compared with the small higher-grade occurrences that usually serve metallurgical purposes.

Ceramic-grade fluorspar, also referred to as "glass" or "enamel" grade, must be not less than 95 percent CaF_2 , with a maximum of 2.5 percent SiO_2 and 0.12 percent Fe_2O_3 . As mentioned

above, it must be fine-ground, ranging in mesh size from coarse to extra fine. From 100 to 1000 pounds of fluorspar for each ton of sand may be used in the manufacture of various types of glass. The vitreous enamels, so familiar on stoves and refrigerators, are made with fine-ground fluorspar as a flux and opacifier.

Acid-grade fluorspar is a fine-ground concentrate with strict chemical specifications. It must contain more than 97 percent CaF_2 , not over 1 percent SiO_2 , and a low content of CaCO_3 , sulphur and metallics. Because this material is used to produce hydrofluoric acid, uniformity and strict quality control are necessary and this concentrate commands the highest price.

Acid- and ceramic-grade concentrates can be produced by milling ores of various grades. Uniform, large-tonnage orebodies, such as those in Newfoundland, are desirable, but many custom fluorspar mills operate on ores of varying grades and produce a uniform concentrate by careful control of the feed and by making small adjustments in their milling process. Such ores are crushed, the fines are screened out, the waste is removed by gravity or heavy-media methods, and the fluorspar is recovered by fine grinding and flotation. These fine concentrates must be shipped in covered transport to avoid wind and rain losses, and are kiln-dried before use in the acid-making plant.

OCCURRENCES OF FLUORSPAR

Little serious attention has been given to a study of the geological factors that control the deposition of fluorspar because,

until recent years, supplies have been adequate and readily available. Fluorspar was obtained from the most convenient source and any scarcity could be overcome by the encouragement of small price increases. Usually, individual mines were small and the operators had neither the means nor the incentive to search for large reserves. Some fluorspar exploration has been carried on, mostly by large chemical and manufacturing companies that have recognized the value of the mineral and wish to assure their future sources of supply. Foremost among these have been E. I. du Pont de Nemours Company, Aluminum Company of America, Allied Chemical Corporation, Reynolds Aluminum Company, and others. In recent years, all these companies have been active in the United States or in Mexico, or in both countries.

Increasing consumption, particularly of acid-grade for the fluorine chemical industry, has caused some concern about future supplies in the United States. This has encouraged exploration and directed attention to the nature of the occurrences in an effort to identify the controlling factors. Characteristics which appear common to certain types of deposit are recognizable and the classification of deposits according to their environment, or origin, provides a better understanding of the occurrences. This, in turn, is of value in the search for new deposits.

Fluorspar has been found in occurrences of two general types: those associated with late granitic intrusions, and those which appear to be related to the last stages of volcanic activity as indicated by minor lava flows and hot springs. Both types are the result of the

migration and deposition of volatile or solution-borne fluorine from cooling magma.

Deposits in or related to granitic intrusive rocks are numerous throughout the world and have been the source of much of the fluorspar produced. Occurrences of this type are known in Britain, France, Germany, Spain, and Canada. The famous deposits of the Illinois-Kentucky area in the United States, although they occur in limestones, are believed to be of this type in spite of the fact that no granitic rocks have been found. The deposition of fluorspar may have been controlled by stratigraphic features or faults. Wide fault or shatter zones in granite may be replaced by fluorspar to form wide bodies. The occurrences are usually within the granitic intrusive but may be found in favourable host rocks adjacent to it. These deposits are usually the largest found and the most consistent in shape and mineralogy. They are normally medium to low in grade and characteristically contain minor amounts of sulphides such as galena and pyrite. Because of their size and consistent mineralization such deposits are usually the most attractive for development, although they may not be the highest grade.

Fluorspar, usually as veins, also occurs in areas where granitic intrusives are not known and with associations and characteristics that suggest a different though related source. The numerous occurrences of fluorspar found in close proximity to hot springs strongly suggest a common origin for both. Occurrences of this type

are known in the Rocky Mountain area from Yukon to Mexico.⁽⁵⁾ The author has seen many deposits of this type in the southwestern United States and in Mexico. These deposits are often high-grade and normally do not contain sulphides. They have been the source of large amounts of fluorspar, although the individual deposits are usually small.

In recent years, extensive occurrences believed to be of this second general type have been found in Mexico and have been the source of large amounts of fluorspar exported to the United States, Canada and other countries. Many of the recently discovered Mexican deposits are unusual in that they consist of extensive flat-lying beds or layers in limestone. They apparently were formed by fluorine depositing in the most favourable host rock of the limestone series. In Mexico these occurrences are referred to as "mantos". They are the most extensive deposits of this type known and they are important as a ready source of supply for United States industry and also because the large amounts of fluorspar already produced from them indicate the value of this particular type of occurrence. These deposits are particularly attractive in Mexico because they are shallow and flat-lying and can be mined cheaply with low-cost labour and hand tools. Flat-lying deposits of fluorspar and witherite that have been found near Lower Liard Crossing in northern British Columbia appear to be similar, although they are too remote to be important at present.⁽⁵⁾

Under varying conditions, fluorspar has been found

associated with many other minerals. The association of galena and pyrite with fluorspar in granitic deposits has been mentioned, and sphalerite also is found. The non-metallic minerals commonly associated with fluorspar are calcite, barite, and quartz; in pegmatitic occurrences, tourmaline, topaz and apatite are common. Dense, fine-grained silica is occasionally found with fluorspar in veins and also as separate occurrences near fluorspar veins. These are unusual occurrences, with no satisfactory explanation. One such occurrence has been seen in Newfoundland, two have been noted in New Mexico (near Socorro and near Deming), and another near Parral, Chihuahua, Mexico. In one instance, silica had completely replaced a shear zone, making it more resistant to weathering than the adjacent wall rocks and causing it to stand prominently above the surface like a siliceous dike. (6)

An association which has been noted in many places is that of uranium and fluorspar. Usually such associations occur in deposits related to granitic rocks, but all granitic fluorspar deposits do not contain uranium. Although occurrences of fluorspar and uranium are numerous, the author knows of none from which both minerals can be recovered economically. The most promising occurrences of this type are primarily fluorspar with a small content of uranium. It has been noted that where these two minerals occur together the fluorspar is almost always a deep blue to indigo colour. Purple fluorspar with uranium is common in the Bancroft area of eastern Ontario and the adjoining area of Quebec, occurs in the Rexspar Minerals and

Chemicals Limited deposit at Birch Island, B.C., and is reported in the Schwondorf fluorspar area of West Germany, and other localities.

Galena and sphalerite frequently occur with fluorspar, and in deposits in England, Germany and United States have sometimes been the primary ores, with fluorspar recovered as a by-product. The Khaidarkan deposit in the U.S.S.R. was primarily a source of mercury and antimony, fluorspar being recovered as a by-product.

Another source of fluorine must be mentioned for its possible importance, although it is not fluorspar and does not as yet produce large amounts. Phosphate rock mined for fertilizer contains minor amounts of fluorine and, in the United States, some plants are recovering part of the fluorine content for its by-product value and also to reduce the danger of air pollution in the surrounding area. United States phosphate rocks contain an average of about 3.5 percent fluorine. It is also reported that fluorine is recovered as a by-product in the processing of apatite-nepheline rock in the Kola Peninsula of the U.S.S.R. Large reserves of both phosphate rock and apatite exist in many countries, and will probably contribute larger amounts to fluorine supplies in the future.

WORLD DISTRIBUTION OF FLUORSPAR

As an industrial raw material with rather specialized uses, fluorspar has been obtained from the source closest to, or most convenient for, the industries consuming it. Major consumption is in

the highly industrialized countries, and major production has been confined to these countries or to nearby areas from which fluorspar can be transported at low cost. Published data on world reserves of fluorspar appear to indicate that future supplies are concentrated in certain countries and areas.* This is because the only information on fluorspar reserves comes from the developed and producing areas. Many other deposits exist but, because they are not readily available to present markets, little is known about them. The present information on fluorspar deposits and future reserves should, therefore, be considered as applying to material most readily available and not as a true measure of future world supplies. This is clearly illustrated by the rapid and large increase in Mexican production and reserves when exploration became active. Compiling reserve figures on a continental basis (as in Table 6) shows the inadequacy of present information. It is unlikely that North America and Europe hold three times the fluorspar reserves of all the rest of the world.

Generally speaking, fluorspar occurs in adequate deposits throughout the world. As the United States report "Resources for Freedom", popularly known as the Paley Report, states, "fluorspar demand is always satisfied", and it seems likely that price increases will be able to encourage production to meet most requirements. There are, however, some consuming areas where supply is becoming a problem, not because fluorspar does not occur in or near these districts, but because continued and increasing production over many years has now consumed the best deposits. An example is the highly

* See Tables 5 and 6, on pages 30 and 31.

industrialized area of the east central United States. To satisfy the demands of these areas, fluorspar deposits in Illinois and Kentucky were developed and have produced large tonnages continuously for more than 60 years. Production from these deposits appears to have reached a peak in the 1940's, and although output and reserves are still substantial new orebodies are becoming increasingly difficult and costly to find. It is probable that production from this district will decline gradually.

Consumption is now rising in the central and eastern industrial regions of the United States and, because the only other United States area with significant amounts of fluorspar lies far to the west in New Mexico, Colorado, Utah, Nevada and Montana and is subject to long, expensive transportation, future supplies have become a matter of concern for consumers. Owing mostly to higher wage rates, fluorspar production costs are greater in the United States than in other countries. This, together with rail freight costs, makes western fluorspar unattractive to eastern consumers. These factors encouraged the discovery and development of deposits in low-wage countries such as Mexico, Spain and Italy. As a consequence, fluorspar production in Mexico has risen very rapidly until in 1956 and 1957 it exceeded that of the United States. The strategic importance of fluorspar and the significance of this trend are more apparent when it is pointed out that Mexico consumes only small amounts of fluorspar. The fluorspar situation in the United States is of interest and has been cited as an example of the importance of the mineral in a highly industrialized nation. As fluorspar-consuming industries expand in Europe, Russia, Japan and China, it seems certain

that fluorspar shortages will occur.

In Europe, supplies have been adequate and in recent years Spain and Italy have exported considerable amounts to the United States. However, the main consuming nations of Europe, such as Germany, the United Kingdom and France, appear to have little more than enough fluorspar for their own needs at present. Any increases in demand would be difficult to supply from present sources. It is expected that the same factors that are increasing fluorspar consumption in the United States, namely the expansion in steel and aluminum production and the development of fluorine chemicals and products, will also eventually affect European industry. It is possible that the fluorine chemical industry, in particular, may develop considerably faster in Europe because many difficult handling and processing problems have already been solved by research and development in the United States. If demands in Europe increase, additional supplies may be obtained from Italy and Spain, possibly at the expense of exports to the United States, but new sources appear necessary. These might be found in North Africa or in the eastern Mediterranean area.

Little reliable information is available on fluorspar production, consumption and reserves in the U.S.S.R. (7) (8) The United States Bureau of Mines has estimated 1958 production at 180,000 short tons, up from 165,000 short tons in 1957, and consumption somewhat greater at 220,000 short tons. It is known that the U.S.S.R. imports fluorspar from satellite countries such as Bulgaria, and from China and Mongolia. In 1956, imports were reported to total 118,400

metric tons and in 1958, 129,600 metric tons. In addition to the fact that imports are increasing, it should be remembered that sources other than fluorspar may be contributing to fluorine supplies in the U.S.S.R. A German author⁽⁸⁾ reports that "alkali fluorides" are produced as a by-product of apatite-nepheline processing in the Kola Peninsula. It is also reasonable to expect that new deposits of fluorspar are more apt to be found in the large undeveloped areas of the U.S.S.R. than in the more crowded and more intensely explored areas of Europe.

Japan does not have adequate domestic supplies and relies almost entirely on imports. In 1958, for example, 50,000 short tons were consumed and less than 10,000 tons were produced. Supplies have been obtained from South Korea and South Africa, and probably from North Korea and China.

Canada is one of the very few industrial nations with adequate supplies of fluorspar available to consuming areas. The Canadian deposits in Newfoundland are not close to consumers but fluorspar can be shipped via the St. Lawrence Seaway to all the industrial areas of eastern Canada. They can also serve the east-central part of the United States through Great Lakes ports, and are well located to supply industrial areas on the east coast of the United States. In fact, except for the very low production cost of Mexican fluorspar, the Newfoundland deposits would be an attractive source of supply both for Canadian and for United States consumers.

WORLD PRODUCTION AND CONSUMPTION

World production and consumption of fluorspar have risen consistently since 1940 (see Table 4). Superimposed on the rather uniform increase due to the steady expansion in steel, aluminum and general manufacturing needs, there are some abrupt increases. Military demands in 1940-45 and 1952-53 spurred production and consumption, and during the past few years technical advances have resulted in sharply increased demands for use in uranium processing, missile-fuel research, and a wide variety of fluorine chemicals.

Countries producing steel and aluminum require fluorspar for every ton of metal produced. The unit amounts are small, about 4.5 pounds of fluorspar per ton of steel and about 200 pounds per ton of aluminum, but producers must have a reliable source of suitable material because there is no adequate substitute for fluorspar. The fluorspar produced in Canada serves these two industries. The present and future importance of fluorspar, however, depends on chemical consumption and will concern those countries that are most advanced industrially. For this reason the production, consumption and reserves available to the highly industrialized and technically aggressive countries, such as the United States, Japan and the U.S.S.R., and to Western Europe, are of considerable interest at the present time.

Table 4 shows the fluorspar shipped by the main producing countries over the past twenty years. It will be noted that United States production has not increased appreciably, while that of the

TABLE 4

World Fluorspar Production ^{1/}, 1940 - 1960

(000's short tons)

| Year | U. S. A. | Mexico | Germany ^{2/} | U. K. | France | Italy | Spain | Canada ^{3/} | U. S. S. R. ^{4/} | China ^{5/} | WORLD ^{6/} TOTAL |
|------|----------|--------|-----------------------|-------|--------|-------|-------|----------------------|---------------------------|---------------------|------------------------------|
| 1940 | 233.1 | 10.2 | 162.5 | 50.1 | 53.0 | 17.9 | 10.0 | 18.4 | N. A. | N. A. | |
| 1941 | 320.0 | 11.6 | 161.5 | 46.4 | 43.7 | 23.0 | 16.9 | 18.2 | " | " | |
| 1942 | 359.5 | 5.9 | 193.2 | 48.3 | 28.7 | 38.5 | 17.9 | 45.0 | " | " | 883.0 |
| 1943 | 405.1 | 24.7 | 218.4 | 60.6 | 25.6 | 33.5 | 39.5 | 122.2 | " | " | 1,137.4 |
| 1944 | 412.9 | 62.1 | 187.0 | 53.8 | 14.0 | 7.4 | 61.1 | 60.4 | " | " | 1,144.0 |
| 1945 | 323.3 | 55.2 | N. A. | 48.7 | 15.1 | 3.6 | 10.6 | 58.0 | " | " | 741.4 |
| 1946 | 277.3 | 24.1 | 34.0 | 51.9 | 23.0 | 8.6 | 9.6 | 30.7 | " | " | 576.4 |
| 1947 | 328.8 | 50.3 | 44.6 | 49.5 | 29.9 | 22.9 | 15.2 | 36.0 | " | " | 718.3 |
| 1948 | 331.0 | 82.9 | 54.3+ | 64.8 | 35.7 | 44.7 | 46.8 | 100.5 | " | " | 871.2 |
| 1949 | 236.2 | 61.3 | 55.0 | 74.5 | 43.2 | 22.9 | 65.5 | 64.4 | " | " | 754.6 |
| 1950 | 300.8 | 72.2 | 101.7 | 70.5 | 38.9 | 34.7 | 35.9 | 64.2 | " | " | 867.9 |
| 1951 | 347.0 | 73.6 | 258.2 | 83.7 | 55.0 | 45.2 | 62.4 | 74.2 | 90.0 | " | 1,130.0 |
| 1952 | 331.2 | 198.6 | 251.5 | 84.9 | 78.8 | 63.5 | 68.9 | 82.1 | 90.0 | " | 1,300.0 |
| 1953 | 318.0 | 173.1 | 267.7 | 88.6 | 69.7 | 83.5 | 56.4 | 88.5 | 90.0 | " | 1,330.0 |
| 1954 | 245.6 | 146.1 | 280.9 | 92.6 | 81.8 | 85.0 | 81.0 | 118.9 | 110.0 | " | 1,350.0 |
| 1955 | 279.5 | 200.2 | 266.3 | 96.2 | 94.8 | 110.7 | 73.6 | 128.1 | 110.0 | 100.0 | 1,545.0 |
| 1956 | 329.7 | 360.1 | 250.9 | 102.5 | 93.4 | 136.6 | 81.2 | 140.0 | 165.0 | 145.0 | 1,860.0 |
| 1957 | 328.8 | 389.8 | 216.8 | 104.4 | 103.0 | 158.9 | 97.4 | 66.2 | 165.0 | 165.0 | 1,920.0 |
| 1958 | 319.5 | 308.2 | 201.9 | 86.7 | 99.0 | 154.3 | 113.5 | 62.0 | 180.0 | 165.0 | 1,760.0 |
| 1959 | 185.1 | 341.2 | 205.7 | 93.1 | 170.9 | 170.9 | 97.3 | 83.0* | 190.0 | 220.0 | 1,854.0 |
| 1960 | | | | | | | | | | | |

Notes: * - Estimate N. A. - Not available

^{1/}Data taken from various sources, which do not always agree.

^{2/}Figures are total of East and West German production, except 1948-1950 which is W. Germany only.

^{3/}Canadian figures include Newfoundland production both before and after union with Canada in 1949.

^{4/}Figures given are estimates rather than official reports. One source gave higher figures up to 1954, i. e. 1953 - 210,000, 1954 - 250,000.

^{5/}There is recent evidence that production is expanding rapidly.

^{6/}World totals include numerous smaller producers not listed.

TABLE 5

World Fluorspar Trade and Reserves, 1958^{1/}

Main Countries
(Short Tons)

| Country | Production | Imports | Exports | Consumption ^{2/} | Reserves ^{5/} |
|----------------------------|------------|---------|---------|---------------------------|------------------------|
| United States | 319,500 | 392,200 | 3,400 | 494,200 | 22,600,000 |
| Mexico | 308,200 | - | 309,800 | Small | 6,600,000 |
| West Germany | 135,400 | 38,700 | 35,200 | 116,400 | 4,400,000 |
| U. S. S. R. ^{3/} | 180,000 | 142,500 | - | 220,000 | 8,800,000 |
| China | 165,000 | None | 113,000 | 20,000? | 1,500,000? |
| Italy | 154,300 | Small | 93,000 | 55,000? | 3,300,000 |
| Spain | 113,500 | None | 73,000 | 15,000? | 6,600,000 |
| France | 93,200 | 6,200 | 5,300 | 60,000 | 1,700,000 |
| United Kingdom | 86,700 | Small | Small | 80,000 | 1,700,000 |
| East Germany and Poland | 72,000 | Small | 28,600 | 50,000 | 1,000,000? |
| Canada | 62,000 | 30,400 | - | 85,000 | 5,500,000 |
| Union of S. Africa | 48,250 | None | 33,900 | 6,400 | 1,000,000 |
| Japan | 5,800 | 41,100 | None | 50,000 | 200,000 |
| South Korea | 1,800 | ? | 13,000 | Small | 50,000 |
| Mongolia ^{4/} | 50,000 | None | 37,500 | ? | ? |
| Total | 1,805,650 | 951,000 | 745,400 | 1,252,000 | 64,950,000 |

- Notes: ^{1/} All grades.
^{2/} Mostly estimated.
^{3/} Production largely in Asiatic Russia; consumption largely in European Russia.
^{4/} Little information available.
^{5/} Indicates only the order of magnitude.

TABLE 6

World Fluorspar Trade and Reserves, 1958

By Continents ^{1/}
(Short Tons)

| Continent | Production | Imports | Exports | Consumption | Reserves |
|----------------------|------------|---------|---------|-------------|------------|
| North America | 689,700 | 150,100 | 18,800 | 580,200 | 34,700,000 |
| South America | 8,800 | Small | None | 10,000 | 450,000 |
| Europe ^{2/} | 745,100 | 112,000 | 142,600 | 496,000 | 17,700,000 |
| Asia ^{1/} | 312,600 | 41,000 | 110,000 | 170,000 | 10,550,000 |
| Africa | 48,200 | None | 28,300 | 11,000 | 6,250,000 |
| Totals | 1,884,400 | 303,100 | 299,700 | 1,267,200 | 69,550,000 |

Notes: ^{1/} Some European and most of Asian figures are estimated.

^{2/} U.S.S.R. production is credited largely to Asia, and imports and consumption are credited largely to Europe.

United Kingdom, France and Germany has approximately doubled. In the same period, Canadian production had increased sevenfold up to 1956 and Mexican production had increased fortyfold until in 1957 it was the largest in the world. It is also of interest to note that the two largest consumers, the United States and the U.S.S.R., import more than half of their fluorspar requirements, as shown in Table 5. (7)

The United Kingdom, France, and East and West Germany each produces and consumes from 50,000 to 120,000 short tons annually. Any additional demands in these countries would probably be difficult to fill from domestic resources. West Germany and Italy appear to have supplies in excess of their own requirements, but both are highly industrialized and can be expected to be among the first in Europe to increase consumption as demands for fluorine chemicals grow. Of the European producers, Spain appears to be about the only country with a significant production and only a small domestic demand.

From information available at present, it appears that Europe has sufficient fluorspar for present demands but that only limited reserves are known for the several industrial nations that can be expected to be active in developing and producing fluorine chemicals and to be aggressive in marketing them.

Little detailed information is available regarding production and consumption of fluorspar in the U.S.S.R. Fluorspar consumption often can be estimated when steel and aluminum production is known, but, because the U.S.S.R. production of these metals is not known with

certainty, the statistics for fluorspar cannot be accurate. It has been suggested that fluorine-based missile fuels have been developed in the U.S.S.R.; if true, this would indicate a research background fully capable of a military and industrial fluorine production comparable to that available in the United States. It is possible that fluorine chemical developments in the U.S.S.R. may be technically advanced but limited at present to military requirements.

Information on U.S.S.R. fluorspar production, capacity and reserves has not been published for many years, and some present estimates are based on data compiled in the 1930's. In view of the aggressive mineral-development policies being pursued, and the evidence of growing ability in research, design and production, it is reasonable to assume an effort has been made to develop fluorspar reserves.

Fluorspar has been mined in China for many years, mainly for export because local demands were small. Recently, however, there has been evidence that production has been rising rapidly. The expanding output of steel is consuming increasing amounts, substantial tonnages have been exported to the U.S.S.R. in recent years, and during 1959 metallurgical-, ceramic- and acid-grade concentrates were offered for sale by a state trading corporation. The United States Bureau of Mines estimates Chinese production as at least 165,000 tons in 1958 and 220,000 tons in 1959.

In South America, Africa and Australia, occurrences of fluorspar are known and a limited production has been recorded. In

the continents, local markets are not large enough to encourage the development of a healthy industry, and transportation to foreign markets is too costly. For reasons such as these, there is a considerable world trade in relatively small amounts of fluorspar by the established low-cost, large-tonnage producers. For instance, the youthful steel industry of India has imported fluorspar from Mexico and China to satisfy its immediate needs, although undeveloped sources are known in that country. These apparent inconsistencies in mineral development and trade become more understandable when it is appreciated that, unlike metallic minerals, which are produced in large plants at low unit costs and for which world markets and trade patterns are well established, fluorspar is produced in smaller operations at higher unit costs and is more expensive to handle and transport. These factors result in fluorspar trade being generally limited to the closest market and the cheapest transportation, and the fact that international transoceanic trade does occur is entirely due to the essential nature of fluorspar and to shortages in the industrial nations.

FUTURE PRODUCTION TRENDS

World production and consumption of fluorspar in past years has been very largely controlled by activity in the steel and aluminum industries. These two industries will continue to be a fairly uniform and basic market.

The additional demands for fluorspar that are expected in order to satisfy the developing fluorine chemical industry will

certainly exert pressure on present sources of supply, and it seems probable that adjustments in price, production and trade patterns will occur. Although larger amounts of metallurgical-grade will be needed, it is expected that most of the future demand will be for acid-grade. Such a market would probably be more uniform and consistent than the present one and might expand to large dimensions. Acid-grade fluorspar can be made without difficulty from the siliceous deposits in granite, which often are large-tonnage but are rarely suitable for metallurgical use. These considerations strongly suggest that larger deposits to feed larger mills and acid plants will be needed, and that, as tonnage increases and unit costs decline, lower grades will be acceptable as mill feed.

It also appears probable that large amounts of fluorspar, or fluorine in other forms, will be recovered from phosphate rock and fluorapatite deposits in the future. In the United States, substantial amounts of fluorine will be available in phosphate-rock deposits when complete and efficient recoveries can be made. The by-product recovery of fluorine from fluorapatite has been reported from the U. S. S. R., and rocks of this or somewhat similar types are known in many other countries. Several large deposits of alkaline rocks containing small amounts of niobium and uranium are known in Canada, and others have been reported in Africa. Some are known to contain fluorine, in fluorapatite, although little attention has been paid to the fluorine content. At present such sources are not attractive but it seems quite probable that large amounts of by-product fluorine will be

recovered from them in the future, possibly by 1980.

FUTURE SOURCES OF FLUORSPAR AND FLUORINE

Assuming that the demand for fluorspar continues to increase as expected--and that shortages develop, as seems certain--it is of interest to review all potential sources of fluorspar, and those fluorine-bearing materials that may supplement fluorspar supplies.

At the present time there are fluorspar deposits in Canada, United States and Mexico which are mineralogically adequate but, because of their location or marginal economics, are not profitable to operate. In some cases a small price increase would stimulate production, and in other cases production might result from entirely independent factors such as the extension of roads and railways in British Columbia or Mexico.

In spite of the low production of fluorspar credited to South America, Africa and Asia, deposits have been found, and it is likely that others are present. The present low production results from a lack of profitable markets, or of transportation to markets, rather than from a lack of fluorspar. It is thus reasonable to expect new sources of supply to appear as demand and price increase.

Such additional sources are reassuring but not entirely satisfactory to present consumers, because they may be affected by political or economic factors in the source country, and by shipping problems and costs, over which the consumer has little or no control. For such reasons, consumers are now becoming interested in other

possible sources of fluorine which show promise of becoming large-scale suppliers--for example, phosphate rock deposits in the United States and fluorapatite deposits in the U. S. S. R.

Discoveries of new deposits of cryolite similar to the one in Greenland are possible, although other large bodies of cryolite are not known. Fluorine does occur in or with a few other minerals, such as cassiterite, topaz and mica, but not in amounts that encourage economic interest.

Fluorine has been recovered, both as a gas and as an artificial fluorspar, from phosphate rock in the United States, although neither the economics nor the tonnage of such production is as yet significant. It has been reported that increasing amounts of fluorine are being obtained from this source and that the Kaiser Aluminum Company contracted for such material in 1957; this report is significant because it indicates that earlier problems in the production of fluoride in a form that could be used by aluminum manufacturers have been solved. Most of the research on the method, and most of the production to date, have been by the Tennessee Valley Authority in the United States. The larger phosphate plants could recover fluorine efficiently but the small operations, which represent a large proportion of the industry, could not. Therefore, although the potential supply from this source is very large, recovery on a large scale is not yet technically efficient or economically attractive. Essentially, the problem is that of producing and processing corrosive and toxic fluorine from large volumes of material. In addition to the profit to be made recovering fluorine as a

by-product, the phosphate operators have been encouraged to make this recovery by recurring litigation concerning the damage to plant and animal life by toxic fluorine that has been wasted to the atmosphere. World reserves of phosphate rock are very large. In 1952, the writers of the Paley Report conservatively estimated reserves of considerably more than 100 billion tons, averaging 20 percent P_2O_5 and about 3 percent fluorine. It is apparent that the phosphate industry can supply large amounts of artificial fluorspar, or fluorine in other forms, when the demand and prices justify the additional equipment necessary to extract it. The Paley Report estimated that by 1975 the equivalent of 650,000 tons annually of artificial fluorspar would be available from phosphate rock. Such figures now appear to have been too optimistic, but they serve to illustrate the potential of this source.

The report⁽⁸⁾ that "alkali fluorides" are being recovered at an apatite-nepheline processing plant in the Kola Peninsula in the U. S. S. R. is of technological interest. The raw material contains about 1 percent fluorine and reserves are estimated at 1,000 million tons. The plant is said to produce apatite and nepheline concentrates, titanium dioxide, vanadium-titanium iron, alkalis, portland cement, aluminum silicate, rare earths, superphosphate, and fluoride. The capacity of this plant is reported to be four million tons yearly, and, assuming an operation of even two million tons, fluoride production may be estimated at about 25,000 tons yearly after allowing for processing losses of 20 percent. There are other plants of this type in the U. S. S. R., although it is not known that fluoride is being recovered at them. The fluorine

content of this raw material is considerably lower than that of the phosphate rocks in the United States, but the large tonnage operation and the several products being recovered may make the operation economically attractive even by Western standards. It also should be noted that the economics of the operation may not be of primary importance in a planned economy such as that of the U.S.S.R., if the production is considered necessary or is a part of long-term plans.

FUTURE DEMANDS FOR FLUORSPAR

Evidence from many sources points to an increasing importance and a greater consumption of fluorspar. The expanding production of steel and aluminum has been estimated by such studies as the Paley Report in the United States (Vol. II, pages 88 and 125), and the Gordon Report (by the Royal Commission on Canada's Economic Prospects, 1957) in Canada (page 218). These suggest that steel production will increase 62 percent in the United States and about 300 percent in Canada by 1975, and that, in this period, aluminum production will increase by 350 percent in the United States and by a larger percentage in Canada. Obviously such increases would demand a much larger consumption of fluorspar than at present and the magnitude of this greater consumption in the United States is suggested, again by the Paley Report, as the difference between the 234,000 tons of fluorspar consumed in steel and aluminum in 1960 and the estimated consumption of 561,000 tons in 1975. Increases of 100 percent are also estimated for fluorspar to be used in glass, ferro-alloy and

miscellaneous industries.

Considering these trends, it seems certain that larger amounts and more reliable sources of metallurgical-grade fluorspar must be found. In 1959, the United States steel industries consumed about 218,700 short tons of metallurgical fluorspar. In this year, imports of metallurgical-grade from Mexico totalled more than 199,400 short tons, and from other countries about 16,800 tons.

In other words, the United States steel industry depends very largely on imports for metallurgical fluorspar. A similar situation exists in Canada, where about 20,000 tons of metallurgical-grade fluorspar are consumed annually, of which about 2,000 tons are produced domestically. If the consumption of metallurgical-grade fluorspar doubles in the next fifteen years, adequate supplies will likely be difficult to obtain. This outlook is clear to the larger United States consumers, although it tends to be obscured by United States producers advocating tariffs in order to retain their markets.

One possible solution to this problem would be to produce metallurgical-grade by agglomerating flotation concentrates from the lower-grade deposits available in the United States. This has been tried, but it has proved difficult to make a product acceptable to the steel industry. Shortages and higher prices for metallurgical-grade would encourage the production and use of more satisfactory pellets. At present, metallurgical-grade fluorspar is obtained from the highest-grade natural deposits and, because these are usually the first to be developed and depleted, it seems certain that shortages will occur and

some other sources of this material will have to be found.

Although the lack of fluorspar for metallurgical purposes seems serious enough, the question of future supplies for hydrofluoric acid and fluorine chemicals is even more pressing. The Paley Report showed that 124,000 tons of fluorspar were used for hydrofluoric acid in 1950 and estimated that 390,000 tons would be required in 1975, an increase of 200 percent. However, in 1960 about 370,000 tons of fluorspar were consumed for this purpose, so it is evident that consumption is rising at a rate considerably steeper than that estimated.

These figures show that the carefully prepared Paley estimates of future U.S.A. fluorspar needs have been too conservative and that the threatened deficiency in 1952 is even more serious in 1961. Estimates for future needs in steel and aluminum can be made with reasonable accuracy, because these are established industries where long-term trends can be studied and plans made to meet them. The fluorine chemical industry, however, is new and, because it is expanding at a very fast rate, its future requirements are difficult to estimate. This uncertainty concerning the amount of future consumption, in an industry which is already consuming almost one-third of the total fluorspar production, has become a critical problem to the major consumers.

Most of the trends of industrial development can be clearly seen, although they are not always clearly appreciated. Energy sources have changed from animal effort, to coal, oil, electricity, and now nuclear fuels. Construction materials have changed from raw, natural materials, such as wood and stone, to highly processed materials such

as steel, cement, aluminum, asbestos and plastics. Textiles have changed from natural fibres to synthetic fibres, and our tools and toys, appliances and conveniences from simple items made from natural materials to complicated machines that no one man can produce and only specialists can understand or repair. These trends are so obvious that they are not worthy of comment except to point out that almost all depend on chemical developments. The fact that many of the new materials do not look like chemicals may be a tribute to designing and manufacturing skills, but it is indisputable that most of the articles we use depend, at some stage, on chemicals and chemistry.

Against the background of these general trends, the potential of fluorine chemicals appears important and impressive. Their wide range of end products helps to produce gasoline, uranium, metals, plastics, fabrics and chemicals--for purposes as varied as fluoridation of water, killing of insects, refrigeration, and propelling of shaving cream out of containers! It has been announced recently that fluorine and fluoride chemicals are being used as oxidizers in rocket fuels. At present, the volume used for this latter purpose is small, but, because these materials appear to approach the ultimate in power sources for rocket fuels, the fantastic power they provide is a rich prize for research. The immediate interest is, of course, in the development of a military asset with tremendous prestige value, but commercial development and applications would certainly follow.

The slackening of industrial activity during 1958 and 1959,

particularly in steel and aluminum production, has tended to relieve the expected shortages in fluorspar. But although supplies are adequate at present, the exploration activity of United States companies, both in that country and in Mexico, and the construction of one hydrofluoric-acid plant in Canada and several in the United States, indicate that future requirements may be expected to increase significantly.

When all these factors are considered and the future potential of fluorspar and fluorine is viewed in the light of developments in the past few years, the possibilities are impressive. It seems certain that there will be further development of fluorine chemical applications and that, eventually, fluorine will occupy a place somewhat analogous to that of sulphur at the present time. Like sulphur, which is rarely seen in its natural form, it will be used in the manufacture of many of the things we use and consume, and like sulphur, it will be the basis of a very large and important acid and chemical industry.

CANADIAN FLUORSPAR DEPOSITS AND PROSPECTS ⁽⁹⁾

Canada is one of the few countries in the world which have adequately developed deposits of fluorspar readily available to industrial areas and large reserves for future demands. The major deposits and the largest reserves are located in the Burin Peninsula of southeastern Newfoundland. These orebodies are more than 1,000 miles from the industrial area of southern Ontario and Quebec, but shipping via the St. Lawrence Seaway ensures relatively cheap and reliable transportation.

Production has also been obtained from numerous small mines near Madoc in eastern Ontario, from the Rock Candy mine in southern British Columbia, and from a few smaller occurrences in Ontario and Nova Scotia. Most of the deposits could produce again if required. In addition to mines and areas that have produced fluorspar, two large-tonnage occurrences of fluorspar have been found in British Columbia. Although it is not certain that either could produce profitably at present because of low grade or distant location, they are important as potential sources.

It might also be noted that Canadian fluorspar reserves are the known resources of a mineral for which no active large-scale search has ever been made. All the deposits of interest at the present time were found at least 20 years ago. It is reasonable to expect that other deposits will be found when it becomes necessary or profitable to search for them.

Newfoundland^{(10) (11)}

The Newfoundland fluorspar deposits occur as veins and mineralized zones in a granitic mass near the village of St. Lawrence on the southeastern coast of the Burin Peninsula. Forty veins have been found in an area about 5 miles square. They range from a few inches to more than 50 feet in width, and some are more than a mile in length. One deposit has been mined to a depth of 900 feet and another to more than 500 feet, with no apparent change in the mineralogy or the conditions that apparently controlled the ore deposition. The narrower, high-grade

veins often contain more than 90 percent CaF_2 and the wider, lower-grade zones contain 35 percent CaF_2 or more. The St. Lawrence area has produced more than 1,300,000 tons of fluorspar to the end of 1958, and by far the largest part of this tonnage has been taken from the two mines mentioned below. The area is only partially explored, because the surface is mostly covered by overburden and there has been little incentive to look for new deposits while large tonnages are available in existing mines. The unexpected discovery of several veins by surface excavation, such as road building and ditching, and by underground development, suggests that the resources are not yet completely known.

Two companies produce fluorspar from the Newfoundland deposits. The St. Lawrence Corporation of Newfoundland Limited has operated since 1933 and has produced from several veins, of which the more important are: Iron Springs, Lord and Lady Gulch, and Blue Beach. Veins range from a few inches to 20 feet in width and assay from 40 to 95 percent CaF_2 . The silica content in the wider veins may be up to 15 percent. Because of this silica content and some dilution by wall rock, the ore as mined normally runs 50 to 55 percent CaF_2 . The company has a heavy-media separation plant that has been used to produce a concentrate, running about 75 percent CaF_2 , for acid plant feed. It also has a flotation mill that produces acid-grade concentrate when markets are available. Other veins on the property are the Hares Ears, Church, and Scrape.

Newfoundland Fluorspar Limited, a subsidiary of the Aluminum Company of Canada Limited, draws all its fluorspar from one mine, the Director. The Director mine is the most important deposit found to date in Newfoundland, and is probably the largest fluorspar mine in the world. The vein has a length of 6,000 feet and a width varying from 0 to 70 feet, and ore lenses carry CaF_2 contents of 60 to 80 percent. Other important deposits on the property are the Tarefare, Grebes Nest, Big Meadow and Canal veins. Milling consists of crushing and heavy-media separation at a plant having a rated capacity of 30 tons per hour. The product of this plant, a concentrate running 75 to 80 percent CaF_2 , is shipped to Arvida, Quebec, where it is improved by flotation and used in aluminum production.

In 1956, a year of full-scale operation, the two Newfoundland producers shipped 139,801 tons of fluorspar concentrate averaging about 75 percent CaF_2 . A higher-grade product could be produced with existing facilities, although the tonnage would be somewhat reduced. Mining presents no serious difficulties, but heavy flows of water in the mines cause operating problems and pumping accounts for a large proportion of the production cost. There has been speculation that the cost of pumping may limit the depth to which the Newfoundland fluorspar deposits can be operated. Although water is certainly a serious problem, and its removal a considerable part of operating cost, it should be noted that the Iron Springs shaft extends to a depth of 901 feet below surface (861 feet below sea level) and the Director shaft to a

depth of 600 feet below surface and these mines have produced large tonnages of fluorspar in spite of water difficulties. Water is a problem but not a critical one.

Fluorspar reserves in Newfoundland are not accurately known, because both operating companies have adequate resources for the immediate future and present market uncertainties discourage long-term exploration expenditures. Unofficial estimates have suggested reserves of between 10 and 20 million tons. Using available data and the standard geological assumptions that veins will have a depth of at least half of their horizontal length and that there will be no appreciable change in mineral content with depth, these estimates appear to have considerable justification. There is no doubt that the reserves are large and will be adequate for many years.

Occurrences of fluorspar have been found at several other places in Newfoundland and in Labrador, but none of economic importance is known at present.

Nova Scotia.

Fluorspar associated with barite and calcite occurs in veins along the east side of Lake Ainslie and near North Cheticamp, on Cape Breton Island. Veins up to 10 feet wide occur near Lake Ainslie but the material is mostly barite with some fluorspar as disseminated grains and in scattered pods. It has been estimated that the best deposits would run about 35 percent CaF_2 , but on the whole the deposits are too small to be attractive. Prior to 1939, attempts were made to

work the veins for barite, with little success. Between 1940 and 1943, about 1,500 tons of fluorspar concentrate were produced by screening and cobbing and were shipped to Canadian steel mills. Grade is reported to have been 60 to 65 percent CaF_2 . The small tonnage, the low grade, and the difficulty in making clean separations of the fluorspar and barite have discouraged operations, except under wartime demands.

Small occurrences of fluorspar have been reported at a few other locations in Nova Scotia.

New Brunswick

Six occurrences of fluorspar have been reported from New Brunswick. All are small and none appears to have economic potential.

Quebec

About 20 occurrences of fluorspar have been reported in the province of Quebec, but none of economic value is known. Most of the discoveries have been made in a narrow band north of the Ottawa River between Ottawa and Montreal. Eighteen tons of clean-picked fluorspar grading 92 to 98 percent CaF_2 were shipped in 1944 from a property in Pontiac county to Dominion Magnesium Limited. This shipment constitutes the total production of fluorspar in Quebec.

Ontario

A large number of fluorspar occurrences and deposits have been found in Ontario in a long arc from Port Arthur, along the north shore of Lake Superior to the lower Ottawa River; most are occurrences only, of no economic interest. The Madoc district has had a fairly

continuous production since 1905. Small shipments have also been made from the Wilberforce-Harcourt area, near Bancroft.

The Madoc area of Ontario has produced about 115,000 tons of fluorspar since 1905. The individual mines have been small, and operations have been hampered by lack of ore reserves, capital, equipment and consistent markets. The highest rates of production have been achieved during war periods and from 1945 to 1951. During World War II, the Federal Government made several small loans of funds, which were nearly completely repaid, to operators in the area, to encourage fluorspar production at a time when demands were high and supplies were not adequate. It is significant that the work done has resulted in the production of more than 90,000 tons of fluorspar since 1940. It appears quite possible that the Madoc area could produce more fluorspar if there were an incentive to search for it and if funds were available for exploration and development work. It is worth noting that mining has been limited to shallow depths (250 feet or less) because of heavy water flows, which the small mines did not have the equipment to control.

Numerous occurrences of fluorspar have been found in the Wilberforce-Harcourt area. Some shipments of ore have been made, but none of the properties has been able to reach consistent production and the possibilities of the area do not appear encouraging. The occurrences found to date have consisted of small veins and zones carrying disseminated fluorspar, sometimes with low uranium values. The area is of interest but cannot be considered promising at the present time.

It is of interest to note that north of Lake Superior and on the long arc referred to above, an area near Chapleau contains large bodies of alkaline rocks in which deposits of magnetite-apatite have been found. These deposits also contain small amounts of niobium and uranium, and fluorine in the form of the CaF radical in apatite. Tests have indicated that iron and apatite could be recovered from one deposit by large-scale operations, and on such a scale the minor constituents, such as niobium, uranium and fluorine, might also be recovered. There are thus two possibilities in the area, that of finding economic deposits of fluorspar and that of by-product fluorine recovery from an iron-apatite plant.

Manitoba, Saskatchewan and Alberta

There appears to be little chance of fluorspar deposits being found in the sedimentary and soil-covered areas of the prairies, and no occurrences have been reported from the Precambrian areas of these provinces.

British Columbia

Three large deposits of fluorspar have been found in British Columbia, and one of them, the Rock Candy, has produced considerable amounts of fluorspar.

The Rock Candy mine, owned by The Consolidated Mining and Smelting Company of Canada Limited, is located near Grand Forks, British Columbia, just north of the international boundary. The deposit was discovered in 1916 and it produced intermittently from 1918 to 1942.

Data available indicate that production totalled more than 42,000 tons of fluorspar concentrate. Consolidated Mining and Smelting no longer requires fluorspar at Trail, since it uses, instead, by-product fluorine recovered from the treatment of phosphate rock in its fertilizer plants.

The Rock Candy deposit occurs in a large body of syenite of Tertiary age, and is in the form of a zone of veins over widths up to 45 feet. The orebody is known to be 550 feet long, and has a vertical depth of at least 450 feet as indicated by surface exposures on a slope and by underground work. The mineralized zone is lengthy and may possibly contain other deposits of fluorspar. Minerals in the zone, in order of abundance, are: fluorspar, barite, chert, quartz, calcite, pyrite, and kaolin. No figures on the percentage of fluorspar are available, but from the production record it is evident that the average grade is satisfactory. Engineers who have examined the deposit believe that large reserves remain. This deposit could probably produce a satisfactory grade of fluorspar on short notice if it were in the interest of the company to resume production.

An occurrence of fluorspar near Birch Island, British Columbia, has been known for many years and recently was further investigated when it was found to have associated uranium. Rexspar Minerals and Chemicals Limited tested the property and attempted to develop it as an uranium producer, with the possibility of recovering fluorspar at a later date. The fluorspar is disseminated and recovery is not simple. Also, the deposits containing the most uranium do not contain the best concentrations of fluorspar. Although a considerable

tonnage of fluorspar has been found, the relatively low grade and the treatment problems make a profitable operation difficult. Recent reports state that production would be by open pit methods.

Numerous occurrences of fluorspar, witherite and barite were found near Lower Liard Crossing in northern British Columbia several years ago. Limited exploration work by Conwest Exploration Company Limited has shown that the mineralization is extensive and has indicated several large deposits. However, the remote location and the high transportation costs make development unattractive at present. From the limited information available, the occurrences appear to be interesting and unusual as compared with other Canadian fluorspar deposits. Fluorspar is found in a roughly horizontal layer, close to the surface, in an area of sedimentary rocks. Hot springs are found in this district, and the description of the deposits makes them seem very similar to extensive, flat-lying deposits from which large tonnages of ore are being obtained in Mexico. The limited and scattered exposures of ore available for study have indicated that satisfactory-grade material is present, and that fluorspar mineralization occurs over a large area. Preliminary estimates indicate a large tonnage, assuming that the ore is continuous between the present exposures. At the present time a deposit at this location could not be operated profitably, but it will undoubtedly become important when fluorspar prices increase and transportation improves.

Yukon, Northwest Territories and Arctic

Several occurrences of fluorspar have been reported from the Yukon and a few from the Northwest Territories. No major deposits have been found. Because of geography, only an exceptional occurrence, for example one similar to the Greenland cryolite body, would be of interest at the present time.

CONCLUSIONS

A study of the occurrences, characteristics and uses of fluorspar shows that it is an unusual and valuable mineral. Its unique properties make it necessary as a flux for steel and ceramics, essential in the electrolyte for the manufacture of aluminum, and the vital raw material for the fluorine chemical industry. On the basis of developments during the past ten years, it is apparent that fluorine chemicals will become important industrially and economically. Their wide range of uses, both as inert materials to contain active and corrosive chemicals and as highly active chemicals in metallurgical and chemical processes, makes them key factors in modern chemical research and industrial development.

Fluorspar is not a scarce mineral, and world reserves are believed to be adequate, but at present many of the producing areas are not close to the main consuming areas. This fact is important, since fluorspar is a heavy mineral with a high weight-to-value ratio. It is particularly noteworthy that both the United States and the U.S.S.R., the largest consumers, must rely on large-scale imports to satisfy

their requirements.

The highly industrialized nations are the main consumers of fluorspar, and consumption is expected to increase steadily as steel and aluminum output expands. In addition, it is expected that large tonnages of high-grade concentrate will be required to satisfy the rapidly expanding fluorine chemical industry. These combined increases will be difficult or impossible to satisfy from present sources; hence production will have to be expanded at these sources, and new ones must be found and brought to production. It thus appears likely that the price of fluorspar will increase and that renewed efforts will be made to recover fluorine from phosphate rock in the United States. Efforts are also being made in the United States to recover more fluorspar from low-grade deposits by improved mining and milling methods.

The increasing importance and the rising value of fluorspar suggest that known occurrences should be evaluated and an active search made for new deposits. Producers should be encouraged to supply concentrate suitable for fluorine chemical manufacturing, and chemical companies should be urged to explore the market opportunities in this industry.

Substantial deposits of fluorspar are known in Canada, particularly in Newfoundland and in British Columbia, and widespread minor occurrences in Ontario and elsewhere suggest that new deposits may be found.

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