STATE OF ILLINOIS
ADLAI E. STEVENSON, *Governor*
DEPARTMENT OF REGISTRATION AND EDUCATION
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DIVISION OF THE
STATE GEOLOGICAL SURVEY
M. M. LEIGHTON, *Chief*
URBANA

REPORT OF INVESTIGATIONS—NO. 141

FLUORSPAR AND FLUORINE CHEMICALS

Part I - Economic Aspects of the Fluorspar Industry

BY

N. T. HAMRICK AND W. H. VOSKUIL

Part II - Fluorine Chemicals in Industry

BY

G. C. FINGER AND F. H. REED

In cooperation with the Office of Naval Research and the University of Illinois

AUG. 26th 1818

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Topographic Mapping in Cooperation with the United States Geological Survey.

This report is a contribution of the Fluorspar Division and the Mineral Economics Section.

November 15, 1948

CONTENTS

PREFACE

THIS CIRCULAR has been prepared for the purpose of presenting the economic aspects of the fluorspar industry and a review of the chemical developments affecting the use of fluorine chemicals in industry. Wide applications of fluorine, derived from fluorspar, and of the compounds of fluorine, are reflected in the rapid increase in overall demand for fluorspar and in the growth in demand for it for the newer uses. This situation leads to an interest in fluorine resources not only as they exist in this country but in foreign countries.

This circular was prepared in conjunction with work in progress on Contract N6ori-71; Task 14, between the Office of Naval Research and the University of Illinois as contracting agent for the State Geological Survey.

M. M. LEIGHTON
Chief

PART I.—ECONOMIC ASPECTS OF THE FLUORSPAR INDUSTRY

ILLUSTRATIONS

PART I

ECONOMIC ASPECTS OF THE FLUORSPAR INDUSTRY*

BY

N. T. HAMRICK AND W. H. VOSKUIL

INTRODUCTION

FLUORSPAR has become a major raw material for the chemical industry. It is also being used in increasing quantities in the steel, aluminum, glass, enamel and other process industries. Elemental fluorine and hydrofluoric acid, derived from fluorspar, are playing an increasingly important role in the manufacture of numerous fluorine compounds of great industrial importance.

Simultaneously with the rapid decrease of reserves of high-grade domestic fluorspar has come this enormously increased demand for a high purity product for the chemical industry.

This has resulted in two things, (1) an increased effort to improve methods of beneficiation, and (2) an increased interest in research to provide an alternate source of fluorine — the chemical which mushroomed into importance during World War II.

Fluorspar (more properly known as fluorite) is the most important source of fluorine today. It is calcium flouride (CaF_2) which in pure form contains 48.7 percent fluorine and 51.3 percent calcium. It has a specific gravity of 3.0 to 3.25, a hardness of approximately 4, and a melting point of 1360°C. It is a fairly heavy, medium-hard crystalline, or massive granular mineral weighing approximately 188 to 203 pounds per cubic foot. It is quite brittle and breaks with a conchoidal or splintery fracture, the crystals having a distinct octahedral cleavage.

It ranges from transparent to a translucent white and in colors from yellow, blue, lavendar, and rose to the rare orange, brown or black. When ground all fluorite is white.

The rare flawless, transparent fluorspar (or optical spar) is used in making optical lenses because it disperses light faintly and has a very low index of refraction.

Fluorspar usually occurs in a gangue of varying quantities of limestone, calcite and quartz with minor amounts of sphalerite, galena, pyrite, and chalcopyrite. It occurs generally in roughly vertical veins in beds of limestone or sandstone and in blanket deposits interspersed with clay.

Since the early war years, fluorspar has become one of our most critical nonmetallic minerals. This resulted from the demand for greatly increased tonnages in the steel industry, in the production of synthetic cryolite for the aluminum industry, and in the production of hydrofluoric acid, a large percentage of which was used during the war as a catalyst in the production of high-octane gasoline and in Freon to be used as a solvent and propellant for insecticides.

This, in conjunction with an upward price trend, has given added impetus to better methods of beneficiation in order to recover a larger percentage of calcium fluoride from the ore.

For many years the United States has been the world's largest producer of fluorspar (fig. 1) with the result that the early lush days of surface mining are over and production costs have risen sharply. In the face of continuing unprecedented demands, we must face this situation of rapid depletion of reserves with a determination to find new sources of supply, better methods of beneficiation, and maintain a national policy of tariffs that will permit importation of ample quantities of foreign spar and at the same time safeguard domestic producers.

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* Presented before the Fall Meeting of the Industrial Minerals Division, A.I.M.E., St. Louis, Mo., October 15, 1948.

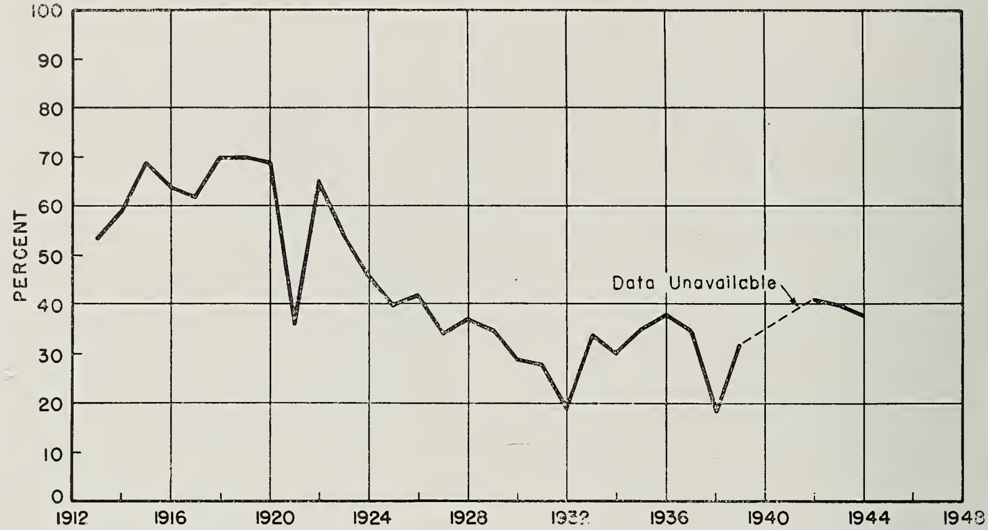


FIG. 1.—Percentage of world fluorspar production in the United States, 1913-1944. Figures for 1945-48 are not yet available as of January 1949.

PRODUCTION

The first recorded technical use of American fluorspar was in 1823 when a few ounces were used in making hydrofluoric acid. It is also reported that some Connecticut spar, selling for $60 per ton, was used with magnetic iron pyrite in smelting copper ores as early as 1837.

Although the Illinois-Kentucky area has produced more than three-fourths of our national supply to date, the first serious attempt at mining in that area seems to have been that of a company headed by President Andrew Jackson which undertook the development of a site in Crittenden County, Kentucky, in 1835.[1] Not far from the original site a mine is still in operation. About four years later, in drilling a well on the Anderson farm across the Ohio River in Illinois, some fluorspar was encountered with galena and discarded as a waste product. This marked the opening of one of the world's richest areas of fluorspar, yet it passed without acclaim since its value was unknown at the time.

Mining and marketing of the mineral did not begin until the early seventies, and then on a very limited scale because the chief uses were in making hydrofluoric acid and in the manufacture of opalescent glass and enamels, which required only small quantities. In 1888 the basic open-hearth process for the manufacture of steel was introduced into the United States and the fluorspar industry was launched on an era of rapid expansion.

Up to that point fluorspar had had a long but relatively unimportant career. Medieval iron and steel makers had probably used fluorspar as a fluxing agent without realizing it, since fluorspar is frequently found with limestone, which was then used as a fluxing agent. Georgius Agricola, early in the Italian Renaissance, mentions fluorspar as a usable agent.

Long before Columbus came to America, the Mound Builders were using fluorspar as their most precious jewel. Birds and animals, frequently turtles, were carved from the highly colored pieces and sometimes these were set in silver. An occasional piece of this early jewelry is to be found in a museum today, although the only known large collection is that of some two hundred pieces at King Mounds, Wickliffe, Kentucky.[21] It is believed, however, that during all this period not more than 25 pounds of fluorspar were mined. Since fluorspar is resistant to weathering agencies that the associated softer materials cannot withstand, it is likely that pebbles became exposed at the surface and were used by these early peoples. These simple uses of fluorspar are in as great contrast with its industrial importance today as are the lives of the people in that day and this.

The industrial importance of fluorspar really dates back to the introduction into America in 1888 of the basic open-hearth process for the manufacture of steel. Our records dating back to 1880 (table 1) show that during the period 1880-1888 production did not exceed 6,000 tons per year and the price ranged from $4.00 to $5.00 per ton. By 1902 production had reached nearly 50,000 tons and the price had increased to $5.66. Continued low prices during these early years stifled the incentive to produce beyond immediate demand. Lack of good transportation and high freight rates did much to localize consumption in a fairly limited area. Because much of the country's steel production was centered around Chicago and Pittsburgh, the Illinois-Kentucky area had the advantage of a relatively short rail haul to Chicago and of barging facilities to the Pittsburgh area. There was no reported production outside of Illinois and Kentucky until 1902.

From then on the demand increased rapidly, so that by the close of the first World War in 1918 production had reached almost 264,000 tons (tables 1 and 2) and the price had skyrocketed to $20.72. After a brief retrenchment following the war, the market recovered and remained fairly constant until the early 1930's when the depression brought about a general curtailment of mineral production.

By 1932 production had fallen to approximately 25,000 tons and the price to $15.54 per ton. From that point on there was a steady increase until 1944, when production reached a peak of almost 414,000 tons with a price of $30.22 per ton. Had it not been for price ceilings, the price would doubtless have been considerably above that figure.

Although the immediate postwar years showed a characteristic decrease in both production and consumption, the price has continued to increase steadily until it has reached the highest point in recorded history (table 3 and fig. 2).

During World War I the United States was producing about 70 percent of the total world production (fig. 1). That percentage has decreased to approximately one-third of the total production today, due not to decreased United States production, but rather to increased production and increased industrial development in other countries. As our supplies decrease and it becomes more necessary to look to foreign sources—or to some new source of fluorine—the foreign situation becomes of vital interest to our own economic structure.

Figure 2 shows that United States production has followed the price curve rather closely except during World War II when price ceilings restricted prices during a period of unprecedented demands. Production declined rather sharply in the final months of 1945 during the adjustment to peacetime activities but has since shown a surprisingly rapid resumption to near wartime levels.

Tables 1-8 in the Appendix give a reasonably complete picture of production figures from 1880 to 1947 insofar as the data are available. Table 1 gives a detailed picture of United States fluorspar production with prices since 1880 by states. A summary of production is given in table 2, and the 1948 prices are given in table 3.

Tables 4 and 5 give a history of Illinois fluorspar production and shipments by grades since 1916 and a comparison of Illinois and the United States prices and production for the last ten-year period. Table 4 gives a thirty-year picture of the crude ore mined, CaF_2 content, and tonnage marketed by grades.

Tables 6 and 7 give the shipments from the country as a whole by industries and by grades and table 8 the world production by countries since 1913, insofar as these data are available. Many countries have not published this information during and since World War II.

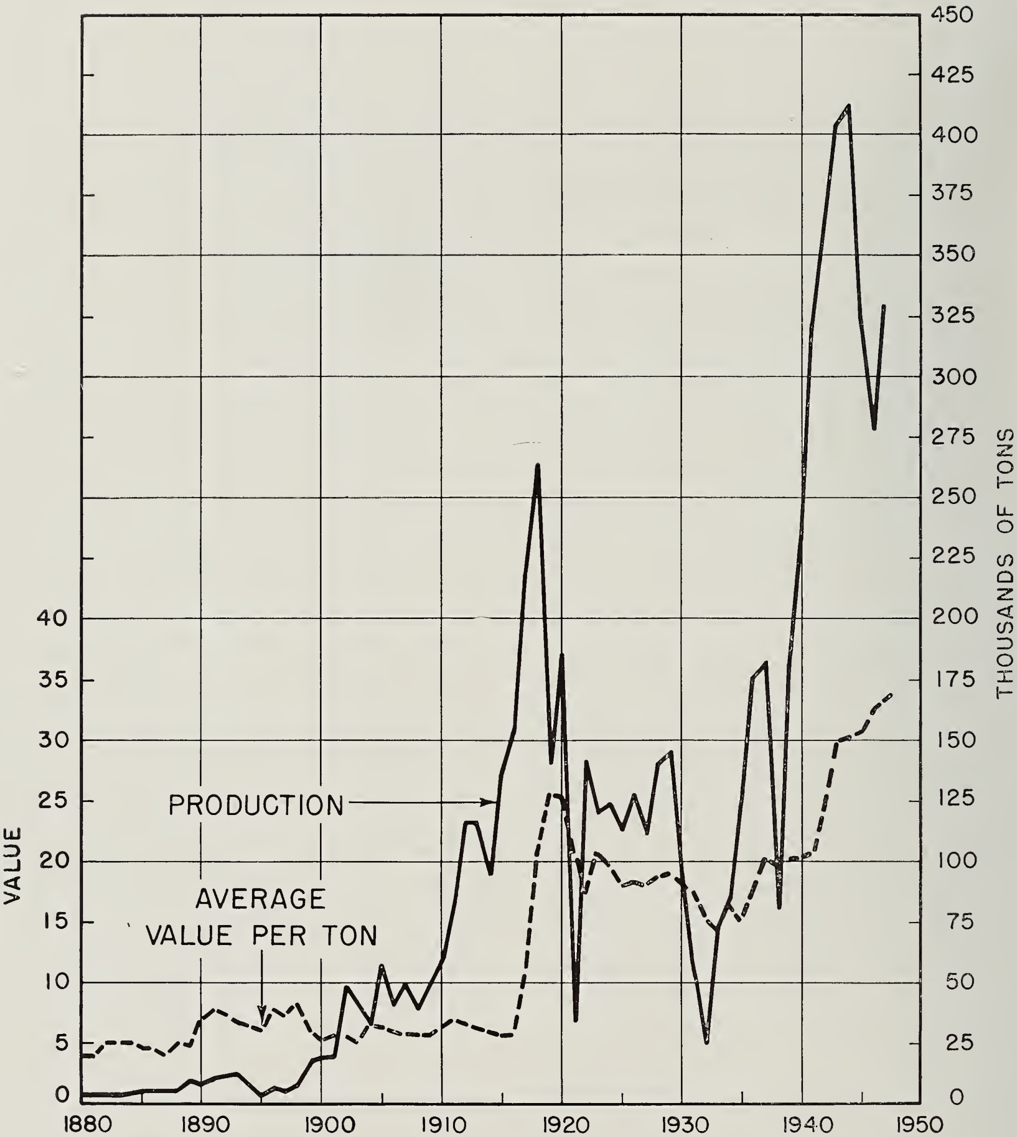


FIG. 2.—United States fluorspar production and value, 1880-1947.

IMPORTS, EXPORTS, AND TARIFFS

Table 9 gives a general survey of salient statistics in our domestic fluorspar industry since 1935. Exports except for a brief period have been negligible. Consumption has consistently exceeded domestic production leaving no incentive for export trade. Production costs in the United States have remained above those in foreign countries, which has also been a factor in curtailing exports.

Just prior to World War II, the United States was virtually independent of imported spar. The rapid expansion of wartime demands, however, found the government encouraging Mexico to develop large deposits, with the result that large quantities were brought into the United States for processing into high-grade spar for military purposes. With the continued high demand for fluorspar since the war it is not likely that imports will again be discouraged.

Table 10 gives a history of imports into the United States since 1910 by country of origin with the value of these imports.

Since 1928 we have had a rather peculiar and interesting tariff provision (table 12). Imports were divided according to CaF_2 content, the rate for fluorspar containing not more than 93 percent CaF_2 being $2.50 per ton more than that on fluorspar containing more than 93 percent CaF_2. In 1930 the percent of CaF_2 was changed from 93 to 97 percent. This was done to protect domestic producers of metallurgical grade spar and to encourage imports of high grade spar. Table 11 gives the imports by grade and by countries since the 1930 tariff became effective.

Table 13 is included to give a twenty-year picture of the relative size of production, imports and consumption. Here again we can note the gradual decrease in percentage of imports to total consumption up to 1940 and the upward trend since that time.

The question of tariffs is of prime importance at this time since it is becoming increasingly vital to the fluorspar industry that our imports be maintained at a relatively high level.

The trend today in general seems to be toward a pronounced reduction of present tariff barriers. This presents a problem worthy of careful consideration in our diminishing mineral industries in view of the various factors involved. Nationally it is imperative that we maintain a sufficient supply to guarantee, as much as is possible, against an emergency. What such a supply would be cannot accurately be foreseen. Nor can the capacity of our own industry to expand under emergency conditions be known beforehand. Production costs in this country are considerably above those in foreign countries and are likely to remain so. As our domestic supplies decrease it becomes increasingly important to make sure that our tariff regulations are high enough to protect our own industry with its increasing costs of mining and beneficiation, yet at the same time low enough to insure adequate imports. It has been suggested that the government import heavily for stockpile purposes, or remove the tariff and buy foreign spar at a world price, paying domestic producers a subsidy for their higher production costs. The consumer using domestic spar would then be given the advantage of buying his spar at the world price. This course of action does not seem unlikely in view of the international political and economic situation, with the United States gradually assuming the status of a creditor nation.

Without some such arrangement the removal or reduction of existing tariffs would seriously injure the competitive position of the domestic producer. Those who fear the extension of any government controls, and the use of subsidies, oppose any lifting of tariff barriers and believe that as domestic production costs increase, protective tariffs should be maintained in order to keep prices in line with increasing costs here, or they outline a plan of long-range tariff reduction whereby both producers and consumers could plan their programs accordingly. Whatever tariff program is needed to assure the nation of a fully adequate supply, with what appears to be a sufficient margin for emergency, is vitally important to our country today. In conjunction with this a program of research for new or extended deposits, conservation of existing supplies and plans for an increased program of imports is definitely in order as our known domestic reserves become insufficient.

BENEFICIATION OF ORES

The Illinois-Kentucky area has long been famous throughout the world for its continued high production of fluorspar. Serious attention has been given to the reserves only since the period of unusual demand during World War II and particularly since the demand appears destined to remain far above prewar levels.

Recently then considerable attention has been given to a more accurate determination of reserves, to better means of beneficiation in order to increase the percentage of recovery, to the problems of concentrating some of the more complex ores of the west and southwest, and to a more economical means of recovering ores from the Illinois-Kentucky area.

Heavy media processes have played an important part in increasing the percentage of recovery. Pulps of high specific gravity are produced by the suspension of a heavy magnetic mineral such as ferrosilicon or magnetite in water. Minerals lighter than the suspension will float and any heavier than the suspension will sink.

Preconcentration has been found to increase the extractions of ore and to decrease the overall cost of producing flotation concentrates. Frequently a mineral deposit cannot be beneficiated economically without the combination of heavy media preconcentration followed by froth flotation.[2]

During recent years the U. S. Bureau of Mines has given much attention to means of increasing our supply of strategic and critical minerals. In connection with this effort several tests were made at the Metallurgical Branch of the Bureau of Mines at Rolla, Missouri,[15] to determine the feasibility of producing acid-grade spar from southern Illinois ores and to determine means for more complete recovery of the CaF_2 content of these ores.

An examination of the ore indicated that approximately half of the fluorite should be recoverable as acid-grade concentrate under favorable conditions.

In the laboratory tests[15] the ore was crushed to a minus 20-mesh in a jaw crusher and rolls and to flotation size (about 100-mesh) by wet grinding. The pulp was then thickened to about 40 percent solids and floated in a mechanically agitated flotation cell. Zeolite-softened water was used in both the grinding and flotation processes.

The zinc was removed first and washed twice to remove as much of the fluorite as possible. The fluorite pulp was then thickened to about 40 percent solids and treated with sodium cyanide and quebracho extract. The cyanide counteracts any residual copper sulphate and the quebracho acts as a depressant for the gangue. The conditioned pulp was then treated with only enough oleic acid to float the cleanest of the fluorite grains. The rougher concentrate was then cleaned four times with additional amounts of quebracho to obtain a concentrate of acid or near acid grade.

The rougher tailings were thickened and refloated to recover a concentrate of metallurgical grade.

They reported recovery of 48.4 percent of the fluorite in an acid grade concentrate of 97.51 percent CaF_2, 0.74 percent $CaCO_3$, and 1.00 percent SiO_2. An additional 39.9 percent of the fluorite was recovered as metallurgical grade of 84.32 percent CaF_2, 7.80 percent $CaCO_3$, and 5.55 percent SiO_2, making a total recovery of 88.3 percent CaF_2.

Additional tests were made on ceramic grade concentrates to produce acid-grade spar. In one of these in which the thickened sample was treated with quebracho, then refloated and cleaned with an additional small amount of quebracho, a recovery of 56.6 percent CaF_2 of acid grade was possible with an analysis of 98.2 percent CaF_2, 0.72 percent $CaCO_3$, and 0.85 percent SiO_2.

In another test on a ceramic grade concentrate the sample was agitated with sulphuric acid to destroy the froth of the oleic acid, thickened to remove soluble salts, and refloated with sodium silicate and sodium oleate. This produced a recovery of 56.2 percent CaF_2 containing 98.3 percent CaF_2, 0.64 percent $CaCO_3$, and 0.85 percent SiO_2.

A third test was made by flotation of the ceramic concentrate with cationic reagents to float the silica and silicate minerals. This produced the highest grade concentrate (98.4 percent CaF_2, 0.41 percent $CaCO_3$, and 0.65 percent SiO_2) but the lowest percentage of recovery (45.2).

The flotation process, developed in 1920, has opened up new possibilities in the beneficiation of low grade ores and has enabled operators to frequently obtain as high as 98 percent merchantable fluorides.

Southern Illinois fluorspar producers were the first to use a flotation process for the removal of both metallic and nonmetal-

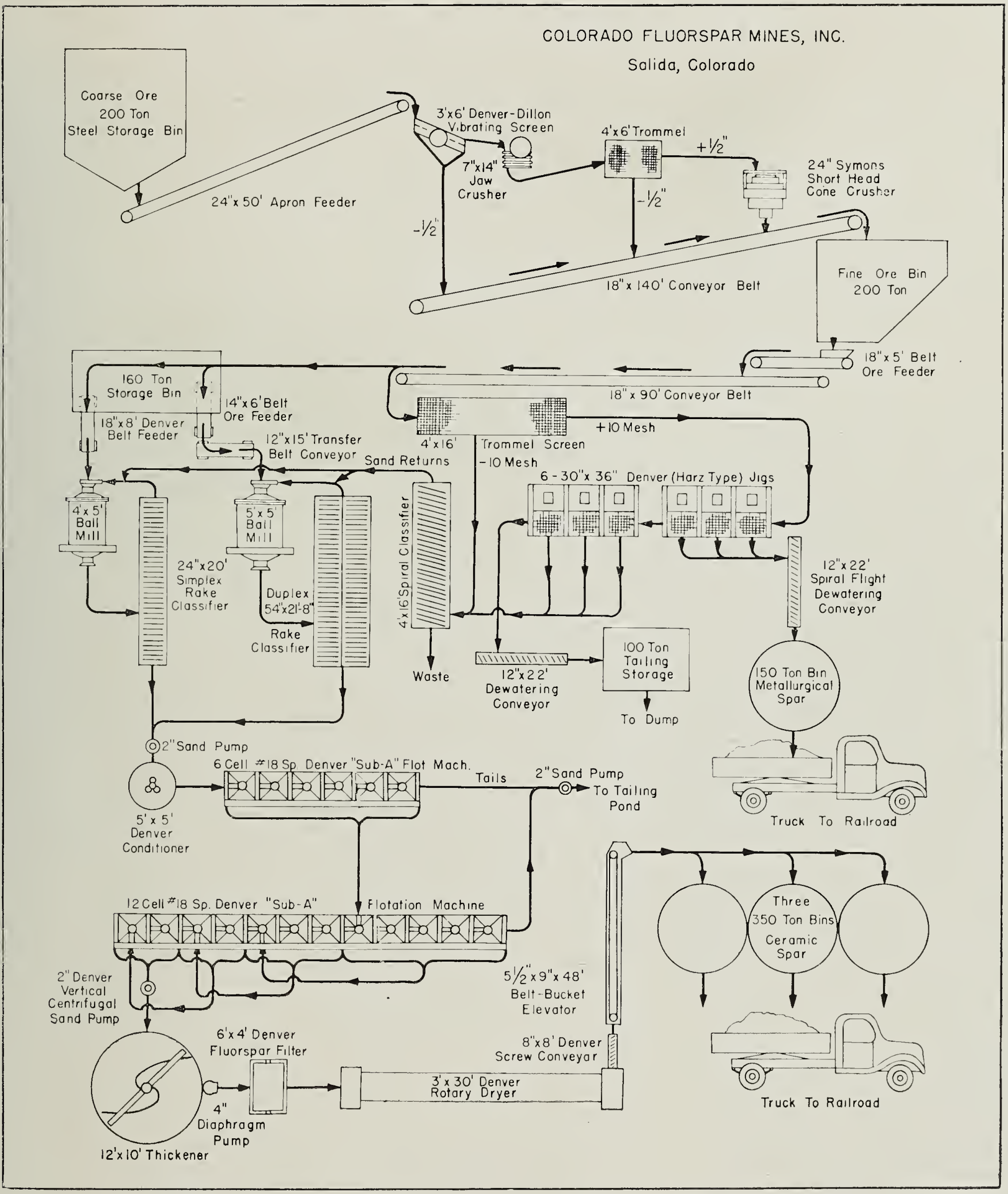
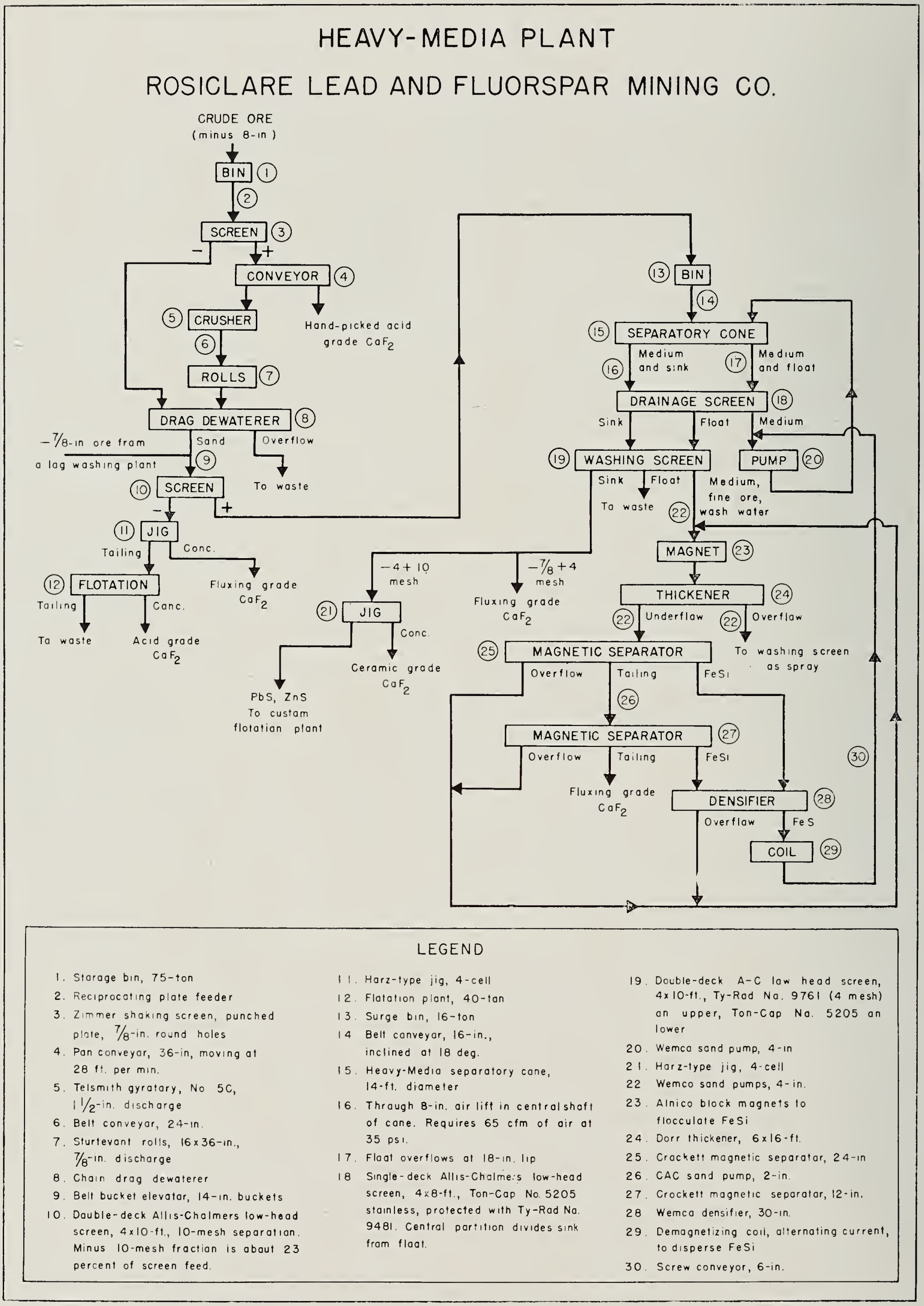


FIG. 3.—Flow sheet for flotation plant of Colorado Fluorspar Mines, Incorporated, at Salida, Colorado.

lic components in a continuous process. This unique process is important both technically and economically. Some of the Illinois - Kentucky fluorspar contains zinc but no lead (as that noted in the Bureau of Mines tests); some contains lead but no zinc; and still other contains both. In the flotation process for material containing both lead and zinc, the zinc is removed first, then the lead, and then the calcium fluoride.

Western fluorspar contains little lead and zinc, has considerable quartz, and a higher silica content. Removal of the quartz presents a different and more difficult problem than the separation of the lead and zinc concentrates.



1. Storage bin, 75-ton
2. Reciprocating plate feeder
3. Zimmer shaking screen, punched plate, $\frac{7}{8}$-in. round holes
4. Pan conveyor, 36-in, moving at 28 ft. per min.
5. Telsmith gyratory, No 5C, $1\frac{1}{2}$-in. discharge
6. Belt conveyor, 24-in.
7. Sturtevant rolls, 16x36-in., $\frac{7}{8}$-in. discharge
8. Chain drag dewaterer
9. Belt bucket elevator, 14-in. buckets
10. Double-deck Allis-Chalmers low-head screen, 4x10-ft., 10-mesh separation. Minus 10-mesh fraction is about 23 percent of screen feed.
11. Harz-type jig, 4-cell
12. Flotation plant, 40-ton
13. Surge bin, 16-ton
14. Belt conveyor, 16-in., inclined at 18 deg.
15. Heavy-Media separatory cone, 14-ft. diameter
16. Through 8-in. air lift in central shaft of cone. Requires 65 cfm of air at 35 psi.
17. Float overflows at 18-in. lip
18. Single-deck Allis-Chalmers low-head screen, 4x8-ft., Ton-Cap No. 5205 stainless, protected with Ty-Rod No. 9481. Central partition divides sink from float.
19. Double-deck A-C low head screen, 4x10-ft., Ty-Rod No. 9761 (4 mesh) on upper, Ton-Cap No. 5205 on lower
20. Wemco sand pump, 4-in
21. Harz-type jig, 4-cell
22. Wemco sand pumps, 4-in.
23. Alnico block magnets to flocculate FeSi
24. Dorr thickener, 6x16-ft.
25. Crockett magnetic separator, 24-in
26. CAC sand pump, 2-in.
27. Crockett magnetic separator, 12-in.
28. Wemco densifier, 30-in.
29. Demagnetizing coil, alternating current, to disperse FeSi
30. Screw conveyor, 6-in.

Fig. 4.—Flow sheet for heavy media plant, Rosiclare Lead and Fluorspar Mining Company, Rosiclare, Illinois.

Flotation Plant

The flotation plant of the Colorado Fluorspar Mines, Incorporated, at Salida, Colorado, (fig. 3) has a total capacity of approximately 260 tons of new feed each 24 hours—100 tons capacity from the jigs and 160 tons from the flotation circuit.[23] Flotation plants are varied according to the particular needs of the company and type of fluorspar to be processed. This was chosen merely as being typical of the process in general. The figure is self-explanatory. Steam under 80 pounds of pressure is used to keep the pulp at a uniform temperature of 90° F.

The following operating data[23] show the average results from this plant:

Assays (Average)	Percent CaF_2	Percent Fe
Heads	35.0	—
Jig concentrate	83.5	0.4
Flotation concentrate	97.0	0.075
Flotation tailings	5.0	—
Percent recovery	90.4	—
Ratio of concentration	3.07	—

The iron content of the concentrates is very low. This is an important factor when the fluorspar is used in the glass industry. Iron will stain glass when it is present in larger quantities. In addition, the concentrates contain no calcium carbonate or sulphides—galena, sphalerite, etc.

Heavy Media Plant

The installation of a heavy-media separation plant[10] at the Rosiclare Lead and Fluorspar Mining Company's property at Rosiclare in February 1944 has enabled the company to lower their milling costs, increase their production, and definitely improve their metallurgy over previous jigging operations. In addition to treating ores direct from the mines, a considerable tonnage of jig-plant tailings are also treated.

The process can be followed quite easily from figure 4 with a few brief explanations. The 16-ton surge bin (13) is placed ahead of the separatory cone (14) to hold the ore long enough to allow excess water to drain from it leaving only approximately 3 percent moisture to minimize dilution in the cone. A double-deck washing screen is not the usual procedure but is used here because of the friability of the fluorspar. Its use produces two different grades of concentrate and makes it possible to market the secondary tailings as metallurgical spar.

This heavy media-process is believed to be definitely superior to the jigging process from both a metallurgical and economic standpoint.

CONSUMPTION

When the basic open-hearth process for the manufacture of steel was introduced into the United States in 1888 the steel industry became the chief consumer of fluorspar. The percentage of fluorspar per ton of steel has been reduced gradually to an average of about 5.4 pounds per ton of steel and the percentage of total fluorspar consumpition used in steel manufacture has dropped from about 80 percent in the 1920's to about 50 percent at present (table 16), yet the total quantity used by the steel industry today shows a definite increase over prewar consumption (table 15). With the rapid increase in the demand for fluorspar in the manufacture of hydrofluoric acid, it is uncertain whether or not steel will long continue the lead in consumption which it has maintained to date (fig. 5).

All but nine or ten states report fluorspar consumption. However, three states—Illinois, Ohio, and Pennsylvania—consume more than half of the total for the country. Pennsylvania has for some time ranked first as a consumer of fluorspar in both steel and glass, whereas Illinois has likewise maintained a lead in the manufacture of hydrofluoric acid.

A history of the fluorspar consumption, both domestic and foreign, by industries, is presented graphically for the period since 1925 (fig. 5). This shows the marked increase in the consumption of fluorspar for the manufacture of hydrofluoric acid during World War II. It is noteworthy that the postwar months of 1945 showed a sudden drop in consumption for this purpose at the close of the war, as the use of hydrofluoric

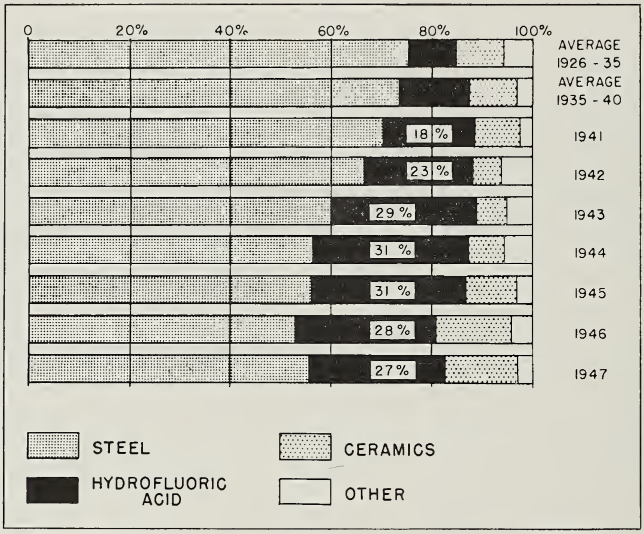


Fig. 5.—Percentage consumption of fluorspar (domestic and foreign) by industries, 1926-1947.

acid shifted from almost entirely military purposes to a resumption of civilian needs. By January 1946, however, the tide had turned and since that time there has been a surprisingly rapid increase in the rate of consumption for this purpose (fig. 6).

Because of the establishment during the war years of so many new uses for fluorspar, as well as the growth of so many old uses for it, there seems little reason to believe that the annual demand will again fall much below 300,000 tons.[17] This figure was based on an estimated consumption of 128,000 to 152,000 tons by the basic open-hearth steel furnaces and foundries, 25,000 to 35,000 tons by the ceramic industries, 25,000 to 38,000 tons by the aluminum-magnesium industries, and 75,000 to 90,000 tons by the chemical industries. Actual consumption figures (table 15) show that the demand since the war has even exceeded these estimates, although ultimate consumption may level off at a slightly lower average. Curtailed production of civilian goods during the war naturally resulted in a backlog of needs that has kept production in most industries at a peak up to the present time.

The chief commercial grades of fluorspar are acid, ceramic, and metallurgical, con-

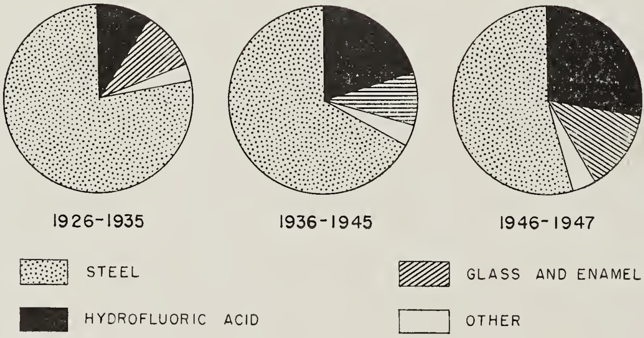


Fig. 6.—Average consumption of fluorspar (domestic and foreign) by industries, 1926-1935, 1936-1945, and 1946-1947.

taining 98.95 and 85 percent CaF_2 respectively (table 18). Improved technology in beneficiation has enabled producers to not only recover a much larger percentage of CaF_2 from the crude ores than formerly but also to control the output by grades according to the current demands, to make economic use of low-grade ores formerly considered impractical to mine, and to recover high-grade concentrates from discarded tailings at the mines.

METALLURGICAL GRADE

Metallurgical spar is largely used by the metal industries because of the desirable fluxing qualities of fluorspar. Although certain substitutes for fluorspar—calcium silicate, ilmenite, borates, etc.—have been tried, none has proved as successful as fluorspar. Most of these substitutes are less expensive than fluorspar and may possibly serve as an economic price ceiling on metallurgical spar. Nevertheless, while the quantities of spar needed by the steel industry remain such a small part of the total cost of production, it would take a considerable increase in the price of fluorspar to make it an important economic factor in the price of steel. Fluorspar used in the steel industry today does not average above 6-10 cents per ton of steel.

The ability to market a pelletized product from the concentration process of making acid-grade spar has made possible the use of second-grade tailings that formerly had no market. The pelletized product has as yet not found favor with the entire steel industry although it has been used with very good success by several companies.

CERAMIC GRADE

The glass industry is consuming ten times as much spar as it did ten years ago. Much of this expansion has come in the field of non-transparent glass using fluorspar as an opacifying agent.

Fluorspar is used in the manufacture of opal, opaque, and colored glass. From 50 to 500 pounds of fluorspar are used per 1000 pounds of sand in the manufacture of glass, depending upon the type of product desired. Substitutes for fluorspar have been tried but offer little competition either because of higher cost or lower efficiency. A more finely ground fluorspar (60 percent through a 100-mesh screen) is required for the manufacture of vitreous enamel than for opaque or colored glass (55 percent through 100-mesh screen). These commodities include sinks, bathtubs, stove parts, refrigerators, toilet fixtures, etc., where vitreous enamel coatings are applied to iron or steel. Similar coatings are also applied to pottery, brick, and tile. Enameled sheets for store fronts, filling stations and as a substitute for tile in bathrooms are proving popular. Since civilian consumption of such products was so drastically curtailed during the war, the market for this mineral for enameling purposes showed a marked upward trend as soon as civilian manufacture of these commodities was again possible.

ACID GRADE

Since the temporary decline in demand for fluorspar for the production of hydrofluoric acid at the close of World War II, there has been a striking increase in demand as the chemical industry adjusted to peacetime uses. Production of hydrofluoric acid (anhydrous and technical, calculated at 100 percent HF) in June 1948 was 3,089 tons or an increase of 34 percent over production in June 1947. Likewise production for the first six months of 1948 (15,699 tons) was a 22 percent increase over the same months of 1947.

During the past decade new uses for hydrofluoric acid have been developing so rapidly that it is altogether possible that eventually more fluorspar will be required for its manufacture than is normally used in the manufacture of open-hearth steel.

UNITED STATES RESERVES

The problem of reserves is one which must be approached cautiously, being ever mindful that the most painstaking estimates may in time be proved erroneous. The fact that fluorspar occurs in relatively small veins makes it more likely that new deposits will be discovered and at the same time more difficult to ascertain the real extent of the known deposits without expending far more labor and capital than has usually been deemed expedient in the past.

Numerous factors must be considered in determining the life span of a given deposit, even when its extent is known with a relative degree of certainty.

(1) The frequent presence of water in the mines—particularly in the Illinois-Kentucky area along the Ohio River—makes uncertain the extent to which even a known deposit will be economically available.

(2) After the first lush days of mining have exhausted the ore that is readily available, it is necessary to determine the ratio of mounting costs in mining less accessible, deeper, and more widely scattered ore bodies to the type of ore available, market value, and demand.

(3) Mining costs increase with the gradual depletion of reserves, and beneficiation of lower grade ores is usually necessary at considerable expense.

Granting then that as ore reserves near depletion relative costs of merchantable concentrates will mount appreciably, will the demand be sufficient to keep prices at a level to warrant this additional expenditure? At present this problem does not seem to enter the picture. Prices never have been so high before and, except for a brief period during World War II, the demand never has been so great. To what extent this condition is due to the general economic level and to what extent it might be affected by a shift in the general price structure is somewhat uncertain today. Should this occur a sudden slump in demand would be certain temporarily but just where it would level off is questionable—certainly well above the prewar level because of the multitude of new uses of fluorspar and fluorine compounds that have developed within the past five or six years.

The table of reserves (table 18) is presented not with the idea of either acclaiming or disclaiming its accuracy, but rather to show how constantly shifting the picture of reserves is. When another estimate is published it will doubtless contain some changes as startlingly different from this one as it was from the one published in 1934. Nor is it a matter of any of these estimates being hastily or carelessly made but rather that at best estimates must be made on incomplete information.

For example, an estimate of 5 million tons (2 million tons for Illinois and 3 million for Kentucky) was given for the Illinois-Kentucky area in 1934.[18] Between 1934 and 1944, when the latest available estimate (table 17) was made, approximately 2 million tons had been mined from this area, yet the estimate for 1944 reserves was listed as 6,200,000 tons.

Likewise, world reserves in 1934 were estimated to be approximately 9.5 million tons, whereas the 1944 report estimates them to be slightly more than 14 million tons, yet during that ten-year interval production had exceeded 3.5 million tons.

This is particularly noteworthy in view of the rapidly increased rate of production during that period and since. In the United States alone the production, 1934-1944, was more than 2.5 million tons, whereas the total United States production up to 1934 was less than 3.5 million tons (table 1).

Thus in the face of an encouraging picture of greatly increased known or indicated reserves is the somewhat alarming factor of a far more rapid rate of demand than had at any time been anticipated. In fact, approximately 50 percent of the total United States production to date has been mined since 1934 (3.4 million tons out of a total to date of 6.9 million tons).

Faced with this situation and the continued high demands, it is to be hoped that a survey of probable reserves in the United States will be published in the near future. Because of the apprehension over the continued high demand, these estimates are likely to be somewhat more accurate than those of the past. We have reached a point where it is imperative that we know what we face for the future.

Considering table 18, since it is the latest estimate on which to base our discussion, the group containing 35 percent or more CaF_2 includes nearly all the known deposits that were considered recoverable under the economic and technologic con-

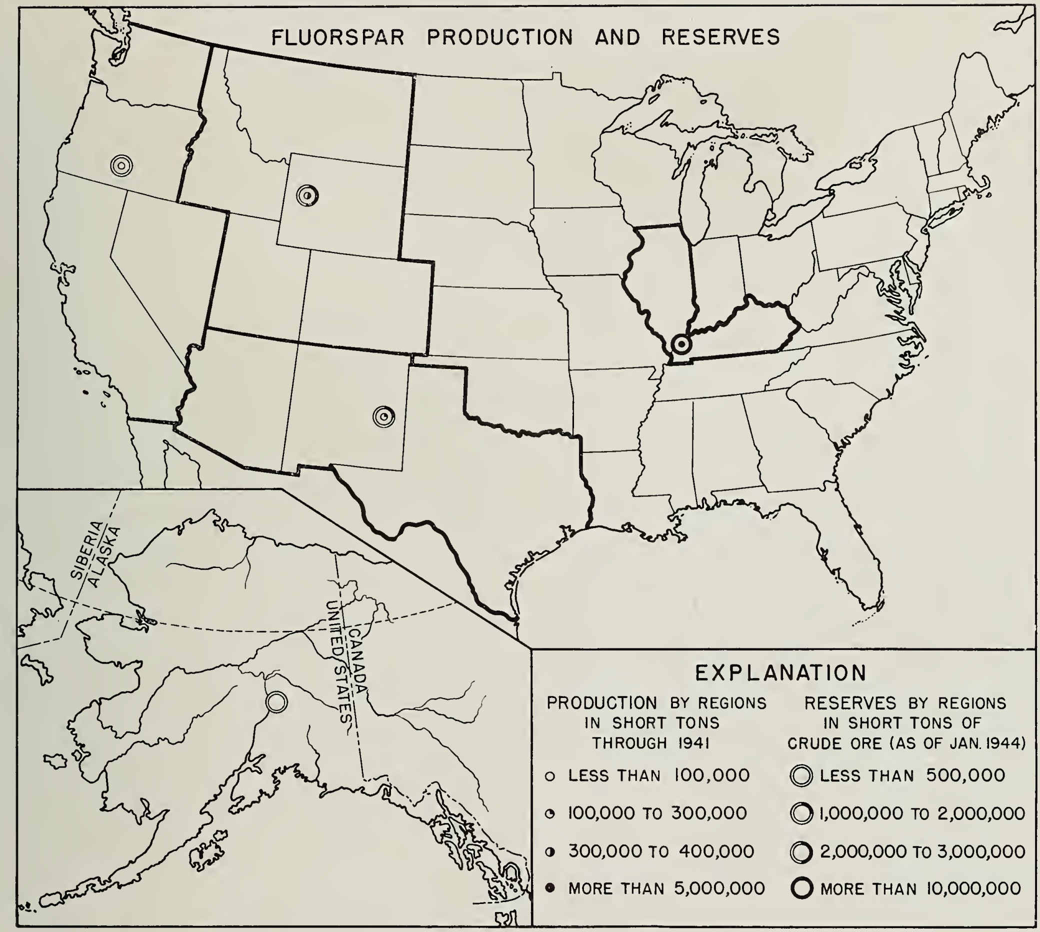


FIG. 7.—Reserves of fluorspar in the United States as of January 1, 1944.

ditions of 1944, as well as some that could not be mined economically because they were subject to excessive mining or milling costs, or because they contained excessive amounts of undesirable impurities. Deposits containing less than 1,000 tons were excluded. A few of the deposits might have been included in this list because of accessibility to markets or ease of mining and milling even though they contain less than 35 percent CaF_2.

The other group (15 to 35 percent CaF_2) is believed to be conservative, although few of these deposits have been investigated. Material containing less than 15 percent CaF_2 could not under present conditions, be economically utilized, although at some future date demand might warrant the extraction of even these small amounts.

From this joint survey (results of which are recorded in fig. 7) the largest deposits are to be found in the states having the largest production: (1) Illinois-Kentucky, considered together since their deposits are so closely associated, with an estimated 15,550,000 tons (6,200,000 tons CaF_2 content); (2) Colorado; and (3) New Mexico. Other western states having important but less-developed deposits are Arizona, Nevada, Utah, California, Idaho, Texas, Montana, and Wyoming. An estimated reserve of more than 8 million tons (over 2½ million tons CaF_2 content) is credited to the western and southwestern states. An additional half million tons (150,000 tons CaF_2 content) is credited to Alaska and other states with small deposits. Fluorspar deposits are known to exist in Alaska, although none has been mined to date.

This estimate, as of January 1944, gave a total of slightly over 9 million tons CaF_2 for the United States as a whole. If we deduct production since that date (approximately 1½ million tons) we arrive at an estimate for today of approximately 7½ million tons. Until another survey is made this estimate must suffice as the latest attempt to determine our reserves and as the best information at hand on which to base our calculations for the future.

From these estimates it was predicted that at the 1935-1939 level of production (around 175,000 tons per year), domestic reserves might be equivalent to a 40-year supply, or at the wartime rate (about 400,000 tons per year) be equivalent to a 20-year supply. This, however, did not take into consideration the declining rate of production that accompanies depletion of any ore deposit. On the other hand there is the possibility always of discovering new deposits that would help to balance the picture of declining reserves or perhaps even lengthen the estimates given. The very nature of fluorspar deposits makes this a greater probability than with many types of minerals and increases the difficulty of making a reasonably accurate estimate.

The fact that the postwar demand is not likely to drop much below the wartime level has made the question of reserves one of strategic importance today.

Those who are charged with the responsibility of providing a stockpile reserve of strategic minerals are particularly alarmed at our situation today with respect to these minerals. What the government is doing toward stockpiling of fluorspar is not generally known, but some of those in a position to know fear the results should a national emergency arise. No one except the producers can know with much certainty how near depletion we really are or what their capacity for rapid expansion would be should the need arise.

Those opposing government stockpiling do so on the grounds that it is likely to upset the price structure by throwing quantities of spar on the market at a time when relatively high prices are imperative to domestic production. This is probably an overly conservative view when we consider the low domestic reserves and the probability of foreign supplies being cut off in case of war.

Many believe that with the increasing demand for acid- and ceramic-grade spar, our entire domestic supply—except the metallurgical marketed as a secondary product in the processing of high grade spars —ought to be reserved for chemical and ceramic use, and our imports ought to be increased to take care of the demand for metallurgical spar in the steel industry.

Without some system of stockpiling it seems unlikely that, if foreign markets were suddenly closed to us, we could increase our production fast enough and far enough to supply the demand. In view of the uncertain world situation today government stockpiling seems not only wise but necessary. Fluorspar stockpiles do not deteriorate. Therefore the danger of a surplus being thrown on the market at an inopportune time for producers seems far less alarming than the danger of a national emergency arising with no means either of being able to supply the demand for fluorspar or of finding an adequate substitute quickly enough to assure adequate production of steel, aluminum and chemicals. With the rapidly increasing demands for acid-grade spar in the chemical industry alone, it would seem a wise move to reserve our domestic supply for processing to acid or ceramic grade.

The following definition of strategic and critical materials, prepared by the Strategic Materials Committee, was approved by the Army and Navy Munitions Board on March 6, 1944:[29]

> Strategic and critical materials are those materials required for essential uses in a war emergency, the procurement of which in adequate quantities, quality, and time is sufficiently uncertain for any reason to require prior provision for the supply thereof.

Recognizing that stockpiling represented only one means of assuring adequate supplies of strategic and critical minerals, these materials were classified into three major subdivisions:[29]

> Group A comprises those strategic and critical materials for which stockpiling is deemed the only satisfactory means of insuring an adequate supply for a future emergency.
>
> Group B comprises additional strategic and critical materials the stockpiling of which is practicable. The Army and Navy Munitions Board recommends their acquisition only to the extent they may be made available for transfer from Government agencies, because adequacy of supply can be insured either by stimulation of existing North American production or by partial or complete use of available substitutes.
>
> Group C comprises those strategic and critical materials which are not now recommended for permanent stockpiling because in each case difficulties of storage are sufficient to outweigh the advantages to be gained by this means of insuring adequate future supply.

Fluorspar has been placed in Group B. However, the placing of a mineral in any one of these groups does not preclude its later transfer to another group if circumstances warrant, nor does it imply that materials in any of the three groups are either more or less important to our national security than those in another group. In general, however, minerals in group C are not suitable for stockpiling.

Sources from which acid-grade fluorspar might be obtained are listed as: United States, Germany, Newfoundland, Union of South Africa, France, Spain, and Mexico. Metallurgical-grade fluorspar may be supplied by the United States, Germany, United Kingdom, U. S. S. R., Newfoundland, France, Spain, Mexico, South Africa, Chosen, and Italy.

FOREIGN RESERVES

Because of the heavy drain upon our domestic reserves and the probability that it will not decrease, it is pertinent that we note where our imports may originate and what volume we might expect to obtain under normal conditions or in an emergency.

Recent estimates are not available and, as with our own reserves, we must bear in mind the uncertainty involved in making these estimates and that at best they are based on indefinite and intangible information.

Mexico, from whom we have been receiving the bulk of our imports for the past several years (table 11) has a potential production far in excess of her domestic demands at present. Mexico has many deposits, including the famous Azul mine, and because of her proximity is our most important prospect for future as well as present imports.

For several years considerable spar has been imported from Newfoundland which has similar advantages. Newfoundland has extensive deposits which appear to be ample for domestic needs and has a sizable surplus of both acid and metallurgical spar for export.

No extensive reserves in Canada are known, although there has been production from time to time. Some Canadian spar has been imported, but our exports to Canada exceed our imports.

Spain probably has the largest reserves of any European country. These are estimated to be at least 5,000,000 tons. Next to Mexico, Spain has furnished our largest source of imports for the past several years. Spain has many mines, of which the Berta is the most important. It appears that Spain will have relatively large tonnages for export for several years.

England reestablished numerous mines during the war which will probably continue to produce more than domestic needs require. English reserves are among the larger European sources.

France has extensive deposits which will be adequate to supply the demand of her steel and aluminum industries, but leave little for export.

German reserves have been relatively large. Although there was considerable exploitation during the war, it is estimated that Bavarian deposits can supply at least 60,000 to 100,000 tons per year for fifty years on a very conservative estimate since the veins are scattered over an area of one hundred square miles.[5] The Gissella mine is estimated to have a reserve of at least 20,000 tons and the Erna and Hermine mines are estimated to be capable of supplying 20,000 tons each for a 50-year period. Total maximum reserves are estimated to be approximately 3,000,000 tons, although nearly half of this amount is not proved. Deposits in Bavaria and the northern part of Baden are in the American zone; those in Harz, Thuringia and Saxony in the Russian zone; and those of Southern Baden and Württemberg-Grunbach are in the French zone. Normal output, of high-grade spar particularly, would be far in excess of German consumption, leaving considerable for possible export trade. Prospects for export, according to the B. I. O. S.* reports, will depend upon political developments in neighboring countries in Europe, on reconstruction of internal transportation facilities, on economic conditions in general and on external shipping facilities.

Switzerland and Italy have reserves that allow some production for export but are not thought to be extensive.

Russia probably has large reserves but is likely to produce for domestic consumption only.

Reserves of South Africa are not large, although they are of a very high quality, and are practically all mined for export. If the South African steel industry can be developed as they hope, there probably will be little or no surplus fluorspar for export.

Future imports will depend largely upon our tariff and general price structure. Under peacetime conditions with a favorable tariff and a price structure that will encourage domestic production and at the same time foster a program of increasingly large imports of fluorspar, our country should be able to supply an annual demand at present day level for at least fifteen to twenty years. Within that period undoubtedly new deposits or additional extensions to known deposits will be found and also improved methods of beneficiation of low-grade ores.

ALTERNATE SOURCES OF FLUORINE

In addition to arousing interest in foreign reserves, the continued high demand for fluorspar and fluorine has made us aware of the need for finding an alternate source of available fluorine to at least supplement the declining reserves of fluorspar.

To date there is no substitute for fluorspar in the manufacture of either hydrofluoric acid or synthetic cryolite, nor is any substitute as effective as a flux in the steel industry. There are, however, other sources of fluorine which may come into importance in the future.

CRYOLITE

Cryolite, which is sodium aluminum fluoride (Na_3AlF_6), contains 54.4 percent fluorine. This means that a ton of cryolite technically contains 1,088 pounds of fluorine, whereas a ton of fluorspar technically contains only 974 pounds of fluorine. Nevertheless, due to the depletion of the cryolite reserves, we cannot consider cryolite among the possible sources of fluorine as a substitute for fluorspar.

The only known commercial deposit of cryolite is the Danish owned quarry at Ivigtut, Greenland. Imports (table 14) have dropped rapidly since the war due partially to the fact that artificial cryolite is replacing natural cryolite in many cases. The chief use for cryolite is in the reduction of aluminum, although small quantities are used in glass, enamels, abrasives, and insecticides. The rapid expansion of the aluminum industry since the early 1940's has made necessary the use of large amounts of cryolite. Fortunately, natural cryolite can be replaced with artificial cryolite after the process is started. Every pound of metallic aluminum produced requires 0.1 lb. of cryolite (54.4 percent fluorine). The 1943 production of aluminum, amounting to approximately 920,000 tons, dropped to less than 600,000 tons in 1947. This meant a drop in cryolite consumption from about

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* British Intelligence Objectives Subcommittee, British Library of Information, 30 Rockefeller Plaza, New York, N. Y.

92,000 tons to less than 60,000 tons. Had this all been artificial cryolite it would have meant a fluorspar consumption in itself of at least 108,500 tons in 1943 and 71,000 tons in 1947. Thus as cryolite reserves become depleted the strain upon fluorspar reserves increases as it becomes necessary to use more synthetic cryolite.

Rock Phosphate

Rock phosphate may well prove to be the important source of fluorine for the future. The fluorine content of rock phosphate averages approximately 3 percent, that from Florida running from 3.5 to 4 percent.

World reserves are currently estimated to be approximately 28 billion net tons, half of which is in the United States. Taking 3 percent of this as the average fluorine content, the potential reserves from this source are around 840 million net tons or an equivalent of 1,750 million tons of fluorspar.

About half of the fluorine is evolved as silicon tetrafluoride vapor which in the presence of water is converted into hydrofluosilicic acid in the production of super phosphates from phosphate rock. A more detailed discussion is given in Part II.

An inexpensive means of converting hydrofluosilicic acid to hydrogen fluoride would mean a tremendous saving toward the conservation of our fluorspar reserves, and at the same time provide a market for a byproduct gas which has caused much concern to the phosphate industry.

Lithium Compounds, Bone Residues

Although some fluorine is available in lithium compounds and bone residues, the amount is so small that their value is negligible at present.

FUTURE TRENDS

In view of the economic factors just considered, what can we expect for the fluorspar industry in the near future?

(1) An enlarged program in exploration and development of new deposits of fluorspar.
(2) Continued technological research for improved methods of beneficiation of low-grade ores.
(3) A program facilitating importation of greatly increased tonnages of foreign fluorspar.
(4) Government stockpiling as an imperative safeguard against a possible emergency.
(5) An expanded research program for new sources of fluorine.
(6) New and increased uses for fluorspar and fluorine compounds in industry.
(7) Rapid expansion of the fluorspar industry in the west and southwest in spite of the wide differential in freight rates.

At present these appear to be likely trends, which will guarantee an immediate future for the fluorspar industry that will be bright indeed. Our problem, then, in facing the future is to take a long-range view to assure locating new reserves, increasing foreign imports and finding an alternate source of fluorine that will be economically available before this unprecedented demand will have depleted our domestic reserves. As Part II shows, fluorine chemistry alone has reached a position of such importance to industry that we must not permit our known reserves to become depleted without the adequate assurance of an alternate source of supply.

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PART II

FLUORINE CHEMICALS IN INDUSTRY

PART II.—FLUORINE CHEMICALS IN INDUSTRY

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FLUORINE CHEMICALS IN INDUSTRY

BY

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THE ADVENT of the Freon refrigerants in 1930, the appearance on the American market of certain brilliantly colored German dyes several years later, and the World War II era with its "atom" bomb, "bug bombs," HF alkylation process for 100-octane aviation gasoline, etc., attracted attention to one of the most unusual chemical elements known to mankind. The element responsible for these unusual products is called fluorine. It is a member of the well-known family of elements called the halogens—namely, fluorine, chlorine, bromine, and iodine. The purpose of this article is to discuss briefly (1) the chief fluorine-containing minerals and their relative significance, (2) the strategic importance of fluorspar as a chemical raw material, (3) the industrial developments and uses of fluorine-containing compounds, and (4) new research frontiers in fluorine chemical industry.

FLUORINE MINERALS

Fluorine is the most reactive element known to chemists in its free or elemental state. Consequently, it is always found in nature in the form of one of its compounds. It is widely distributed in the earth's crust[8] to the extent of about 0.03 percent. This low percentage makes it appear that it might be a rare element. It is, to the contrary, three times as abundant as copper, fifteen times as abundant as lead, thirty times as abundant as cobalt, and two-thirds as abundant as chlorine. Just as the other elements mentioned are obtained commercially from minerals that contain a high percentage of them, so it is with fluorine. The chief fluorine-containing minerals of commercial significance are fluorapatite (rock phosphate), cryolite, and fluorspar. Fluorspar, also called fluorite, and known to the chemists as calcium fluoride, CaF_2, is the most important fluorine-containing mineral for the chemical industry.

There are several miscellaneous fluorine minerals such as amblygonite, $AlPO_4 \cdot LiF$, and lepidolite, $KLi[Al(OH,F)_2]Al(SiO_3)_3$ containing 13.5 and 9.5 percent of fluorine respectively. They are of no importance to the fluorine chemical industry, and are used solely in the ceramic industry or as a source of lithium.

FLUORAPATITE OR ROCK PHOSPHATE

Fluorapatite, also called apatite or rock phosphate, has an approximate chemical composition of $CaFCa_4(PO_4)_3$ with a fluorine content of about 3.7 percent. It is a very common mineral and rather widely distributed throughout the world. Due to its wide distribution and the immense deposits, it can be considered to be the world's largest known fluorine reserve. Unfortunately the fluorine in fluorapatite is not readily available in a usable form for the chemical industry. On the other hand the rock phosphate industry merits attention. (1) The industry produces a certain class of fluorine-containing compounds known as the silicofluorides as by-products, and (2) this industry may serve as an alternate source of fluorine when the need arises. The silicofluorides are discussed in detail under the section on fluorine chemicals.

In order to appreciate the magnitude of the fluorine reserve in the rock phosphate deposits of the United States, a few simple calculations can be made. According to table 21 (appendix), the inferred reserves of phosphate rock in 1943 were estimated to be approximately 11 billion tons. Assuming the fluorine content to be approximately 3 percent, the potential fluorine reserve is over 300 million tons and is equivalent to about 600 million tons of fluorspar. On the basis of a million ton world production of fluorspar in 1943, the phosphate rock reserves in the United States alone represent a world fluorspar reserve of approximately 600 years.

Cryolite

A natural occurring mineral called cryolite, Na_3A1F_6, has the highest fluorine content of any known commercial mineral, 54 percent by weight. It is mined at only one place—Ivigtut, Greenland. The Danish government owns the mine and has a world monopoly. Its chief use is in the manufacture of metallic aluminum where the molten cryolite in the cells serves as a solvent for the alumina which is being electrolyzed. Other minor uses for cryolite are in the ceramic and insecticidal industries, and in some fluxing mixtures. Due to its cost and limited availability, it is not used as a raw material for a fluorine chemical industry. As a matter of fact, natural cryolite is seriously confronted with competition from synthetic cryolite prepared from fluorspar.

Fluorspar

The most important fluorine-containing mineral in industry today is fluorite, commonly called fluorspar, CaF_2. It contains 48.7 percent fluorine and 51.3 percent calcium, by weight, and is distributed widely in nature. In the United States, as pointed out in the section on economic aspects, the Illinois-Kentucky field accounts for 80 to 90 percent of the domestic production. The close proximity of this district, with its modern processing equipment, to industrial centers makes it the world's outstanding fluorspar area.

In general, fluorspar is associated chiefly with limestone and sandstone. Fluorspar associated with igneous rock of the quartz matrix type is the most difficult to process. Other minerals commonly found with it are galena, sphalerite, calcite, barite, etc. As the Illinois-Kentucky fluorspar generally occurs in beds of limestone or sandstone, it can be processed readily to a high-grade product unmatched in quality by a quartz matrix type. Generally, fluorspar is processed into metallurgical, acid, and ceramic grades as indicated in table 18. Almost all of the domestic spar is processed by some mechanical means. The modern installations use a heavy media and/or a flotation process, when a very high-grade product is desired. The flotation process enables the industry to recover such valuable by-products as lead and zinc ores which may run as high as 10 percent of the "as mined" product. The lead and zinc content varies considerably between mines, and in some places very little of the sulfide ore may be present. The heavy media process depends upon finely divided ferrosilicon to control the density of the slurry for efficient separation of the fluorspar from its gangue material. A plant equipped with such a process has a very large production capacity, can handle readily an ore containing less than 40 percent CaF_2, and can produce a satisfactory metallurgical grade. As the heavy media process can be used economically on a low-grade ore, it is frequently used ahead of the flotation process to provide a much higher grade of feed for the flotation cells. In order to produce an acid or ceramic grade of fluorspar and at the same time recover the lead and zinc, a froth flotation is the standard process. This froth flotation process is unique in that it is the first continuous process devised to obtain two metallic minerals and a nonmetallic product all in the same operation. In the Illinois-Kentucky district most of the processing is done in the Illinois area.

USES OF FLUORSPAR

Metallurgical

The largest user of fluorspar is the steel industry. Approximately 60 percent of the fluorspar produced is of the metallurgical grade. It is used in the basic open hearth process as a flux to give fluidity to the slag, thus allowing the furnaces to be operated much more efficiently. In addition, it is of assistance in the removal of impurities such as sulfur and phosphorous. Depending upon economic conditions, the quantity of fluorspar used varies from one to fifty pounds per ton of steel with the average being five to eight pounds. Where speed and a maximum production are at stake, amounts higher than the above are used. A smaller amount of fluorspar is consumed in the electric-furnace steel, Bessemer steel, ferro-alloys, and iron foundry industries.

CHEMICAL

Since 1936 the chemical industry has not only established itself as the second largest consumer of fluorspar, but has had a profound effect upon the technical development of the fluorspar industry in general. When the chemical industry increased its acid spar consumption from 20,000 tons in 1936 to a phenomenal demand of 129,000 tons in 1944, the fluorspar industry realized that here was an almost ideal type of customer from the standpoint of economic stability. Fortunately, the Illinois-Kentucky fluorspar interests met this challenge in a most positive way by installing suitable equipment and thus becoming the world's outstanding producers and processors of high quality acid spar. Circumstances are such now that the chemical industry need not hesitate to base its developments on a uniform and constant quality of raw material.

The chemical industry requires a high quality fluorspar with a maximum calcium fluoride content and a minimum of silica and calcite, as indicated in table 18. This grade is known as acid spar and, as the name implies, is used in the manufacture of hydrofluoric acid.

Fluorspar or calcium fluoride is quite inert chemically and so is not used directly in many chemical operations. The chemical industry circumvents this difficulty by treating the acid spar with sulfuric acid to form hydrofluoric acid. This acid has many desirable features: (1) By weight it contains 95 percent fluorine; (2) its fluorine is readily available for many chemical reactions; and (3) it is a very useful chemical in many nonfluorinating types of reactions. The summation of these features is reflected in the fact that hydrofluoric acid is now considered a major industrial chemical. Due to the fact that hydrofluoric acid is used, directly or indirectly, in almost every fluorine chemical process, it can be called the "key chemical." This is further verified by the fact that the production trends of hydrofluoric acid accurately portray the activities of industry in fluorine chemicals.

Outside of the manufacture of hydrofluoric acid, fluorspar is used directly in very few chemical reactions for reasons stated previously. Recently a new process has been announced for "winning the fluoride values from fluorspar" which avoids the usual hydrofluoric acid route. In brief, the process involves the interaction of fluorspar, sulfuric acid and boric acid in an aqueous medium to form fluoboric acid (HBF_4). A low-grade of fluorspar may be used. The fluoboric acid can be used as such or converted to fluoborate salts, or used in the production of synthetic cryolite.

CERAMIC

The ceramic industry is the third largest user of fluorspar. A high quality product is required as indicated by the specifications under the ceramic grade. It is essential that the product not only have a high calcium fluoride content, but should be relatively free from iron or other coloring material. It is used in glass manufacture where opaque, colored, and clear glass is desired. Manufacturers of enamel and vitrolite use it as a fluxing and opacifying agent. The separation of the fluorides as solid crystallites is probably the important factor in opacity.

MISCELLANEOUS

The miscellaneous uses of fluorspar are rather numerous. A small amount of fluorspar is used in the electrolytic cells in the manufacture of aluminum. The magnesium industry requires a small amount to satisfy its special needs. It is used in the manufacture of calcium carbide and cyanamide to facilitate the fusion and contact of ingredients. Occasionally some is used in the clinkering process for the manufacture of cement, and the rock wool industry in certain instances requires a small amount to reduce the viscosity of its rock melts. It is used as a paint pigment, as a binder in abrasives, as a mineralizer in certain ceramic operations, in the manufacture of carbon electrodes, as a catalyst, welding fluxes and rods, and in heat resistant brick. Since a very small amount of fluorine prevents dental caries, some new dentrifices contain a small amount of fluorspar. It is reported that 1-3 parts per million of fluorine in drinking water is sufficient to prevent dental caries; larger amounts are undesirable due to the possibility of causing a condition called mottled teeth. Some of the colored material has been used in inexpensive jewelry and stone ornaments.

A clear and colorless fluorspar called optical spar is used in various optical instruments because (1) it has a low index of refraction, (2) it has a high transmissibility to light, especially to ultra-violet, and (3) it displays no double refraction. Due to the great scarcity of natural optical material, a process for the production of synthetic crystals of fluorspar has been developed. The process involves the very carefully controlled cooling of molten calcium fluoride so as to produce a large single crystal. This development of growing synthetic crystals has revolutionized the optical instrument field due to the ready availability of crystal types and sizes.

MAJOR FLUORINE CHEMICALS IN INDUSTRY

Any attempt to compile an extensive list of fluorine chemicals in the order of their relative economic importance would be almost impossible. The reason for such a situation is the lack of statistical information, and the reluctance of manufacturers to release production figures for competitve reasons. However, a few isolated facts stand out from which deductions can be made as to the major fluorine chemicals. According to table 6, approximately 90,000 tons of acid spar valued at $3,500,000 was shipped from the mines for the manufacture of hydrofluoric acid and derivatives in 1947. The production of anhydrous and technical hydrofluoric acid for the same year was about 27,000 tons.[22] As early as 1944, plant construction facilities were underway to achieve a monthly production of 2,400 tons of Freon. Turning to the silicofluorides, the Manufacturing Chemists Association[7] reported a domestic production of more than 10,000 tons of sodium silicofluoride in 1944. These facts not only speak for themselves as to the stature of certain fluorides, but also give the market analysts an opportunity to speculate on the value of the entire fluoride industry. For the purposes of our discussion, the major fluorine chemicals will be listed as hydrofluoric acid, organic fluorides (the Freons), silicofluorides, synthetic cryolite, and aluminum fluoride.

Hydrofluoric Acid

The largest production of any fluorine chemical is represented by hydrofluoric acid. This acid is one of the most unique chemicals in industry for two reasons, (1) it is a "key chemical" in almost all fluorine chemical processes, and (2) it finds extensive application in non-fluorinating processes as a catalyst, reaction medium, etc. Hydrofluoric acid production in 1944 reached its peak of 45,700 tons (calculated as 100 percent HF). This tonnage of acid on an anhydrous basis represents over 2,100 tank cars, 21.6-ton capacity, or a train more than 12 miles long. The relaxation of war demands caused a recession in hydrofluoric acid production to a low of 21,000 tons in 1946, but its recovery since then has been steady as indicated by a production of 3,000 tons in August 1948.[25] All indications are that this is a steady recovery due to greater diversification of uses and the development of new products. Anhydrous hydrofluoric acid of over 99 percent purity is available in carload lots at a current price of 16 to 16½ cents per pound (November 1948).

AQUEOUS AND ANHYDROUS HYDROFLUORIC ACID

Two types of hydrofluoric acid are commercially available, namely aqueous acid and anhydrous. The difference is that the aqueous acid is a water solution of hydrogen fluoride whereas the anhydrous product contains no water of solution. The anhydrous product is known in the trade 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 types of chemicals. Both are made by the same basic reaction, namely by the interaction of acid spar with sulfuric acid in suitably heated kilns:

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

The manufacture of aqueous acid preceded the production of the anhydrous product by many years. The hydrogen fluoride gases from the preceding reaction are absorbed in water in suitable lead cooling and absorbing towers. By recycling the absorption liquors, various strengths of acid can be obtained. Occasionally certain strengths are redistilled to give a higher quality acid. The usual strengths are 30, 40, 48, 52, and 60 percent; other strengths are available upon contract specifications. Those acids below 60 percent are generally shipped in lead or hard rubber containers, whereas 60 percent or higher may be handled in steel. More recently, the trend has been to dilute the anhydrous grade to the desired strengths. This arrangement is much more convenient as the anhydrous product can be stored in steel.

Anhydrous acid is made by the same general reaction, but under more rigidly controlled conditions.[3,6] The retort is a large revolving steel kiln which is heated at 300-800°C. Finely ground acid spar is mixed with a slight excess of sulfuric acid in a hopper and then fed into the kiln. A large vent pipe serves as a collector for the HF and other gaseous products. At the far end of the kiln, the by-product calcium sulfate is usually expelled by a screw drive into water. The vent gases are passed countercurrently into sulfuric acid absorption towers. Some of the HF, some water, and most of the SO_2 and SO_3 are absorbed in the sulfuric acid. The sulfuric acid builds up in HF content, and the HF is recovered by heating. Both the recovered and the unabsorbed HF are combined and distilled through suitable columns. Besides the anhydrous HF (b.p. 19°C.) which is condensed to a liquid by a refrigerating system, an aqueous residue is obtained also. The SiF_4 formed from the silica present in the fluorspar passes through the entire system as a gas. The aqueous residue is fortified with sulfuric acid and returned to the scrubbing towers.

The silicon tetrafluoride gas (SiF_4) is passed into water absorption towers to form fluosilicic acid (H_2SiF_6). It is because of this by-product that hydrofluoric acid manufacturers prefer a low silica fluorspar as it minimizes the loss of available fluorine. The fluosilicic acid derived from this source is channeled into industry in the same manner as the by-product acid derived from phosphate fertilizer plants.

Formerly, the type of equipment and the handling of hydrofluoric acid or its anhydrous product was of serious concern to the industry. Remarkable strides have been made in handling such a corrosive product so that all the operations are now within the realm of engineering materials well known to the chemical industry. Concentrations of acid above 60 percent can be conveniently handled in iron as well as magnesium, copper, monel, nickel, and brass. Lower acid strengths find lead a suitable engineering material; bakelite, wax, hard rubber, various plastics, such as polyethylene, are used also for container fabrication.

USES OF HYDROFLUORIC ACID

The uses of aqueous and anhydrous acid are many, and it is difficult to determine the consumption, value, and all of the specific uses for each type of acid. The Bureau of Census, Chemicals Unit,[25] reports the production of the acid on a 100 percent HF basis and does not differentiate between the types of acid. In 1944 about 50 percent (24,900 tons)[24] of the total acid production (45,700 tons as 100 percent HF) was earmarked as anhydrous acid. Indications as of 1948 are such that more anhydrous acid is being generated than aqueous. This agrees with the fact that the industrial trend is toward the anhydrous acid with subsequent dilution to the desired aqueous strengths.

Large tonnages of anhydrous hydrofluoric acid are used in the production of "alkylate" for the manufacture of 100-octane aviation gasoline and the Freon refrigerants. These items together account for the major consumption of the anhydrous product. The manufacture of the refrigerants is discussed below. Due to the development of HF-alkylation process by Universal Oil Products in 1942,[13,15] the wartime demand for HF was very large. The HF functions as a catalyst for the conversion of olefines and isoparaffins into an "alkylate" that consists of a mixture of isomers of heptane, octane, etc. Unconfirmed reports indicate that some reactors use 50 tons of HF. Because the process is catalytic, very little "make-up" HF is needed to maintain the reactors at their capacity.

As the properties of anhydrous hydrofluoric acid or pure hydrogen fluoride (HF) are quite different from those of the aqueous acid, a brief resume of its outstanding properties will help to explain its unusual applications. It is a clear colorless liquid that freezes at -83° and boils at 19.5°C. Because its boiling point is close to room temperature, it can be handled either as a liquid or as a gas, and in many instances can be readily recovered from a reaction mixture. In the liquid state its density is about the same as water, and it is very hygroscopic which makes it fume in moist air and react vigorously with water or ice; it has a high dielectric constant, its surface tension is extremely low, and it has a high fluidity. Complete details on the properties of this acid and materials of construction for handling are available in a number of publications and trade bulletins.[9,18,21,26]

Anhydrous hydrofluoric acid is used in the preparation of inorganic fluorides, especially those compounds which are unstable in water solution, in the production of elemental fluorine, as the basis for a new electrochemical process[20] for the direct synthesis of organic "fluorocarbons," as a stripping agent for enamel coatings in salvaging steel from defective enamelware, and it is a suitable reaction medium for effecting nitration with sodium or potassium nitrate. Organic sulfonation reactions are performed also in hydrogen fluoride with a measure of success. Cellulose dissolves very rapidly in it to form glucose, and a wood sugar process[14,17] developed in Germany depends upon this principal as a means of converting wood to sugar for fermentation to alcohol. Lignin can be recovered quantitatively from this process along with a certain amount of acetic acid.

The broadest field for the use of HF is in the organic chemical industry. This versatile material plays a dual role in organic syntheses: (1) It is used in the synthesis of organic fluorine compounds, and (2) it finds application in the synthesis of various types of nonfluorine-containing compounds. It can be used in such fields[21,26] as fluorination, hydrofluorination, polymerization, esterification, catalysis, alkylation, reaction media, nitrations, sulfonations, diazotizations, molecular rearrangements, degradations, ring closures, etc. Some of these applications will be discussed later. The aqueous acid finds use in the manufacture of many inorganic fluorides and acid fluorides; frosting, etching, and polishing of glass; as an antiseptic in breweries and distilleries; electroplating; cleaning of copper and brass; in the making of filter paper and carbon electrodes; and for the removal of silica from graphite; also in the removal of efflorescence from stone and brick, extraction of tantalum and columbium, pickling and galvanizing metals. Occasionally hydrofluoric acid is used in acidizing oil wells to increase oil production.

In any discussion on the manufacture, handling, and uses of hydrofluoric acid attention must be called to the personal hazards involved. Both the liquid and vapors produce very serious and painful burns which heal very slowly if not properly treated. A bulletin, "The Treatment of Hydrofluoric Acid Burns," published by the National Institute of Health, Washington, D. C., covers the subject very thoroughly and every organization is strongly advised to obtain copies as a Safety First measure.

Organic Fluorides (the Freons)

The phenomenal growth of the Freon refrigerants since their inception in 1930 to a proposed production capacity of 2,400 tons per month, as reported in 1944, represents one of the most outstanding developments in the synthetic organic chemical industry. Organic fluorine compounds prior to the advent of the Freons were considered laboratory curiosities, and the impact of these new refrigerants has been the development of new types of fluorine-containing fumigators, plastics, dielectrics, dyes, solvents, lubricants, etc. In spite of their cost, these new products have found application where their unusual properties are unmatched by any other materials. Furthermore, these developments represent only "surface scratches" as to what can be expected in the future.

Most of these new developments trace their origin, directly or indirectly, to fundamental research by Swarts, a pioneer Belgian chemist. In 1892 he discovered a chemical reaction which enabled him to synthesize the Freons and many other compounds. In tribute to 40 years of pioneering research devoted exclusively to organic fluorine compounds, chemists have perpetuated his name in the Swarts reaction.

REFRIGERANTS

In 1930, Midgley and Henne by means of the Swarts reaction announced the commercial production of a new group of refrigerants, called the Freons. The Swarts 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 hydrofluoric acid. To illustrate the mechanics of this reaction, the synthesis of dichlorodifluoromethane (F-12), CCl_2F_2, is indicated by a chemical equation along with a description of the commercial process.

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

Into a heated autoclave or reactor containing antimony trifluoride and a catalyst, both carbon tetrachloride and anhydrous hydrofluoric acid are fed continuously in a definite ratio. Antimony pentachloride is the catalyst most frequently used. The anhydrous hydrofluoric acid continuously regenerates the active fluorinating agent, antimony trifluoride. The reaction products pass into a distillation column where the free acids (HCl and HF) are separated from the Freon, and the insufficiently fluorinated raw material is returned to the reactor. For each chlorine atom that is replaced by a fluorine atom, there is a lowering of the boiling point by about 52° C., making the distillation operation very simple. The final product, after passing through scrubbing and drying towers, is condensed and shipped in steel cylinders, drums, and tank cars. By substituting carbon tetrachloride with other polychlorinated methanes and ethanes, various other Freons can be produced. It is obvious also from this discussion that these refrigerants are chlorofluoro derivatives of methane and ethane.

Since Freon is a family trade name, the various members are differentiated by code symbols for simplicity. F-12 is CCl_2F_2, the most common, and is loosely spoken of as Freon. Other members are F-11, CCl_3F; F-13, $CClF_3$; F-21, $CHCl_2F$; F-22, $CHClF_2$; F-113, CCl_2FCClF_2; and F-114, $CClF_2CClF_2$. In general, their outstanding features are stability, noninflamability, nontoxicity, and noncorrosiveness. They find extensive use in refrigeration and air conditioning equipment. The application and the type of compressor determines to a great extent the choice of refrigerant. General Chemical Company[1] in 1946 announced the availability of two fluorinated ethanes, CH_3CHF_2 and CH_3-$CClF_2$, and called them "Genetrons" 100 and 101, respectively. A brief resume of the research on refrigerants in Germany appeared in a recent bulletin[12] of the Office of Technical Services. In the chemical industry some of these compounds are used as intermediates in the manufacture of other fluorinated products. Certain fluorinated derivatives of propane and butane have been discussed in research circles as having practical application.

AEROSOL FUMIGATORS

An interesting application for F-11 and F-12 came as a result of the development of the aerosol fumigator or "bug bomb." The extermination of mosquitoes, flies, and other disease carrying insects in enclosed places became a matter of minutes with these fumigators. Briefly, the fumigator is a small, hand-sized cylinder filled with an insecticide, oil and Freon mixture, capable of fumigating a space of 150,000 cu. ft. When the ejection valve is opened, the Freon begins to boil, thus discharging the contents as a very fine mist which remains suspended in air for a long period of time. These fumigators were first delivered to the Armed Services in huge quantities and are available now as a household item. By far the largest percentage of Freon that is produced is consumed as a refrigerant and as a propellant for the aerosol fumigators.

Fluosilicic Acid and the Silicofluorides

The position of fluosilicic acid and its salts is unique as far as a fluorine chemical industry is concerned. The fertilizer phosphate industry confronted with a disposal problem of by-product gases that contain fluorine, developed a silicofluoride chemical industry. In other words, fluorine has always been considered a necessary evil by the phosphate interests. The magnitude of this by-product fluorine has been pointed out already, and its potential implications for the future cannot be ignored. Even though the phosphate industry is considered almost the exclusive producer of silicofluorides, the anhydrous hydrofluoric acid manufacturers also produce a small amount of this material as a secondary product. It should also be pointed out that it is possible to develop a silicofluoride industry based on low-grade fluorspar (high in silica) if economic conditions ever warrant it.

In the acidulation process for the manufacture of fertilizer phosphate, the rock phosphate is treated with sulfuric acid and approximately one-half of the fluorine is evolved in the form of a gaseous mixture. This toxic gaseous mixture of hydrofluoric acid, silicon tetrafluoride, and fluosilicic acid is passed through water absorption towers. Fluosilicic acid (H_2SiF_6) and a precipitate of silica are formed. Approximately one-half of the fluorine in the gases is recovered in this process. The fluosilicic acid liquor is concentrated to commercial strengths by recycling or distillation.

Fluosilicic acid is sold generally in strengths of 30 to 35 percent, although other concentrations are available. A large use for this acid is in the brewing industry as a disinfectant for copper and brass vessels. It is sold also for use as a preservative, in electroplating, as a concrete hardener, and in the manufacture of silicofluoride salts.

Sodium silicofluoride (Na_2SiF_6) is the most common salt, and is readily prepared by the addition of sodium chloride or soda ash to the acid. It precipitates from solution as a white finely-divided product. In many recovery plants this salt is considered as the sole means of disposal. It is used extensively as an insecticide, laundry sour, fluxing and opacifying agent in the ceramic industry, and as a protective agent in the casting of light metals. With a production of over 10,000 tons in 1944, its value for that year can be estimated to be about one million dollars.

Ammonium fluosilicate is prepared by neutralizing fluosilicic acid with strong ammonia. This salt is used extensively in the laundry and light metal casting industry. The magnesium and zinc fluosilicates also are prepared from the acid by neutralization. Both salts are used as concrete or wall hardeners, and the magnesium salt finds application also in magnesium foundries. The zinc and copper salts are useful as impregnating compounds for the prevention of wood decay. Barium silicofluoride is a common insecticide and is also used in ceramics. Lead fluosilicate is used primarily in the electrolytic refining and plating of lead. Occasionally salts such as calcium, iron, aluminum, cobalt, nickel, and potassium are mentioned as having special limited uses. It is interesting to note that zinc, magnesium, copper, and lead fluosilicates are all quite soluble in contrast to the sodium and potassium salts.

Synthetic Cryolite and Aluminum Fluoride

The aluminum industry is one of the heaviest consumers of fluorine compounds. Cryolite comprises the molten bath in the electrolytic cells. Aluminum fluoride and fluorspar are added directly in small amounts from time to time while the cells are operating. It is difficult to arrive at exact consumption figures for each component, although it is stated in Part I that 0.1 lb. of cryolite is required for each pound of metallic aluminum produced. On this basis, 60,000 tons of cryolite was required in 1947 to produce 600,000 tons of aluminum.

It has long been known that the aluminum industry is not dependent upon natural cryolite and is consuming large quantities of the synthetic material derived from fluorspar. Unofficial statements indicate that the natural cryolite is favored usually when the cells are put into operation. In general, synthetic cryolite is prepared by reacting a mixture of alumina and hydrofluoric acid, and neutralizing it with soda ash or alkali. A more recent process was mentioned previously. The synthetic processes enable the manufacturers to produce a uniform and high quality cryolite. Aluminum fluoride can be readily prepared by simply reacting alumina with hydrofluoric acid.

Both synthetic cryolite and aluminum fluoride are used in the ceramic industry. The insecticidal industry offers a ready market for cryolite, especially in the form of fruit orchard sprays. One of the prerequisites for insecticidal purposes is that the material be very finely divided in order to be effective.

MINOR FLUORINE CHEMICALS IN INDUSTRY

The fluorine chemicals discussed in this section have been arbitrarily grouped together for the sake of brevity. Some compounds may be produced in tonnage lots at a fairly low unit cost, whereas others may have a limited market and demand a high price. The real purpose of this discussion is to point out the wide range of uses along with the wartime and more recent developments of the fluorine industry.

Inorganic Fluorides

Simple inorganic fluorides may be classified into two groups, depending upon their stability in water. Those stable in water solution can be prepared by reacting their carbonates, oxides, or hydroxides with aqueous hydrofluoric acid. This group comprises practically all of the well known fluorides. Some of them form acid fluorides with an excess of acid. The double fluorides are obtained by reacting two basic components in the proper proportions in hydrofluoric acid. The second group, fluorides which hydrolyze in water, are prepared usually from the chlorides with anhydrous acid; examples of this group are boron trifluoride (BF_3) and antimony pentafluoride (SbF_5). Still another group of fluorides requires gaseous fluorine in their synthesis. Examples are cobalt trifluoride (CoF_3), chlorine trifluoride (ClF_3), sulfur hexafluoride (SF_6), and uranium hexafluoride (UF_6).

The uses of inorganic fluorides extend over a broad range, but relatively few are used in tonnage lots. Most common salts are the sodium, ammonium, potassium, barium, zinc, magnesium, chromium, aluminum and antimony salts. The sodium, potassium, and ammonium salts find use in preservatives and insecticides (a common roach powder uses sodium fluoride). The ceramic industry utilizes salts of lithium, sodium, copper, beryllium, barium, strontium, zinc and aluminum. Beryllium fluoride and its sodium double salt are used in the production of metallic beryllium. Sodium fluoride is used in the steel industry for promoting soundness in the outer layer of a steel ingot and in rim steel production. Zinc fluoride is used in insecticides and for wood preserving. The chromium salt finds application in the textile printing and dyeing industries. Antimony, mercury, zinc, and potassium fluorides are used in the synthesis of organic fluorine compounds. Boron trifluoride is used as a catalyst in the manufacture of some synthetic rubbers and fine organic chemicals. Rare earth fluorides are used in the cores of carbon electrodes for anti-aircraft searchlights. Synthetic fluoride crystals of lithium and calcium are used in optical instruments. Cobalt trifluoride finds extensive use in the synthesis of "fluorocarbons." Chlorine trifluoride was contemplated for use in incendiary bombs, and can be used in certain types of fluorinations. Due to its high dielectric value, sulfur hexafluoride is used as a gaseous insulator in x-ray equipment and the like where extremely high voltages are involved. It possesses the additional features of being non-toxic, extremely stable (more inert than nitrogen), non-inflammable, and five times as heavy as carbon dioxide gas.

Uranium hexafluoride, UF_6, merits special attention because of its basic use in atomic energy and the first "atom bomb." Uranium possesses certain isotopes required for nuclear reactions, and in order to separate and concentrate these isotopes by some suitable means, it became necessary to find a thermally stable uranium compound with a high vapor pressure near room temperature.[5] The only compound meeting these specifications is UF_6 with a sublimation point of 56° C. In other words, a fluorine compound was instrumental in opening the door to an atomic energy world. The amount of uranium hexafluoride which has been produced or will be in the future is relegated appropriately to the secret archives of the Atomic Energy Commission.

In commerce, the acid fluorides are usually represented by the sodium, potassium, and ammonium salts. They are used as laundry sours, for etching glass, in welding fluxes, and in fusion mixtures for the extraction of various metals. The potassium salt is used exclusively in the commercial preparation of fluorine. Fluoboric acid, HBF_4, is used in electroplating, aluminum reflectors, and in the manufacture of dyes and organic fluorine chemicals.

Among the double salts, synthetic cryolite, Na_3AlF_6, is the most important. Sodium antimony fluoride is used as a mordant in dyes and in the synthesis of organic fluorides. The sodium, potassium, and ammonium fluoborates find application as sand agents in the casting of aluminum and magnesium, in electro-chemical processes, and chemical research.

FLUORINE GAS

Henri Moissan in 1886 succeeded in preparing fluorine, as a free element, by the electrolysis of potassium acid fluoride. Almost sixty years elapsed before scientists in Germany and the United States solved the problem of handling fluorine safely and producing it in large quantities. It is interesting to note that this was achieved almost simultaneously and independently by two groups of scientists on opposing sides during World War II. The development of the modern cells is described in detail in a number of publications. [2,10]

Two types of cells have been developed, one operating at about 100° and the other at 250° C. Both types use potassium acid fluoride as the electrolyte and anhydrous HF is fed into the cells to maintain the proper composition. According to reports from Germany, 2,000 ampere cells operating at 8-15 volts with a current efficiency of 95 percent were capable of producing almost 2,000 pounds of fluorine per month. They reached a total output of 50 tons of fluorine per month. The fluorine gas is piped through steel or copper pipes, and stored in steel cylinders. Small laboratory cells are available as well as small cylinders of fluorine for experimental purposes. Fluorine being the most reactive element known, unusual precautions must be strictly observed in its generation, handling, and application.

The uses of fluorine are very limited at the present time. Presumably, large quantities were and are being used in the preparation of uranium hexafluoride from a uranium oxide for nuclear reactions. Sulfur hexafluoride is prepared by the direct combination of sulfur and fluorine. Higher metallic fluorides (CoF_3, AgF_2, CeF_4, MnF_3, etc.) and halogen fluorides (ClF_3 and BrF_3), useful in certain organic fluorinations, can be prepared only by the use of fluorine gas because of its high oxidation potential.

One of the methods developed during the war for the production of "fluorocarbons" involves the direct fluorination of organic compounds. These compounds and other methods of synthesis are discussed later.

ORGANIC MISCELLANEA

The synthetic organic chemical industry, with its diversity of compounds and extensive applications, offers unlimited opportunities for the development of organic fluorine compounds in many fields of interest. In order to show that this industry is beginning to recognize these possibilities, a number of compounds which have appeared in the trade are discussed.

DYES AND DYE INTERMEDIATES

The I. G. Company of Germany introduced a group of fluorine-containing dyes[13] to the American market in the 1930's. These brilliant dyes of yellow, orange and red colors exhibited unusual color clearness and possessed excellent light and laundry fastness. Fast Orange Salt RD and Fast Orange Golden Salt GR are two examples of this group, and supposedly they are benzotrifluoride derivatives. Benzotrifluoride ($C_6H_5CF_3$) is a very stable organic fluorine compound and the American production of this compound has been announced recently. It is interesting to note that once these dyes appeared on the market, imports increased each year until the Nazi miltary machine began its European expansion program.

Concurrently with these dyes, the above company also introduced certain stabilized diazo salts containing the fluoborate radical. In other words, they were diazonium salts of fluoboric acid (HBF_4). Fast Red Salt RL, 2-methyl-4-nitrobenzene diazonium fluoborate, is a typical example. Besides fluoboric acid, certain metallic fluorides, fluorosulphonic acid, and borofluorosulfonic acid can be used as diazo stabilizers.

"FLUOROCARBONS"

The "atom bomb" was responsible not only for the large-scale production of gaseous fluorine and uranium hexafluoride, but also for the development of a group of completely fluorinated organic compounds. In order to separate the isotopes of uranium by a gaseous diffusion process, it became necessary to develop a liquid[2] which possessed unusual thermal and chemical stability. The completely fluorinated hydrocarbons provided the answer and are known under variously coined terms such as "perfluoro" hydrocarbons, "fluorocarbons," and "fluocarbons."

The synthesis of these compounds depended upon the development of controlled methods of fluorination of hydrocarbons without the usual explosions or extensive scission of carbon-carbon linkages. This is due to the fact that fluorine is the most reactive element known, and its heat of reaction is so high that very few organic systems can absorb the heat impact directly without disintegrating. Two general methods were developed, (1) fluorination with gaseous fluorine, and (2) fluorination with CoF_3, etc. It is interesting to compare the heats of reaction in the two methods.

$$(1)\quad C_7H_{16} + 16F_2 \longrightarrow C_7F_{16} + 16HF + 1660 \text{ kg.-cal.}$$

$$(2)\quad C_7H_{16} + 32CoF_3 \longrightarrow C_7F_{16} + 32CoF_2 + 16HF + 1000 \text{ kg.-cal.}$$

The second method has the lower heat of reaction, due to the fact that part of the energy has been dissipated previously in a separate system in converting CoF_2 to CoF_3. Complete details of both methods of fluorination and the various fluorinating agents which can be used have been described in the March 1947 issue of *Industrial and Engineering Chemistry.*

A new and novel process for the preparation of fluorocarbons has recently been announced by Simons and co-workers[20] which appears to accomplish the same objectives as direct fluorination. It is an electrochemical process involving the electrolysis of organic substances in liquid hydrogen fluoride.

One of the uses for the liquid "fluorocarbons" has been mentioned already in connection with the "atom bomb." Due to their unusual stability and non-inflammability, their use as lubricants, coolants, and hydraulic liquids has been suggested.

PLASTICS

Today there are two fluorine-containing plastics on the market. Teflon derived from tetrafluoroethylene is produced by the du-Pont Company. The other, Kel-F, derived from trifluorochloroethylene is marketed by the M. W. Kellogg Company.

Both plastics are produced from a Freon type of compound. They are non-inflammable, insoluble in organic solvents, very stable to chemical agents, possess high thermal stability, and are excellent dielectric materials. One of the first uses for Teflon was as a gasket material in fluorine cell construction. Due to their high cost they will find use only where very unusual conditions exist.

INSECTICIDES—DFDT

During the recent war, in Germany considerable use was made of a fluorine compound related to DDT. It is called DFDT and chemically it is known as 4,4'-difluorodiphenyl trichloroethane. Instead of using chlorobenzene as in the synthesis of DDT, fluorobenzene is used. Production of DF-DT must have reached sizable proportions, as fluorobenzene was produced at the rate of 12 tons per month for the manufacture of this insecticide.[11] It appears that for certain insects it is more effective than DDT. The production cost of this insecticide is considerably higher due to the higher cost of fluorobenzene over that of chlorobenzene. It remains to be seen if this insecticide will find a place on the American market.

"1080"

During the war years the sodium salt of monofluoroacetic acid ($CH_2FCOONa$) was discovered to be the most toxic rodenticide known. For secrecy reasons it was given the code number "1080." It possesses high toxicity to all rodents tested, excellent acceptance, quick action, absence of objectionable taste and odor, chemical stability and non-volatility, and lack of toxicity to the skin. Its distribution is very carefully controlled, as it is very poisonous also to humans if taken internally, plus the fact that there is no known antidote for it.

The commercial process for its manufacture has been described by Jenkins and Koehler.[16] About 10,000 pounds per year meet the present commercial demand. During the war it was used extensively for rodent control around military installations.

"There is nothing new under the sun" aptly applies to "1080." Nature has endowed a plant in South Africa with the ability to synthesize this toxic principle, and its identification in the plant was not accomplished until 1944 by Marais.[19] This is the first recorded synthesis of an organic fluorine compound in nature. To add a bit of irony to the great war secret, the natives in the natural habitat of the plant have been aware of its poisonous properties to cattle and rodents for many years.

DRUGS

Pardinon (3-fluorotyrosine) and Epidermin (4,4'-difluorobiphenyl) appeared on the German drug market before the war.[13] The sodium salt of *para*-fluorobenzoic acid has been mentioned as an internal antiseptic. Di-isopropyl fluorophosphate, called DFP, is a very toxic material, but in very low concentrations it can be used in medical work.

FUTURE PROSPECTS IN FLUORINE CHEMISTRY

After reviewing the position of fluorine and its compounds in industry, it is obvious that fluorine chemicals are finding their industrial niches by the impact of their unique properties. By the same token, industry has found a new tool in fluorine chemistry that has fabricated and will fabricate for tomorrow new products of majestic quality. In view of these facts, it is very much to the point to discuss briefly some fundamental concepts of fluorine chemistry. Fluorine is the most reactive and electronegative element known. It has the distinction of being the first member of the well-known halogen family (F, Cl, Br, and I). Due to its distinguished position in the family, the element and its compounds exhibit not only some of the usual family characteristics, but many unique properties quite foreign to the other members. These concepts lead to a research philosophy that anything can happen in fluorine chemistry. The achievements of the last decade are but a feeble introduction to the many frontiers still waiting to be challenged and probed. In short, fluorine promises to write one of the most brilliant chapters in academic and industrial chemistry.

A synthetic fluorine chemical industry is based essentially on fluorspar and hydrofluoric acid, and an industrial fluorine economy will continue to revolve around these basic materials for many years to come.

Much has been said about the availability of fluorspar, the primary raw material. It is true that it is a strategic mineral, but by shifting the demand for metallurgical spar under emergency conditions, through a good neighbor policy, to Mexico and other sources, the domestic industry should be able to produce adequate tonnages of acid spar for many years. This is further enhanced by the fact that the Illinois-Kentucky fluorspar district has the facilities, the "know-how," and the capability of producing increased tonnages of high grade acid spar of constant and uniform quality.

Very little needs to be said about hydrofluoric acid, the key chemical, except in retrospect. It is available in all strengths, on a large tonnage basis, and at a fairly reasonable price. It is interesting to note that the demand for the acid is increasing steadily since the war recession. This means that the chemical industry is expanding its fluorine chemical interests in a peacetime economy.

Research and development in fluorine chemicals is no longer relegated to the isolated recesses of a few intrepid academic investigators. Modern technology has solved many of the difficult problems of handling, control, and operation. In fact, many process industries are capable of embarking upon a fluorine program because of the calibre of their research staffs, experience in handling other operations just as hazardous, and the availability of modern equipment. Immediate success is not to be expected, but a long-range program based upon an experienced and capable staff, and synchronized with materials already within the organization, is bound to achieve commercial objectives.

The opportunities for research with fluorine chemicals is almost unlimited. Since fluorine in its compounds exhibits very unusual properties, advantage must be taken of the unusual. Fluorine compounds will be expensive and they must find their place on the industrial market where their superiority will not have any close competitors. In general, fluorine exhibits unusual stability in its compounds in contrast to chlorine or other halogen atoms. There are many changes in properties, induced by it in compounds, such as volatility, surface tension, index of refraction, etc. Such fields as solvents, plastics, medicine, pharmaceuticals, dyes, insecticides[4] and many others offer unusual opportunities. Fluorine compounds run the extreme in toxicity; some are as inert as nitrogen, whereas others such as "1080" are very poisonsous. Very few studies have been made on toxicity and the effect of fluorine in biological systems. In retrospect, fluorine chemistry is one of the newest fields of chemical endeavor and promises to increase in stature in the future.

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APPENDIX

STATISTICAL SUMMARY OF THE FLUORSPAR INDUSTRY

PRODUCTION—SHIPMENTS

IMPORTS—EXPORTS—TARIFFS

CONSUMPTION

RESERVES

TABLE 1.—FLUORSPAR SHIPPED FROM MINES IN THE UNITED STATES BY STATES, 1880–1947[a, b]

Year	ILLINOIS			KENTUCKY		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1880	4,000	$ 16,000	$ 4.00	—	—	—
1881	4,000	16,000	4.00	—	—	—
1882	4,000	20,000	5.00	—	—	—
1883	4,000	20,000	5.00	—	—	—
1884	4,000	20,000	5.00	—	—	—
1885	5,000	22,500	4.50	—	—	—
1886	3,500	15,400	4.40	1,500	$ 6,600	$ 4.40
1887	3,500	14,000	4.00	1,500	6,000	4.00
1888	6,000	30,000	5.00	—	—	—
1889	9,500	45,835	4.82	—	—	—
1890	8,250	55,328	6.71	—	—	—
1891	10,044	78,330	7.80	—	—	—
1892	12,250	89,000	7.27	—	—	—
1893	12,400	84,000	6.27	—	—	—
1894	7,500	47,500	6.33	—	—	—
1895	4,000	24,000	6.00	—	—	—
1896	5,000	40,000	8.00	1,500	12,000	8.00
1897	3,562	25,159	7.06	1,500	12,000	8.00
1898	—	—	—	7,675	63,050	8.21
1899	3,300	23,000	6.97	12,600	73,650	5.85
1900	3,000	12,600	4.20	15,450	81,900	5.30
1901	6,086	37,405	6.15	13,500	76,398	5.66
1902	18,360	121,550	6 62	29,030	143,410	4.94
1903	11,413	57,620	5.05	30,835	153,960	4.99
1904	17,205	122,172	7.10	19,096	111,499	5.84
1905	33,275	220,206	6.62	22,694	132,362	6.83
1906	28,268	160,623	5.68	11,868	79,802	6.72
1907	25,128	141,971	5.65	21,058	133,971	6.36
1908	31,727	172,838	5.45	6,323	48,642	7.69
1909	41,852	232,251	5.55	7,800	53,233	6.82
1910	47,302	277,764	5.87	17,003	124,574	7.33
1911	68,817	481,635	7.00	12,403	96,574	7.79
1912	103,937	695,467	6.69	10,473	61,186	5.84
1913	85,854	550,815	6.42	19,622	113,903	5.80
1914	73,811	426,063	5.77	19,077	128,986	6.76
1915	116,340	624,040	5.36	19,219	129,873	6.76
1916	126,369	746,150	5.90	19,698	123,596	6.27
1917	156,676	1,373,333	8.77	43,639	697,566	15.98
1918	132,798	2,887,099	21.74	87,604	2,069,185	23.62
1919	92,729	2,430,361	26.21	32,386	883,171	27.27
1920	120,299	3,096,767	25.74	46,091	1,246,942	27.05
1921	12,477	315,767	25.31	15,266	294,513	19.29
1922	83,855	1,493,188	17.81	52,484	970,059	15.48
1923	65,045	1,443,490	22.19	45,441	945,402	20.81
1924	62,067	1,288,310	20.76	47,847	988,940	20.67
1925	54,428	1,024,516	18.82	44,826	833,794	18.60
1926	53,734	1,012,879	18.85	62,494	1,167,129	18.68
1927	46,006	863,909	18.78	57,495	1,040,338	18.09
1928	65,884	1,154,983	17.53	69,747	1,426,766	20.46
1929	67,009	1,284,834	19.17	70,827	1,390,603	19.63
1930	44,134	836,473	18.95	39,181	763,370	19.48
1931	28,072	468,386	16.69	23,462	437,642	18.65
1932	9,615	156,279	16.25	14,725	225,052	15.28
1933	36,075	543,060	15.05	34,614	469,451	13.56
1934	33,234	587,396	17.07	43,163	690,990	16.01
1935	44,120	685,794	15.54	68,679	1,017,451	14.81
1936	82,056	1,525,606	18.59	80,241	1,409,433	17.56
1937	78,664	1,730,585	22.00	87,296	1,710,122	19.59

Table 1.—Fluorspar Shipped from Mines in the United States by States, 1880–1947 [a, b]—(Continued)

Year	ILLINOIS			KENTUCKY		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1938	35,368	$ 751,227	$21.24	34,803	$ 678,094	$19.48
1939	75,257	1,638,693	21.77	89,563	1,773,063	19.30
1940	104,698	2,313,747	22.10	103,939	2,043,866	19.66
1941	133,333	3,047,247	22.85	142,862	2,957,982	20.71
1942	161,949	4,306,750	26.59	134,133	3,266,257	24.35
1943	198,789	6,292,789	31.66	109,849	3,122,513	28.43
1944	176,259	5,954,991	33.79	112,791	3,363,788	29.82
1945	147,251	5,014,807	34.06	95,142	2,832,945	29.78
1946	154,525	5,493,642	35.55	63,143	1,889,454	29.92
1947	167,157	6,148,654	36.78	90,256	2,713,508	30.06
Total	3,676,113	$72,912,784	$19.83	2,365,413	$47,286,558	$19.99
	COLORADO			NEW MEXICO		
1880	—	—	—	—	—	—
1881	—	—	—	—	—	—
1882	—	—	—	—	—	—
1883	—	—	—	—	—	—
1884	—	—	—	—	—	—
1885	—	—	—	—	—	—
1886	—	—	—	—	—	—
1887	—	—	—	—	—	—
1888	—	—	—	—	—	—
1889	—	—	—	—	—	—
1890	—	—	—	—	—	—
1891	—	—	—	—	—	—
1892	—	—	—	—	—	—
1893	—	—	—	—	—	—
1894	—	—	—	—	—	—
1895	—	—	—	—	—	—
1896	—	—	—	—	—	—
1897	—	—	—	—	—	—
1898	—	—	—	—	—	—
1899	—	—	—	—	—	—
1900	—	—	—	—	—	—
1901	—	—	—	—	—	—
1902	—	—	—	—	—	—
1903	—	—	—	—	—	—
1904	—	—	—	—	—	—
1905	1,156	$ 8,200	$ 7.09	—	—	—
1906	300	1,800	6.00	—	—	—
1907	3,300	11,400	3.45	—	—	—
1908	701	4,266	6.09	—	—	—
1909	350	2,100	6.00	710	$ 3,728	$ 5.25
1910	268	1,608	6.00	4,854	26,250	5.41
1911	721	4,226	5.86	4,307	22,612	5.25
1912	1,639	9,834	6.00	196	1,176	6.00
1913	4,432	26,592	6.00	5,372	42,976	8.00
1914	1,978	12,992	6.57	—	—	—
1915	247	1,482	6.00	485	3,880	8.00
1916	8,669	42,457	4.90	—	—	—
1917	17,104	196,633	11.50	—	—	—
1918	38,475	416,780	10.83	3,437	64,348	18.72
1919	9,687	150,739	15.56	2,346	37,643	16.05
1920	12,852	251,308	19.55	6,353	101,460	15.97

TABLE 1.—FLUORSPAR SHIPPED FROM MINES IN THE UNITED STATES BY STATES, 1880–1947 [a, b]—(Continued)

Year	COLORADO			NEW MEXICO		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1921	3,143	$ 39,907	$12.70	3,507	$ 60,186	$17.16
1922	2,309	20,169	8.73	2,180	30,992	14.22
1923	6,044	59,710	9.88	4,328	50,861	11.75
1924	12,301	135,411	11.01	2,580	35,178	13.63
1925	11,776	153,707	13.05	2,639	40,325	15.28
1926	10,440	128,211	12.28	1,989	33,058	16.62
1927	6,432	82,503	12.83	2,613	47,978	18.36
1928	1,815	18,040	9.94	2,589	50,162	19.38
1929	4,808	56,607	11.77	2,438	35,682	14.64
1930	9,248	101,758	11.00	2,312	30,775	13.31
1931	529	5,921	11.19	1,026	13,629	13.28
1932	333	3,330	10.00	529	6,956	13.15
1933	742	6,778	9.13	994	[c] 19,889	[c]13.27
1934	6,537	83,132	12.72	2,040	[c] 49,887	[c]17.49
1935	6,978	88,454	12.68	2,726	[c] 68,823	[c]17.39
1936	9,412	109,411	11.62	2,045	[c] 66,818	[c]14.78
1937	7,883	98,493	12.49	3,324	[c] 105,733	[c]18.02
1938	1,704	27,543	12.73	4,066	[c] 142,802	[c]17.70
1939	7,569	107,459	14.20	4,869	[c] 132,408	[c]20.44
1940	11,032	163,285	14.80	6,616	[c] 139,675	[c]17.49
1941	15,566	225,069	14.46	17,591	[c] 355,951	[c]18.65
1942	31,743	640,938	20,19	22,542	[c] 530,025	[c]22.76
1943	49,145	1,164,868	23.70	37,050	986,094	26.62
1944	65,209	1,604,043	24.60	42,973	1,205,830	28.06
1945	52,437	1,333,735	25.43	14,449	390,331	27.01
1946	32,539	925,867	28.45	17,584	489,607	27.84
1947	32,153	950,882	29.57	27,526	841,095	30.56
Total	501,156	$9,477,648	$18.91	263,185	(g)	(g)
	ARIZONA			NEVADA		
1880	—	—	—	—	—	—
1881	—	—	—	—	—	—
1882	—	—	—	—	—	—
1883	—	—	—	—	—	—
1884	—	—	—	—	—	—
1885	—	—	—	—	—	—
1886	—	—	—	—	—	—
1887	—	—	—	—	—	—
1888	—	—	—	—	—	—
1889	—	—	—	—	—	—
1890	—	—	—	—	—	—
1891	—	—	—	—	—	—
1892	—	—	—	—	—	—
1893	—	—	—	—	—	—
1894	—	—	—	—	—	—
1895	—	—	—	—	—	—
1896	—	—	—	—	—	—
1897	—	—	—	—	—	—
1898	—	—	—	—	—	—
1899	—	—	—	—	—	—
1900	—	—	—	—	—	—
1901	—	—	—	—	—	—
1902	500	—	—	—	—	—
1903	79	$6,593	$10.08	—	—	—

Table 1.—Fluorspar Shipped from Mines in the United States by States, 1880–1947 [a, b]—(Continued)

Year	ARIZONA			NEVADA		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1904	75	—	—	—	—	—
1905	—	—	—	—	—	—
1906	—	—	—	—	—	—
1907	—	—	—	—	—	—
1908	34	$ 252	$ 7.41	—	—	—
1909	30	435	14.50	—	—	—
1910	—	—	—	—	—	—
1911	—	—	—	—	—	—
1912	—	—	—	—	—	—
1913	100	800	8.00	—	—	—
1914	—	—	—	—	—	—
1915	—	—	—	—	—	—
1916	199	2,587	13.00	—	—	—
1917	135	1,080	8.00	—	—	—
1918	364	5,537	15.21	—	—	—
1919	45	450	10.00	400	$ 5,600	$14.00
1920	181	3,264	18.03	532	8,672	16.30
1921	—	—	—	—	—	—
1922	—	—	—	—	—	—
1923	—	—	—	—	—	—
1924	—	—	—	—	—	—
1925	—	—	—	—	—	—
1926	—	—	—	—	—	—
1927	—	—	—	—	—	—
1928	—	—	—	455	6,603	14.51
1929	—	—	—	1,357	23,400	17.24
1930	—	—	—	974	14,267	14.65
1931	—	—	—	395	5,697	14.42
1932	—	—	—	49	882	18.00
1933	—	—	—	505	(c)	(c)
1934	—	—	—	631	(c)	(c)
1935	—	—	—	1,040	(c)	(c)
1936	40	(c)	(c)	2,126	(c)	(c)
1937	610	(d)	(d)	2,544	(c)	(c)
1938	1,093	(c)	(c)	2,909	(c)	(c)
1939	1,608	(c)	(c)	3,520	[f] 53,336	[f]13.66
1940	1,370	(c)	(c)	5,803	[f] 84,235	[f]14.17
1941	1,428	(c)	(c)	8,967	[f]138,533	[f]14.11
1942	714	(c)	(c)	8,020	[f]153,779	[f]16.72
1943	1,328	26,441	19.91	8,653	(d)	(d)
1944	976	21,983	22.52	7,293	(d)	(d)
1945	1,126	21,016	18.66	7,038	(d)	(d)
1946	389	7,959	20.46	6,234	(d)	(d)
1947	1,601	—	—	8,042	(d)	(d)
Total	14,025	(g)	(g)	77,487	(g)	(g)
	OTHER STATES			UNITED STATES		
1880	—	—	—	4,000	$16,000	$4.00
1881	—	—	—	4,000	16,000	4.00
1882	—	—	—	4,000	20,000	5.00
1883	—	—	—	4,000	20,000	5.00
1884	—	—	—	4,000	20,000	5.00
1885	—	—	—	5,000	22,500	4.50
1886	—	—	—	5,000	22,000	4.40

TABLE 1.—FLUORSPAR SHIPPED FROM MINES IN THE UNITED STATES BY STATES, 1880–1947 [a, b]—(Continued)

Year	OTHER STATES			UNITED STATES		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1887	—	—	—	5,000	$ 20,000	$ 4.00
1888	—	—	—	6,000	30,000	5.00
1889	—	—	—	9,500	45,835	4.82
1890	—	—	—	8,250	55,328	6.71
1891	—	—	—	10,044	78,330	7.80
1892	—	—	—	12,250	89,000	7.27
1893	—	—	—	12,400	84,000	6.77
1894	—	—	—	7,500	47,500	6.33
1895	—	—	—	4,000	24,000	6.00
1896	—	—	—	6,500	52,000	8.00
1897	—	—	—	5,062	37,159	7.34
1898	—	—	—	7,675	63,050	8.21
1899	—	—	—	15,900	96,650	6.08
1900	—	—	—	18,450	94,500	5.12
1901	—	—	—	19,586	113,803	5.81
1902	128	—	—	48,018	271,832	5.66
1903	196	$ 3,400	$ 8.50	42,523	213,617	5.02
1904	76	—	—	36,452	234,755	6.44
1905	260	1,720	6.62	57,385	362,488	6.32
1906	360	1,800	5.00	40,796	244,025	5.98
1907	—	—	—	49,486	287,342	5.81
1908	—	—	—	38,785	225,998	5.83
1909	—	—	—	50,742	291,747	5.75
1910	—	—	—	69,427	430,196	6.20
1911	800	6,400	8.00	87,048	611,447	7.02
1912	300	1,500	5.00	116,545	769,163	6.60
1913	200	1,200	6.00	115,580	736,286	6.37
1914	250	2,000	8.00	95,116	570,041	5.99
1915	650	5,200	8.00	136,941	764,475	5.58
1916	800	7,864	9.83	155,735	922,654	5.92
1917	1,274	19,110	15.00	218,828	2,287,722	10.45
1918	1,139	22,532	19.78	263,817	5,465,481	20.72
1919	697	17,610	25.26	138,290	3,525,574	25.49
1920	470	10,134	21.56	186,778	4,718,547	25.26
1921	567	13,721	24.20	34,960	724,094	20.71
1922	768	16,757	21.82	141,596	2,531,165	17.88
1923	330	6,356	19.26	121,188	2,505,819	20.68
1924	184	3,292	17.89	124,979	2,451,131	19.61
1925	—	—	—	113,669	2,052,342	18.06
1926	—	—	—	128,657	2,341,277	18.20
1927	—	—	—	112,546	2,034,728	18.08
1928	—	—	—	140,490	2,656,554	18.91
1929	—	—	—	146,439	2,791,126	19.06
1930	—	—	—	95,849	1,746,643	18.22
1931	—	—	—	53,484	931,275	17.41
1932	—	—	—	25,251	392,499	15.54
1933	—	—	—	72,930	1,039,178	14.25
1934	6	(c)	(c)	85,786	1,391,405	16.22
1935	373	(c)	(c)	123,741	1,860,638	15.04
1936	311	(c)	(c)	176,231	3,111,268	17.65
1937	909	21,696	14.28	181,230	3,666,629	20.23
1938	460	(e)	(e)	80,403	1,599,666	19.90
1939	385	(f)	(f)	182,771	3,704,959	20.27
1940	142	(f)	(f)	233,600	4,744,808	20.31
1941	922	(f)	(f)	320,669	6,724,782	20.97
1942	1,215	(f)	(f)	360,316	8,897,749	24.69
1943	1,202	207,900	21.19	406,016	11,802,255	29.07
1944	8,280	352,452	22.66	413,781	12,503,487	30.22

Table 1.—Fluorspar Shipped from Mines in the United States by States, 1880–1947 [a], [b]—(Concluded)

Year	OTHER STATES			UNITED STATES		
	Net tons	Value		Net tons	Value	
		Total	Av.		Total	Av.
1945	6,518	$375,665	$22.70	323,961	$ 9,896,879	$30.55
1946	3,526	232,440	23.82	277,940	9,038,969	32.52
1947	2,749	300,736	24.27	329,484	10,954,875	33.25
Total	37,093	—	—	6,935,022	$138,097,245	$19.91

[a] U. S. Bureau of Mines, Minerals Yearbooks and Mineral Market Report No. 1596.

[b] Figures from 1880-1905 represent production.

[c] Value for Nevada, 1933-1938; Arizona, 1936 and 1938-1942; New Hampshire and Utah, 1935 and 1936; Texas, 1941 and 1942; included with New Mexico.

[d] Value for Arizona in 1937 and Nevada, 1943-1947, included in "other states." Except where otherwise stated, "other states" includes California, New Hampshire, Tennessee, Texas, Utah, Washington and Wyoming.

[e] Value for Utah and New Hampshire included with Colorado, 1938.

[f] Value for Utah 1939-1942 and Washington 1941-1942 included with Nevada.

[g] Data for individual states not available for complete value and average.

Table 2.—Summary of Fluorspar Shipped* from Mines in the United States, 1880–1947, by States [a], [b]
(In net tons)

Year	Arizona	Colorado	Illinois	Kentucky	Nevada	New Mexico	Other states [c]	Total
1880–1909 [d]	718	5,807	330,120	203,929	—	710	1,020	542,304
1910–19 [d]	843	83,220	1,004,633	281,124	400	20,997	6,110	1,397,327
1920–29 [d]	181	71,920	630,804	512,518	2,344	31,216	2,319	1,251,302
1930–39 [d]	3,351	50,935	466,595	515,727	14,693	23,931	3,090	1,078,322
1940	1,370	11,032	104,698	103,939	5,803	6,616	142	233,600
1941	1,428	15,566	133,333	142,862	8,967	17,591	922	320,669
1942	714	31,743	161,949	134,133	8,020	22,542	1,215	360,316
1943	1,328	49,145	198,789	109,849	8,653	37,050	1,202	406,016
1944	976	65,209	176,259	112,791	7,293	42,973	8,280	413,781
1945	1,126	52,437	147,251	95,142	7,038	14,449	6,518	323,961
1946	389	32,539	154,525	63,143	6,234	17,584	3,526	277,940
1947	1,601	32,153	167,157	90,256	8,042	27,526	2,749	329,484
Total	14,025	501,706	3,676,113	2,365,413	77,487	263,185	37,093	6,935,022

* Figures for 1880-1905 represent production.

[a] U. S. Bureau of Mines, Preprint Minerals Yearbook, 1946, and Mineral Market Report No. 1596.

[b] Figures on production not recorded for Colorado before 1905, for Illinois before 1880, and for Kentucky before 1886 and for 1888-95; total unrecorded production, chiefly from Illinois, estimated at 25,000 tons.

[c] California, New Hampshire, Tennessee, Texas, Utah, Washington, and Wyoming.

[d] Figures by years for 1880-1909 are given in Mineral Resources of the United States, 1925, pt. II, p. 13; for 1910-39 in Minerals Yearbook, Review of 1940, p. 1297.

TABLE 3.—FLUORSPAR PRICES[a]

Grade	1948	
	July	September
Fluorspar, acid grade, bags, carload lots at mine . . . ton	$45.50	$ 47.50
less than carload lots at mine . . . ton	47.50	49.50
bulk, contract, c.l. mine . . . ton	40.00	42.00
noncontract, c.l. mine . . . ton	43.00	45.00
l.c.l. mine . . . ton	45.00	47.00
Ceramic grade, No. 1 ground, 90–92% CaF_2, bulk, c.l., mine . . . net ton	38.50	39.00–41.00
Washed gravel, 70% or more CaF_2 bulk, c.l. mine . . . ton	34.00	35.00–37.00
65%, bulk, c.l. mine . . . ton	33.00	34.00–36.00
60%, bulk, c.l. mine . . . ton	32.00	33.00–35.00
less than 60%, bulk, c.l. mine . . . ton	30.00	32.00–34.00

[a] Oil, Paint and Drug Reporter, July 12, 1948, and Sept. 6, 1948.

TABLE 5.—U. S. AND ILLINOIS FLUORSPAR PRODUCTION AND VALUE 1938–1947[a]

Year	Illinois			United States		
	Production (net tons)	Av. value per ton	Total value	Production (net tons)	Av. value per ton	Total value
1938....	46,000	$21.24	$ 977,040	99,000	$19.90	$ 1,981,100
1939....	71,000	21.77	1,545,670	([b])	20.27	([b])
1940....	105,000	22.10	2,320,500	([b])	20.31	([b])
1941....	135,000	22.85	3,084,750	313,000	20.97	6,563,610
1942....	145,000	26.59	3,855,550	337,000	24.69	8,320,530
1943....	204,000	31.66	6,458,640	405,600	29.07	11,790,792
1944....	177,000	33.79	5,980,830	413,700	30.22	12,502,014
1945....	151,400	34.06	5,156,684	325,200	30.55	9,934,860
1946....	149,900	35.55	5,328,945	277,300	32.52	9,017,796
1947....	169,400	36.78	6,230,532	343,700	33.25	11,428,025

[a] Compiled from U. S. Bur. Mines, Mineral Market Reports.
[b] Not available.

Table 4.—Illinois Fluorspar Production and Net Tons Marketed by Grades, 1916–1947[a]
(In net tons)

Year	Total tonnage crude mined	Merchantable equivalent	Fluorspar marketed			
			Gravel	Lump	Ground	Total
1916....	144,689	([b])	110,543	11,166	4,660	126,369
1917....	201,489	([b])	136,954	11,758	7,964	156,676
1918....	167,013	134,039	122,721	3,480	6,597	132,798
1919....	134,865	103,113	81,026	3,738	7,965	92,729
1920....	162,175	124,953	103,486	8,332	8,481	120,299
1921....	30,661	24,904	8,208	1,099	3,170	12,477
1922....	117,457	82,309	76,537	1,722	5,596	83,855
1923....	178,204	93,845	52,249	5,659	7,137	65,045
1924....	109,946	54,896	54,541	2,766	4,760	62,067
1925....	97,023	42,185	46,195	3,366	4,867	54,428
1926....	84,575	50,053	47,254	1,780	4,700	53,734
1927....	81,121	44,990	38,970	2,471	4,565	46,006
1928....	117,241	62,288	56,555	819	5,263	65,884
1929....	121,684	67,882	59,101	2,926	4,982	67,009
1930....	111,325	63,763	38,702	2,107	3,325	44,134
1931....	57,829	32,013	23,632	1,098	3,342	28,072
1932....	7,499	3,837	7,460	542	1,613	9,615
1933....	65,959	29,970	29,694	357	6,024	36,075
1934....	68,699	29,672	28,922	572	3,740	33,234
1935....	87,136	40,031	36,766	1,013	6,341	44,120
1936....	136,446	76,261	68,191	3,546	9,263	81,000
1937....	138,000	81,000	57,722	9,548	10,077	77,347
1938....	75,000	46,000	26,324	4,203	4,841	35,368
1939....	128,000	71,000	57,586	6,330	11,341	75,257
1940....	213,000	105,000	90,864	2,277	11,557	104,698
1941....	248,000	135,000	110,811	5,743	16,779	133,333

Year	Crude	Merchantable equivalent	Metallurgical	Acid	Ceramic	Total
1942....	282,000	145,000	82,919	69,752	9,278	161,949

Year	Crude	Merchantable equivalent	Metallurgical	Lump	Ground and flotation concentrate	Total
1943....	350,883	204,000	84,929	—	113,860	198,789
1944....	342,754	177,000	64,072	—	112,187	176,259
1945....	368,663	151,400	63,573	336	83,342	147,251
1946....	316,381	149,900	65,344	838	88,343	154,525
1947....	345,795	169,400	70,694	1,822	94,641	167,157

[a] U. S. Bur. Mines, Tabulations of Illinois Fluorspar Production.
[b] Not available.

TABLE 6.—FLUORSPAR SHIPPED FROM MINES IN THE UNITED STATES, BY USES, 1930-1947[a]

Uses	1930		1931		1932	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	76,837	$16.13	39,832	$14.16	18,881	$12.13
Foundry	2,209	18.69	1,123	16.10	524	14.57
Glass	3,158	32.92	5,279	30.74	3,596	28.30
Enamel and vitrolite	2,188	33.61	1,996	32.79	1,261	28.80
Hydrofluoric acid and derivatives	9,834	26.45	4,386	24.65	738	19.79
Miscellaneous	1,342	16.32	557	14.13	226	11.91
	95,568	18.22	53,173	17.41	25,226	15.54
Exports	281	21.92	311	18.00	25	22.12
Total	95,849	$18.22	53,484	$17.41	25,251	$15.54

Uses	1933		1934		1935	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	60,279	$12.77	70,672	$15.03	100,988	$13.77
Foundry	1,039	13.27	1,489	15.99	2,336	12.44
Glass	6,778	21.83	7,343	22.77	10,256	22.22
Enamel and vitrolite	3,100	24.82	2,590	26.20	4,087	24.64
Hydrofluoric acid and derivatives	950	19.58	1,666	21.43	3,333	22.42
Miscellaneous	713	15.44	1,504	17.55	2,248	13.76
	72,859	14.25	85,264	16.22	123,248	15.04
Exports	71	13.62	522	16.48	313	14.86
Total	72,930	$14.25	85,786	$16.22	123,561	$15.04

Uses	1936		1937		1938	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	142,264	$16.20	137,040	$18.51	51,991	$17.54
Iron Foundry	2,326	15.79	2,566	18.42	2,041	16.54
Glass	11,014	24.27	12,697	26.79	8,702	25.78
Enamel	5,249	24.62	6,054	27.45	4,100	26.63
Hydrofluoric acid	12,627	25.82	17,879	26.93	11,484	24.84
Miscellaneous	3,157	16.19	4,538	19.01	1,297	20.03
Exports	176,637	17.64	180,774	20.23	79,615	19.98
	240	17.00	456	19.94	788	11.50
Total	176,877	$17.64	181,230	$20.23	80,403	$19.90

Table 6.—Fluorspar Shipped from Mines in the United States, by Uses, 1930–1947[a]—(Concluded)

Uses	1939		1940		1941	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	125,371	$17.83	162,772	$18.42	214,120	$18.91
Foundry	2,391	17.74	2,829	17.94	2,724	19.47
Glass and enamel	21,884	26.02	20,269	27.04	32,051	26.19
Hydrofluoric acid	27,463	26.60	33,608	25.36	52,674	25.81
Miscellaneous	2,686	19.87	5,640	20.80	6,916	21.16
Foreign consumption	179,795	20.19	225,118	20.28	308,485	20.90
	2,976	25.01	8,482	21.04	12,184	22.80
Total	182,771	$20.27	233,600	$20.31	320,669	$20.97

Uses	1942		1943		1944	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	225,233	$22.58	220,809	$27.20	219,361	$27.75
Iron Foundry	3,408	19.09	3,398	25.23	4,044	27.17
Glass	20,890	27.59	19,487	29.87	27,174	32.85
Enamel	1,923	29.50	1,572	32.20	2,685	33.68
Hydrofluoric acid	88,083	28.85	123,680	32.72	121,084	35.11
Miscellaneous	11,763	28.16	19,956	30.00	13,057	31.91
Government stockpile	—	—	8,070	23.01	24,396	24.15
Foreign consumption	9,016	26.90	9,044	27.31	1,980	33.29
Total	360,316	$24.69	406,016	$29.07	413,781	$30.22

Uses	1945		1946		1947	
	Net tons	Av. value per ton	Net tons	Av. value per ton	Net tons	Av. value per ton
Steel	186,073	$27.85	134,295	$28.62	165,427	$29.01
Iron Foundry	3,422	27.72	4,855	28.32	4,439	30.13
Glass	32,300	32.00	39,837	32.78	40,843	35.13
Enamel	3,660	35.14	7,540	34.82	8,716	36.20
Hydrofluoric acid	80,155	36.13	79,047	39.36	89,667	40.84
Miscellaneous	7,482	34.02	6,730	32.84	10,103	34.30
Government stockpile	9,449	27.61	3,907	24.01	9,109	24.00
Foreign consumption	1,420	32.35	1,729	36.90	1,180	37.02
Total	323,961	$30.55	277,940	$32.52	329,484	$33.25

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[a] U. S. Bur. Mines, Minerals Yearbooks and Mineral Market Reports, Nos. 1164, 1392 and 1596.

TABLE 7.—FLUORSPAR SHIPPED FROM MINES IN THE UNITED STATES, BY GRADES AND INDUSTRIES, 1943–1947[a]
(In net tons)

Grade and industry	1943	1944	1945	1946	1947
Fluxing gravel and foundry lump:					
Ferrous	215,530	210,930	[c]184,645	[e]134,822	[e]165,281
Nonferrous	3,313	1,264	1,170	1,410	1,734
Cement	1,094	646	326	661	812
Miscellaneous	205	389	158	175	3,489
Government stockpile	4,374	23,825	7,225	3,907	9,109
Exported	1,945	55	—	—	—
Total	226,461	237,108	193,524	[e]140,975	180,425
Acid lump:					
Ferrous	20	20	36	15	—
Nonferrous	1	—	2	2	1
Hydrofluoric acid	547	1,572	593	267	—
Total	568	1,592	631	284	1
Ground and flotation concentrates:					
Ferrous	[b]13,446	[b]14,715	[b,d]6,791	[b,e]5,939	[b,e]6,581
Nonferrous	6,875	6,157	2,211	2,231	783
Glass and enamel	21,059	29,857	35,960	47,377	49,559
Hydrofluoric acid	121,133	119,512	79,562	78,780	89,667
Miscellaneous	3,679	2,341	1,638	625	1,288
Government stockpile	3,696	572	2,224	—	—
Exported	7,099	1,925	1,420	1,729	1,180
Total	178,987	175,081	129,806	[b,e]136,681	[b,e]149,058
Total:					
Ferrous	228,996	225,665	191,472	140,776	171,862
Nonferrous	10,189	7,421	3,383	3,643	2,518
Cement	1,094	646	326	661	812
Glass and enamel	21,059	29,859	35,960	47,377	49,559
Hydrofluoric acid	123,680	121,084	80,155	79,047	89,667
Miscellaneous	3,884	2,730	1,796	800	4,777
Government stockpile	8,070	24,396	9,449	3,907	9,109
Exported	9,044	1,980	1,420	1,729	1,180
Total	406,016	413,781	323,961	277,940	329.484

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[a] U. S. Bur. Mines, Mineral Market Reports, Nos. 1278, 1392 and 1596.
[b] Includes pelletized gravel.
[c] Includes 4,182 tons of flotation concentrates which were blended with fluxing gravel.
[d] Excludes 4,182 tons of flotation concentrates which were blended with fluxing gravel.
[e] Fluxing gravel includes (and flotation concentrates exclude) the following quantities of flotation concentrates blended with fluxing gravel: 9,129 tons in 1946; 19,110 tons in 1947.

Table 8.—World Production of Fluorspar, 1913–1946[a]
(In metric tons)

Country*	1913	1914	1915	1916	1917	1918	1919	1920	1921
Argentina[b]	—	—	—	—	—	—	—	—	—
Australia:									
New South Wales	—	—	424	1,407	1,326	2,315	2,046	1,213	—
Queensland	—	—	—	—	72	—	—	613	545
South Australia	—	—	—	—	—	—	—	—	—
Victoria	—	—	—	—	—	102	319	13	199
Canada	—	—	—	1,165	3,855	6,679	4,593	10,192	5,007
China	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Chosen	—	—	—	—	—	—	—	—	—
France	7,524	(c)	(c)	(c)	(c)	(c)	4,894	8,997	5,776
Germany:									
Anhalt	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Baden	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Bavaria	4,731	3,729	1,500	4,198	6,470	6,011	6,396	6,272	7,210
Prussia	16,977	12,316	7,874	9,333	7,856	9,387	10,444	7,339	11,989
Saxony	3,260	3,725	3,045	2,763	1,410	2,332	2,906	2,918	4,763
Thuringia	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Great Britain	54,522	34,357	33,653	55,607	65,912	54,357	37,452	55,561	23,508
Italy	—	—	—	800	800	876	900	810	1,600
Mexico	(c)	(c)	(c)	(c)	(c)	(c)	(c)	[d]500	[d]500
Newfoundland (shipments)	—	—	—	—	—	—	—	—	—
Norway	—	—	180	140	—	155	560	—	—
Russia	—	—	—	—	—	—	—	—	—
South-West Africa	—	—	—	—	—	—	—	—	—
Spain	351	79	370	277	250	350	280	416	176
Switzerland	—	—	—	—	—	—	—	—	—
Union of South Africa	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
United States	104,853	86,289	124,230	141,282	198,519	239,333	125,454	169,441	31,715
Estimated total	217,000	160,000	198,000	244,000	327,000	356,000	196,000	270,000	97,000

TABLE 8.—WORLD PRODUCTION OF FLUORSPAR, 1913–1946[a]—(Continued)
(In metric tons)

Country*	1922	1923	1924	1925	1926	1927	1928	1929	1930
Argentina[b]	—	—	—	—	—	24	—	—	—
Australia:									
New South Wales	—	—	478	—	—	—	—	96	205
Queensland	—	—	1,894	4,295	2,348	1,050	1,143	602	763
South Australia	—	—	—	—	—	—	—	—	—
Victoria	—	—	—	—	—	—	—	—	—
Canada	4,085	126	69	3,525	—	—	—	16,211	73
China	(c)	165	(c)	4,498	(c)	3,436	(c)	(c)	(c)
Chosen	—	—	—	—	—	—	950	1,470	2,297
France	9,251	12,913	23,047	24,430	41,670	44,210	46,650	52,968	58,600
Germany:									
Anhalt	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Baden	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Bavaria	13,221	10,543	21,663	31,454	32,475	51,001	48,552	50,797	48,063
Prussia	8,630	10,810	13,078	24,101	29,729	36,607	37,365	37,717	30,272
Saxony	8,509	5,761	9,032	16,141	17,442	22,027	16,422	18,491	11,871
Thuringia	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Great Britain	33,878	49,818	50,286	39,706	36,459	40,362	47,614	42,432	30,266
Italy	1,395	3,362	6,831	7,770	6,320	5,577	4,520	5,740	6,655
Mexico	[d]500	[d]500	[d]500	—	937	(c)	(c)	(c)	(c)
Newfoundland (shipments)	—	—	—	—	—	—	—	—	—
Norway	—	—	—	—	—	—	(c)	(c)	821
Russia	[e]42	[e]14	[e]215	[e]1,211	[e]3,765	[e]840	[e]3,100	[e]5,700	16,900
South-West Africa	—	—	(c)	(c)	(c)	995	872	565	—
Spain	392	—	4,474	2,436	14,011	757	2,082	13,478	11,296
Switzerland	—	(c)	(c)	(c)	(c)	[d]1,000	[d]1,000	[d]1,000	[d]1,000
Union of South Africa	(c)	10,975	10,192	4,883	8,403	7,582	5,582	2,715	1,520
United States	128,453	109,939	113,378	103,118	116,715	102,099	127,450	132,847	86,952
Estimated Total	218,000	224,000	269,000	286,000	311,000	339,000	374,000	416,000	335,000

Table 8.—World Production of Fluorspar, 1913–1946[a]—(Continued)
(In metric tons)

Country*	1931	1932	1933	1934	1935
Argentina[b]	—	10	200	311	(c)
Australia:					
New South Wales	12	—	51	203	420
Queensland	529	1,240	749	1,328	815
South Australia	—	41	201	234	91
Victoria	—	—	—	—	—
Canada	36	29	66	136	204
China	7,100	3,510	4,800	5,050	(c)
Chosen	2,648	7,577	9,076	12,099	9,722
France	23,800	15,200	15,050	14,100	22,750
Germany:					
Anhalt	(c)	(c)	(c)	7,357	8,068
Baden	(c)	(c)	(c)	6,527	3,941
Bavaria	26,780	21,915	26,364	29,661	31,277
Prussia	12,842	7,794	10,653	21,555	24,618
Saxony	6,937	2,656	3,672	4,945	6,938
Thuringia	(c)	(c)	(c)	(c)	23,572
Great Britain	20,242	15,675	28,508	34,765	31,646
Italy	5,850	6,450	7,714	9,668	9,500
Mexico	[d]900	[d]900	[d]900	[d]900	[d]900
Newfoundland (shipments)	—	—	1,451	2,535	4,082
Norway	630	571	507	673	(c)
Russia	16,600	11,200	19,300	27,000	49,100
South-West Africa	—	610	—	—	—
Spain	6,017	7,018	3,564	6,365	(c)
Switzerland	[d]1,000	[d]1,000	[d]1,000	[d]1,000	—
Union of South Africa	2,197	1,317	445	1,393	1,955
United States	48,520	22,907	66,161	77,823	112,255
Estimated Total	194,000	135,000	214,000	286,000	354,000

Table 8.—World Production of Fluorspar, 1913–1946[a]—(Concluded)
(In metric tons)

Country*	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946
Argentina (shipments)	450	350	1,406	739	597	(c)	2,328	4,000	(c)	(c)	(c)
Australia:											
New South Wales	339	55	—	—	(c)	(c)	—	—	—	—	(c)
Queensland	487	1,410	2,479	20	(c)	(c)	311	544	520	801	875
Victoria	—	—	804	—	(c)	(c)	344	468	266	145	326
Canada	68	136	197	218	(c)	(c)	5,624	10,169	6,281	6,685	6,853
France	30,600	51,430	51,920	(c)	(c)	(c)	27,447	24,160	13,400	13,749	21,528
Germany:											
Anhalt	11,225	13,662	10,462	11,157	(c)	(c)	12,470	—	—	—	—
Baden	7,359	13,637	21,350	22,480	(c)	(c)	31,625	—	—	—	—
Bavaria	49,153	62,455	59,919	69,870	(c)	(c)	59,640	[d]190,000	[d]170,000	(c)	(c)
Prussia	36,271	30,514	22,956	24,414	(c)	(c)	27,841	—	—	—	—
Saxony	7,990	8,074	12,063	10,002	(c)	(c)	11,806	—	—	—	—
Thuringia	18,792	16,117	22,405	24,040	(c)	(c)	32,290	—	—	—	—
India	—	—	—	20	(c)	(c)	4,110	1,667	1,249	(c)	(c)
Italy	11,437	13,385	12,186	13,243	(c)	(c)	35,034	(c)	(c)	(c)	(c)
Japan	(c)	(c)	(c)	1,960	(c)	(c)	7,800	7,282	7,967	3,207	(c)
Korea (Chosen)	8,740	8,084	[f]34,207	[f]22,000	(c)	(c)	47,847	[d]50,000	[d]60,000	(c)	(c)
Mexico (exports)	900	(c)	(c)	—	(c)	(c)	5,365	22,469	56,450	50,251	20,114
Newfoundland	8,498	8,479	8,944	11,227	14,697	11,581	[d]32,660	66,170	58,290	49,841	[f]25,266
Norway	1,013	1,692	1,676	2,411	(c)	(c)	1,920	905	3,119	(c)	(c)
Southern Rhodesia	—	—	156	—	(c)	(c)	(c)	(c)	(c)	(c)	(c)
South-West Africa	—	—	585	105	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Spain	(c)	4,250	8,596	8,408	(c)	(c)	16,297	35,911	55,595	9,642	[i]6,477
Sweden	—	—	—	—	(c)	(c)	468	2,107	1,836	3,448	(c)
Switzerland	—	—	—	—	(c)	(c)	486	582	520	—	(c)
Tunisia	—	1,676	2,060	2,010	(c)	(c)	(c)	16	—	—	(c)
Union of South Africa	3,123	3,615	4,736	10,322	7,421	[h]1,836	4,185	4,646	3,481	3,657	4,004
U.S.S.R.	65,000	[d]70,000	(g)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
United Kingdom	33,491	42,837	33,866	38,786	(c)	(c)	43,920	55,106	48,927	44,281	46,644
United States (shipments)	160,459	164,408	72,940	165,806	211,917	290,905	326,871	368,330	375,374	293,891	252,142
Total (estimated)	465,000	510,000	456,000	577,000	(c)	(c)	883,000	1,022,000	1,086,000	(c)	(c)

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* In addition to the countries listed, Japan produced 36 tons in 1922.

[a] Data for 1913-1935 from Hatmaker and Davis, Illinois State Geol. Survey, Bulletin No. 59; for 1936-1946 from U. S. Bureau Mines, Minerals Yearbooks.

[b] Railroad shipments.

[c] Data not available; estimate included in total.

[d] Estimated.

[e] Data for year ended Sept. 30.

[f] Exports.

[g] Estimate included in total.

[h] January to June.

[i] January to September.

TABLE 9.—SALIENT STATISTICS OF FLUORSPAR IN THE UNITED STATES, 1935–1947[a]

(In net tons)

Year	Shipments from domestic mines	Foreign trade		Consumption	Stocks at end of year			
		Imports for consumption	Exports		Consumers' plants	Domestic mines	Government stock pile	Total
1935	123,741	16,340	313	137,400	58,000	40,043	—	98,043
1936	176,877	25,504	240	182,400	72,600	29,958	—	102,558
1937	181,230	37,063	456	194,300	90,100	30,539	—	120,639
1938	80,403	19,622	788	115,100	71,800	34,996	—	106,796
1939	182,771	16,302	2,976	176,800	90,400	38,619	—	129,019
1940	233,600	11,873	8,482	218,500	102,100	43,866	—	145,966
1941	320,669	7,524	12,184	303,600	108,900	31,997	—	140,897
1942	360,316	2,151	9,020	360,800	96,000	19,429	—	115,429
1943	406,016	43,769	9,068	388,885	105,933	19,026	36,223	161,182
1944	413,781	87,200	1,980	410,170	98,446	19,021	129,885	247,352
1945	323,961	103,133	1,420	356,090	103,148	20,249	198,856	322,253
1946	277,940	29,852	1,729	303,190	98,663	18,957	29,254	146,874
1947	329,484*	78,379	([b])	376,138	114,150	33,101	([b])	([b])
1948:								
1st quarter	63,918	20,014	([b])	97,292	103,748	41,524	([b])	([b])
2nd quarter	83,327	24,553	([b])	97,235	104,904	40,179	([b])	([b])

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* Includes exports and government stockpiles.

[a] U. S. Bur. Mines, Minerals Yearbooks and Fluorspar Report No. 45, May 28, 1948.

[b] Data not available.

Table 10.—Fluorspar Imported into the United States by Countries, with Total Value, 1910–1947[a]

Year	Africa		Argentina		Australia		Austria-Hungary		Belgium		Canada	
	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value
1910	—	—	—	—	—	—	11	$50	—	—	—	—
1911	—	—	—	—	—	—	—	—	—	—	—	—
1912	—	—	—	—	—	—	—	—	—	—	—	—
1913	—	—	—	—	—	—	—	—	—	—	—	—
1914	—	—	—	—	—	—	—	—	—	—	—	—
1915	—	—	—	—	—	—	—	—	—	—	—	—
1916	—	—	—	—	—	—	—	—	—	—	—	—
1917	—	—	—	—	—	—	—	—	—	—	618	$ 3,813
1918	—	—	—	—	—	—	—	—	—	—	913	21,973
1919	—	—	—	—	—	—	—	—	—	—	902	13,532
1920	30	$ 1,080	—	—	11	$426	—	—	—	—	7,068	110,532
1921	—	—	—	—	—	—	—	—	—	—	4,370	52,855
1922	486	8,415	—	—	—	—	—	—	71	$1,187	2,877	32,679
1923	10,380	157,625	—	—	—	—	—	—	35	712	(c)	5
1924	11,125	147,977	—	—	—	—	—	—	6	75	213	3,216
1925	7,906	108,647	—	—	—	—	—	—	78	1,624	—	—
1926	8,506	136,502	—	—	—	—	—	—	31	566	1,109	10,310
1927	7,069	90,966	—	—	—	—	—	—	21	449	560	4,250
1928	2,661	36,471	20	$360	—	—	—	—	—	—	—	—
1929	6,387	75,856	—	—	—	—	—	—	21	519	—	—
1930	2,712	31,069	—	—	—	—	—	—	—	—	—	—
1931	3,672	40,375	—	—	—	—	—	—	11	170	280	2,313
1932	1,587	14,809	—	—	(d)	196	—	—	—	—	—	—
1933	712	12,449	—	—	—	—	—	—	—	—	—	—
1934	1,997	31,872	—	—	—	—	—	—	—	—	187	2,962
1935	1,347	23,739	—	—	—	—	—	—	—	—	1	14
1936	948	19,424	—	—	—	—	—	—	—	—	—	—
1937	538	11,223	—	—	—	—	—	—	—	—	—	—
1938	1,787	38,047	—	—	—	—	—	—	—	—	—	—
1939	—	—	—	—	—	—	—	—	—	—	—	—
1940	—	—	—	—	—	—	—	—	—	—	—	—
1941	—	—	—	—	—	—	—	—	—	—	—	—
1942	—	—	—	—	—	—	—	—	—	—	(d)	10
1943	570	7,500	—	—	—	—	—	—	—	—	—	—
1944	3,557	44,715	—	—	—	—	—	—	—	—	69	1,951
1945	—	—	—	—	—	—	—	—	—	—	[f]2,361	[f]75,085
1946	—	—	—	—	—	—	—	—	—	—	310	8,934
1947	—	—	—	—	—	—	—	—	—	—	284	7,594
Total	73,977	$1,038,761	20	$360	11	$622	11	$50	274	$5,302	22,122	$352,028

Table 10.—Fluorspar Imported into the United States by Countries, with Total Value, 1910–1947[a]—(Continued)

Yr.	Mexico		Netherlands		Newfoundland		Norway		Spain	
	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value
1910	—	—	—	—	—	—	—	—	—	—
1911	—	—	—	—	—	—	—	—	—	—
1912	—	—	—	—	—	—	—	—	—	—
1913	—	—	—	—	—	—	—	—	—	—
1914	—	—	—	—	—	—	—	—	—	—
1915	—	—	—	—	—	—	—	—	—	—
1916	—	—	—	—	—	—	—	—	—	—
1917	—	—	—	—	—	—	—	—	—	—
1918	—	—	—	—	—	—	—	—	—	—
1919	—	—	—	—	—	—	—	—	—	—
1920	—	—	—	—	—	—	—	—	—	—
1921	—	—	—	—	—	—	—	—	—	—
1922	—	—	—	—	—	—	—	—	—	—
1923	—	—	11	$ 180	—	—	—	—	—	—
1924	—	—	1,177	13,951	—	—	—	—	—	—
1925	—	—	—	—	—	—	—	—	—	—
1926	—	—	—	—	—	—	—	—	2,948	$ 33,915
1927	—	—	—	—	—	—	—	—	978	3,650
1928	—	—	—	—	—	—	—	—	680	5,178
1929	—	—	—	—	—	—	—	—	7,168	52,039
1930	—	—	—	—	—	—	—	—	6,784	53,612
1931	—	—	—	—	—	—	—	—	4,068	31,786
1932	—	—	—	—	—	—	—	—	2,659	24,881
1933	—	—	—	—	320	$ 2,646	—	—	4,262	28,690
1934	—	—	—	—	745	10,460	—	—	4,914	35,316
1935	465	$ 7,418	—	—	—	—	—	—	5,094	35,432
1936	1,557	21,466	—	—	4,317	31,497	—	—	5,701	31,365
1937	—	—	—	—	5,520	67,723	—	—	566	4,464
1938	85	1,263	—	—	4,752	103,909	—	—	309	3,535
1939	465	7,418	—	—	2,268	61,775	1	$15	168	2,542
1940	1,555	21,466	—	—	3,640	69,825	—	—	112	841
1941	4,452	57,331	—	—	—	—	—	—	3,070	22,772
1942	2,151	35,519	—	—	—	—	—	—	—	—
1943	20,515	237,404	—	—	7,144	175,829	—	—	15,540	224,432
1944	58,324	980,089	—	—	16,072	431,232	—	—	9,177	222,080
1945	62,575	1,054,692	—	—	[f]10,875	[f]332,556	—	—	27,322	694,125
1946	24,063	384,757	—	—	2,688	80,640	—	—	2,791	42,484
1947	51,619	771,933	—	—	10,307	275,076	—	—	12,042	158,834
Tot.	227,826	$3,580,756	1,188	$14,131	68,648	$1,643,168	1	$15	116,353	$1,711,973

TABLE 10.—FLUORSPAR IMPORTED INTO THE UNITED STATES BY COUNTRIES, WITH TOTAL VALUE, 1910–1947[a]—(Continued)

Year	China		Czecho-slovakia		France		Germany		Italy	
	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value
1910	—	—	—	—	—	—	142	$ 1,386	—	—
1911	—	—	—	—	—	—	198	1,919	—	—
1912	—	—	—	—	—	—	256	2,444	—	—
1913	—	—	—	—	—	—	320	3,073	—	—
1914	—	—	—	—	—	—	184	1,818	—	—
1915	—	—	—	—	—	—	127	1,154	—	—
1916	—	—	—	—	—	—	—	—	—	—
1917	—	—	—	—	—	—	—	—	—	—
1918	—	—	—	—	—	—	—	—	—	—
1919	—	—	—	—	—	—	—	—	—	—
1920	—	—	—	—	—	—	407	9,450	—	—
1921	—	—	—	—	—	—	215	4,420	—	—
1922	—	—	34	$ 761	—	—	5,804	49,196	—	—
1923	90	$ 1,183	—	—	—	—	8,580	67,595	268	$ 2,471
1924	506	5,089	—	—	232	$ 2,782	6,834	69,357	1,585	14,804
1925	559	5,816	27	591	2,537	20,887	11,680	103,845	4,278	32,208
1926	645	5,992	—	—	11,163	90,737	20,465	171,769	1,379	15,434
1927	449	3,961	—	—	11,711	86,279	31,829	230,821	449	5,969
1928	756	8,200	—	—	15,072	141,434	17,601	150,872	1,033	9,600
1929	1,345	11,534	—	—	16,850	159,059	16,488	140,860	1,258	10,528
1930	739	7,957	—	—	23,313	184,238	23,797	189,587	1,802	17,198
1931	202	1,811	—	—	4,462	33,646	6,491	77,067	1,523	24,267
1932	112	671	—	—	1,578	9,588	5,842	70,294	1,457	11,848
1933	27	413	—	—	204	1,247	4,333	54,836	533	4,533
1934	112	990	—	—	—	—	8,224	98,565	60	587
1935	—	—	—	—	—	—	9,843	119,275	55	589
1936	—	—	—	—	1,595	16,039	12,943	160,937	—	—
1937	—	—	—	—	14,158	80,816	14,501	219,393	1,124	5,752
1938	—	—	—	—	7,411	67,097	3,062	51,304	—	—
1939	—	—	—	—	13,094	100,769	19	603	—	—
1940	—	—	—	—	5,735	47,345	—	—	—	—
1941	—	—	—	—	—	—	—	—	—	—
1942	—	—	—	—	—	—	—	—	—	—
1943	—	—	—	—	—	—	—	—	—	—
1944	—	—	—	—	—	—	—	—	—	—
1945	—	—	—	—	—	—	—	—	—	—
1946	—	—	—	—	—	—	—	—	—	—
1947	—	—	—	—	—	—	—	—	4,126	40,793
Total	5,542	$53,617	61	$1,352	129,115	$1,041,963	210,185	$2,051,840	20,930	$196,581

Table 10.—Fluorspar Imported into the United States by Countries, with Total Value, 1910–1947[a]—(Concluded)

Year	Tunisia		United Kingdom		U.S.S.R.		Total	
	Net tons	Value	Net tons	Value	Net tons	Value	Net tons	Value
1910	—	—	42,335	$ 133,716	—	—	42,488	$ 135,152
1911	—	—	32,566	78,673	—	—	32,764	80,592
1912	—	—	25,920	69,172	—	—	26,176	71,616
1913	—	—	22,362	68,390	—	—	22,682	71,463
1914	—	—	10,021	37,125	—	—	10,205	38,943
1915	—	—	7,040	21,724	—	—	7,167	22,878
1916	—	—	12,323	54,000	—	—	12,323	54,000
1917	—	—	12,998	110,785	—	—	13,616	114,598
1918	—	—	11,659	147,391	—	—	12,572	169,364
1919	—	—	6,041	94,099	—	—	6,943	107,631
1920	—	—	17,096	144,142	—	—	24,612	265,630
1921	—	—	1,644	12,031	—	—	6,229	69,306
1922	—	—	23,836	206,950	—	—	33,108	299,188
1923	—	—	22,862	202,548	—	—	42,226	432,319
1924	—	—	29,365	298,391	—	—	51,043	555,642
1925	—	—	21,635	195,229	—	—	48,700	468,847
1926	—	—	29,407	281,735	18	$277	75,671	747,237
1927	—	—	18,449	168,840	—	—	71,515	595,185
1928	—	—	9,360	56,585	—	—	47,183	408,700
1929	—	—	4,828	30,580	—	—	54,345	480,975
1930	—	—	5,756	60,995	—	—	64,903	544,656
1931	—	—	—	—	—	—	20,709	211,435
1932	—	—	[e]1	378	—	—	13,236	132,665
1933	—	—	17	229	—	—	10,408	105,043
1934	—	—	466	2,534	—	—	16,705	183,286
1935	—	—	—	—	—	—	16,340	179,049
1936	—	—	—	—	—	—	25,504	259,262
1937	656	$ 8,256	—	—	—	—	37,063	397,627
1938	1,572	18,251	644	4,237	—	—	19,622	287,643
1939	231	2,919	56	650	—	—	16,302	176,691
1940	829	3,454	—	—	—	—	11,873	142,931
1941	—	—	2	32	—	—	7,524	80,135
1942	—	—	—	—	—	—	2,151	35,529
1943	—	—	—	—	—	—	43,769	627,165
1944	—	—	1	37	—	—	87,200	1,680,104
1945	—	—	—	—	—	—	103,133	2,156,458
1946	—	—	—	—	—	—	29,852	516,815
1947	—	—	1	169	—	—	78,379	1,254,399
Total	3,288	$32,880	368,691	$2,481,367	18	$277	1,246,241	$14,160,159

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[a] U. S. Bur. Mines, Minerals Yearbooks and Mineral Market Report No. 1596.

[b] Imports Aug. 1 to Dec. 31, 1909, 6,971 tons, valued at $26,377; not recorded separately prior to Aug. 1, 1909.

[c] Quantity not recorded.

[d] Less than 1 ton of optical fluorspar.

[e] Optical fluorspar.

[f] Bur. Mines has determined that 1,691 tons, valued at $56,918, credited to Canada by the U. S. Dept. Commerce, originated in Newfoundland.

Table 11.—Fluorspar Imported for Consumption in the United States, by Countries of Origin and by Grades, 1930–1947[a]

Year and country	Containing more than 97% calcium fluoride		Containing not more than 97% calcium fluoride		Total	
	Net tons	Value	Net tons	Value	Net tons	Value
1930:						
Africa	2,146	$ 24,998	566	$ 6,071	2,712	$ 31,069
China	739	7,957	—	—	739	7,957
France	4,922	42,127	18,391	142,111	23,313	184,238
Germany	13,835	112,889	9,962	76,698	23,797	189,587
Italy	911	7,409	891	9,789	1,802	17,198
Spain	559	6,736	6,225	46,876	6,784	53,612
United Kingdom	—	—	5,756	60,995	5,756	60,995
Total	23,112	$202,116	41,791	$342,540	64,903	$544,656
1931:						
Belgium	—	—	11	$ 170	11	$ 170
Canada	—	—	280	2,313	280	2,313
China	90	$ 1,155	112	656	202	1,811
France	654	7,163	3,808	26,483	4,462	33,646
Germany	3,990	59,975	2,501	17,092	6,491	77,067
Italy	—	—	1,523	24,267	1,523	24,267
Spain	98	1,603	3,970	30,183	4,068	31,786
Union of South Africa	3,672	40,375	—	—	3,672	40,375
Total	8,504	$110,271	12,205	$101,164	20,709	$211,435
1932:						
Australia	(b)	$ 196	—	—	(b)	$ 196
China	—	—	112	$ 671	112	671
France	—	—	1,578	9,588	1,578	9,588
Germany	3,903	62,938	1,939	7,356	5,842	70,294
Italy	66	537	1,391	11,311	1,457	11,848
Spain	595	8,996	2,064	15,885	2,659	24,881
Union of South Africa	1,587	14,809	—	—	1,587	14,809
United Kingdom	[c]1	378	—	—	[c]1	378
Total	6,152	$87,854	7,084	$44,811	13,236	$132,665
1933:						
China	27	$ 413	—	—	27	$ 413
France	—	—	204	$ 1,247	204	1,247
Germany	3,773	51,585	560	3,251	4,333	54,836
Italy	—	—	534	4,533	534	4,533
Newfoundland	—	—	320	2,646	320	2,646
Spain	635	8,728	3,626	19,962	4,261	28,690
Union of South Africa	713	12,449	—	—	713	12,449
United Kingdom	17	229	—	—	17	229
Total	5,165	$73,404	5,244	$31,639	10,409	$105,043
1934:						
Canada	—	—	187	$ 2,962	187	$ 2,962
China	2	$ 31	110	959	112	990
Germany	7,518	94,291	706	4,274	8,224	98,565
Italy	—	—	60	587	60	587
Newfoundland	297	6,460	448	4,000	745	10,460
Spain	818	12,800	4,096	22,516	4,914	35,316
Union of South Africa	1,997	31,872	—	—	1,997	31,872
United Kingdom	—	—	466	2,534	466	2,534
Total	10,632	$145,454	6,073	$37,832	16,705	$183,286

Table 11.—Fluorspar Imported for Consumption in the United States, by Countries of Origin and by Grades, 1930–1947[a]—(Continued)

Year and country	Containing more than 97% calcium fluoride		Containing not more than 97% calcium fluoride		Total	
	Net tons	Value	Net tons	Value	Net tons	Value
1935:						
Canada	—	—	1	$ 14	1	$ 14
Germany	8,585	$115,562	1,258	3,713	9,843	119,275
Italy	—	—	55	589	55	589
Spain	646	10,522	4,448	24,910	5,094	35,432
Union of South Africa	1,347	23,739	—	—	1,347	23,739
Total	10,578	$149,823	5,762	$29,226	16,340	$179,049
1936:						
France	224	$ 2,293	1,371	$ 13,746	1,595	$ 16,039
Germany	6,802	102,117	6,142	58,820	12,944	160,937
Newfoundland	1,870	9,500	2,447	18,997	4,317	28,497
Spain	185	3,625	5,516	27,740	5,701	31,365
Union of South Africa	947	19,424	—	—	947	19,424
Total	10,028	$136,959	15,476	$119,303	25,504	$256,262
1937:						
France	11	$ 295	14,147	$ 80,521	14,158	$ 80,816
Germany	6,883	115,898	7,618	103,495	14,501	219,393
Italy	—	—	1,124	5,752	1,124	5,752
Newfoundland	2,160	26,473	3,360	41,250	5,520	67,723
Spain	—	—	566	4,464	566	4,464
Tunisia	656	8,256	—	—	656	8,256
Union of South Africa	538	11,223	—	—	538	11,223
Total	10,248	$162,145	26,815	$235,482	37,063	$397,627
1938:						
France	39	$ 924	7,372	$66,173	7,411	$ 67,097
Germany	3,062	51,304	—	—	3,062	51,304
Mexico	85	1,263	—	—	85	1,263
Newfoundland	3,390	87,343	1,362	16,566	4,752	103,909
Spain	—	—	309	3,535	309	3,535
Tunisia	853	13,588	719	4,663	1,572	18,251
Union of South Africa	1,787	38,047	—	—	1,787	38,047
United Kingdom	—	—	644	4,237	644	4,237
Total	9,216	$192,469	10,406	$95,174	19,622	$287,643
1939:						
France	144	$ 3,181	12,950	$97,588	13,094	$100,769
Germany	19	603	—	—	19	603
Mexico	465	7,418	—	—	465	7,418
Newfoundland	2,268	61,775	—	—	2,268	61,775
Norway	—	—	1	15	1	15
Spain	168	2,542	—	—	168	2,542
Tunisia	231	2,919	—	—	231	2,919
United Kingdom	56	650	—	—	56	650
Total	3,351	$79,088	12,951	$97,603	16,302	$176,691
1940:						
France	151	$ 1,932	5,584	$45,413	5,735	$ 47,345
Mexico	1,555	21,466	—	—	1,555	21,466
Newfoundland	1,344	36,000	2,296	33,825	3,640	69,825
Spain	—	—	112	841	112	841
Tunisia	—	—	829	3,454	829	3,454
Total	3,050	$59,398	8,821	$83,533	11,871	$142,931

TABLE 11.—FLUORSPAR IMPORTED FOR CONSUMPTION IN THE UNITED STATES, BY COUNTRIES OF ORIGIN AND BY GRADES, 1930–1947[a]—(Concluded)

Year and country	Containing more than 97% calcium fluoride		Containing not more than 97% calcium fluoride		Total	
	Net tons	Value	Net tons	Value	Net tons	Value
1941:						
Mexico	1,516	$29,850	2,936	$27,481	4,452	$57,331
Spain	—	—	3,070	22,772	3,070	22,772
United Kingdom	—	—	2	32	2	32
Total	1,516	$29,850	6,008	$50,285	7,524	$80,135
1942:						
Canada	—	—	(d)	$ 10	(d)	$ 10
Mexico	1,882	$31,951	269	3,568	2,151	35,519
Total	1,882	$31,951	269	$3,578	2,151	$35,529
1943:						
Mexico	1,854	$41,635	18,661	$195,769	20,515	$237,404
Newfoundland	—	—	7,144	175,829	7,144	175,829
Spain	—	—	15,341	222,676	15,341	222,676
Union of South Africa	—	—	570	7,500	570	7,500
Total	1,854	$41,635	41,716	$601,774	43,570	$643,409
1944:						
Canada	—	—	69	$ 1,951	69	$ 1,951
Mexico	3,210	$ 67,837	55,114	912,252	58,324	980,089
Newfoundland	2,352	85,613	13,720	345,619	16,072	431,232
Spain	—	—	9,177	222,080	9,177	222,080
Union of South Africa	—	—	3,557	44,715	3,557	44,715
United Kingdom	—	—	1	37	1	37
Total	5,562	$153,450	81,638	$1,526,654	87,200	$1,680,104
1945:						
Canada	—	—	[e]2,361	$ [e]75,085	[e]2,361	$ [e]75,085
Mexico	6,176	$128,920	56,399	925,772	62,575	1,054,692
Newfoundland	4,099	125,880	[e]6,776	[e]206,676	[e]10,875	[e]332,556
Spain	—	—	27,322	694,125	27,322	694,125
Total	10,275	$254,800	92,858	$1,901,658	103,133	$2,156,458
1946:						
Canada	—	—	310	$ 8,934	310	$ 8,934
Mexico	3,933	$ 78,219	20,130	306,538	24,063	384,757
Newfoundland	2,688	80,640	—	—	2,688	80,640
Spain	—	—	2,791	42,484	2,791	42,484
Total	6,621	$158,859	23,231	$357,956	29,852	$516,815
1947:						
Canada	—	—	284	$ 7,594	284	$ 7,594
Italy	—	—	4,126	40,793	4,126	40,793
Mexico	7,090	$130,662	44,529	641,271	51,619	771,933
Newfoundland	8,257	206,360	2,050	68,716	10,307	275,076
Spain	275	9,277	11,767	149,557	12,042	158,834
United Kingdom	1	169	—	—	1	169
Total	15,623	$346,468	62,756	$907,931	78,379	$1,254,399

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[a] U. S. Bur. Mines, Minerals Yearbooks and Mineral Market Report No. 1596.

[b] Less than 1 ton of optical spar.

[c] Optical fluorspar.

[d] Less than 1 ton.

[e] Bur. Mines has determined that 1,691 tons, valued at $56,918, credited to Canada by the U. S. Dept. Commerce, originated in Newfoundland.

Table 12.—Tariffs on Fluorspar, 1909–1947[a]

The rates of duty on fluorspar beginning with 1909 have been as follows:

- Act of 1909, effective August 1909, $3 per long ton (equivalent to $2.68 per short ton).
- Act of 1913, effective October 1913, $1.50 per long ton (equivalent to $1.34 per short ton).
- Act of 1922, effective September 22, 1922, $5.60 per long ton (equivalent to $5 per short ton).
- Act of 1922, effective November 16, 1928, $8.40 per long ton (equivalent to $7.50 per short ton) on fluorspar containing not more than 93 percent of calcium fluoride. The rate of duty on fluorspar containing more than 93 percent of calcium fluoride remained $5 per short ton.
- Act of 1930, effective June 18, 1930, $8.40 per long ton (equivalent to $7.50 per short ton) on fluorspar containing not more than 97 percent of calcium fluoride. The rate of duty on fluorspar containing above 97 percent remained $5 per short ton.

Note: The $5.60 rate was reduced to $4.20 per long ton (equivalent to $3.75 per short ton) effective January 1, 1939, pursuant to the trade agreement with the United Kingdom; and the $8.40 rate was reduced to $6.30 per long ton (equivalent to $5.625 per short ton), effective January 30, 1943, pursuant to the trade agreement with Mexico.

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[a] Hatmaker and Davis, Illinois Geol. Survey Bull. No. 59, 1938; and Report of U. S. Tariff Commission in Response to Senate Resolution No. 341 (78th Congress).

Table 14.—Cryolite Imported into the United States, 1922–1946[a]

Year	Net tons	Value	
		Total	Per ton
1922	4,367	$ 196,302	$44.95
1923	7,140	319,959	44.81
1924	7,078	320,670	45.30
1925	11,025	690,651	62.64
1926	8,511	557,598	65.51
1927	5,672	410,876	72.44
1928	7,735	529,176	68.41
1929	8,711	670,841	77.01
1930	9,313	695,794	74.71
1931	8,857	580,621	65.56
1932	4,236	291,357	68.78
1933	4,638	298,316	64.32
1934	4,984	376,868	75.62
1935	9,295	646,390	69.54
1936	14,130	1,076,538	76.19
1937	18,693	1,482,141	79.29
1938	13,569	785,606	57.89
1939	11,435	712,096	62.27
1940	28,961	1,329,788	45.92
1941	29,886	1,462,725	48.94
1942	72,213	3,859,875	53.45
1943	51,968	3,117,888	59.99
1944	17,562	1,155,787	65.81
1945	20,106	1,349,678	67.13
1946	11,424	815,627	71.39

[a] 1922-1936, Hatmaker and Davis, The Fluorspar Industry, Illinois Geol. Survey, Bull. No. 59, 1938; Minerals Yearbooks and Mineral Market Report No. 1596, U. S. Bur. Mines.

Table 13.—Average Production, Consumption and Imports of Fluorspar, 1926–1947[a]

Year	Production	Imports	Consumption	Imports to total consumption (Percent)
1926–1930	124,796	62,723	175,991	35.6
1931–1935	72,238	15,480	96,520	16.1
1936–1940	170,847	22,073	177,420	12.4
1941–1945	364,949	48,755	363,909	13.4
20-yr. av.	183,208	37,258	228,460	16.3
1946–1947	303,712	54,116	339,664	15.9

[a] Based on U. S. Bur. Mines data.

TABLE 15.—FLUORSPAR (DOMESTIC AND FOREIGN) CONSUMED IN THE UNITED STATES, 1927–1947[a]
(In net tons)

Year	Steel	Hydro-fluoric acid	Glass	Enamel	Iron foundry and ferro-alloys	All other	Total
1927	142,700	15,500	6,800	5,800	3,900	1,500	176,200
1928	158,100	20,500	6,200	5,700	4,100	1,600	196,200
1929	162,100	15,600	6,600	5,200	3,800	1,500	194,800
1930	112,600	12,600	4,300	4,000	2,700	2,000	138,200
1931	69,300	12,000	7,100	3,000	1,300	1,300	94,000
1932	38,400	7,000	6,700	2,400	800	700	56,000
1933	64,700	7,800	7,000	3,200	1,200	700	84,600
1934	85,300	11,000	7,700	3,500	2,100	1,000	110,600
1935	105,000	12,900	11,000	4,900	2,600	1,000	137,400
1936	140,800	20,100	11,600	5,400	2,700	1,800	182,400
1937	146,400	24,100	11,600	5,900	3,700	2,600	194,300
1938	77,600	18,900	10,500	4,000	2,800	1,300	115,100
1939	123,800	26,300	15,300	6,100	3,500	1,800	176,800
1940	155,500	37,000	13,400	5,500	4,600	2,500	218,500
1941	210,400	56,000	20,300	7,300	5,100	4,500	303,600
1942	242,600	81,600	18,500	3,100	7,800	7,200	360,800
1943	234,148	113,614	20,592	1,726	7,260	11,545	388,885
1944	230,201	129,553	27,315	2,547	7,815	12,739	410,170
1945	197,916	109,315	31,874	3,695	6,786	6,504	356,090
1946	160,735	83,901	39,852	6,739	6,969	4,944	303,190
1947	209,395	100,363	42,130	8,938	6,567	8,745	376,138
1948:							
First Quarter	56,750	25,037	8,844	2,308	([b])	[b]4,353	97,292

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[a] U. S. Bureau of Mines, Preprint Minerals Yearbook, 1946, Mineral Market Report No. 1596 and Fluorspar Report No. 45, May 28, 1948.

[b] Iron foundry and ferro-alloys included in "all other."

TABLE 16.—ANNUAL FLUORSPAR CONSUMPTION IN THE UNITED STATES IN PERCENT, BY INDUSTRIES, 1926–1947[a]

Industry	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937
Basic open-hearth steel	81.3	78.3	77.5	79.9	78.9	70.4	64.8	72.5	73.2	72.2	73.4	71.7
Electric-furnace steel	2.7	2.7	3.1	3.3	2.6	3.3	3.7	4.0	3.9	3.9	3.8	3.9
Foundry	2.5	1.9	1.7	1.4	1.2	1.1	1.1	1.1	1.4	1.4	1.0	1.3
Ferro-alloys	0.3	0.3	0.4	0.5	0.8	0.3	0.4	0.3	.04	0.5	0.4	0.6
Hydrofluoric acid and derivatives	4.4	8.8	10.4	8.0	9.1	12.8	12.5	9.2	10.0	9.3	11.0	12.4
Enamel and vitrolite	3.8	3.3	2.9	2.7	2.9	3.2	4.3	3.8	3.2	3.6	3.0	3.0
Glass	4.6	3.9	3.2	3.4	3.1	7.5	12.0	8.3	7.0	8.4	6.4	6.0
Miscellaneous	0.4	0.8	0.8	0.8	1.4	1.4	1.2	0.8	0.9	0.7	1.0	1.1

Industry	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947	Average		
											1926–1935	1936–1945	1946–1947
Basic open-hearth steel	64.0	65.6	65.7	63.0	60.0	52.8	49.0	49.6	48.0	50.4	74.9	61.5	66.5
Electric-furnace steel	3.5	4.3	5.4	6.0	7.0	7.3	6.6	5.8	4.9	5.2	3.3	5.4	4.4
Foundry	1.7	1.4	1.2	0.9	1.0	0.9	1.0	1.1	1.6	1.1	1.5	1.2	1.3
Ferro-alloys	0.7	0.6	0.9	0.8	1.2	1.0	0.9	0.8	0.7	0.7	0.4	0.8	0.6
Hydrofluoric acid and derivatives	16.5	14.8	17.0	18.5	22.7	29.2	31.6	30.7	27.7	26.7	9.5	20.4	16.1
Enamel and vitrolite	3.5	12.2	8.7	9.1	0.9	0.4	0.6	1.0	2.2	2.4	3.4	1.8	2.6
Glass	9.1				5.1	5.3	6.7	8.9	13.1	11.2	6.1	7.2	7.2
Miscellaneous	1.0	1.1	1.1	1.7	2.1	3.1	3.6	2.1	1.8	2.3	0.9	1.8	1.3

[a] Data based on Minerals Yearbooks, U. S. Bur. Mines.

Table 17.—Fluorspar Consumption in Steel and Hydrofluoric Acid by Tonnage and Percentage of Total Consumption 1938–1947[a]

Year	Thousands of net tons			Percentage		
	Steel	HF	Total	Steel of total	HF of total	HF of steel
1938	78	19	115	67	17	24
1939	124	26	177	70	15	21
1940	156	37	219	71	17	24
1941	210	56	304	69	18	27
1942	243	82	361	67	23	34
1943	234	114	389	60	29	49
1944	230	130	410	55	31	57
1945	198	109	356	56	31	56
1946	161	84	303	53	28	52
1947	210	100	372	56	27	48

[a] Compiled from Bur. Mines data.

Table 18.—Chief Commercial Grades of Fluorspar[a]

General classification	Industrial use	Form	Specifications, percent		
			CaF_2 (Min.)	SiO_2 (Max.)	Fe_2O_3 (Max.)
Metallurgical	Basic open-hearth steel	Washed gravel, less than 1 inch (not over 15 percent fines)	85	5	—
Ceramic	Glass and enamel	Ground: coarse, fine, and extra fine	95	2.5	0.12
Chemical	Hydrofluoric acid and its products	Lump gravel and fines	98	1	—

[a] June 1945.

Table 19.—Estimated Fluorspar Reserves of the United States as of January 1944, by Regions[a]
(In net tons)

Region	Ore containing 35 percent or more CaF_2						Ore containing 15 to 34% CaF_2* (Measured, indicated and inferred)			Total	
	Measured	Indicated	Inferred	Total crude ore	CaF_2 content	Av. grade (est. % CaF_2)	Crude material	CaF_2 content (est.)	Av. grade (est. % CaF_2)	Crude ore	CaF_2 content
Kentucky and Illinois	1,722,000	2,328,000	7,000,000	11,050,000	5,525,000	50	4,500,000	675,000	15	15,550,000	6,200,000
Rocky Mountain States (Colo., Utah, Idaho, Wyoming and Montana)	104,000	782,000	1,250,000	2,136,000	961,200	45	3,500,000	700,000	20	5,636,000	1,661,200
Southwestern States (Ariz., New Mexico, and Texas)	102,000	209,000	800,000	1,111,000	610,500	55	1,000,000	200,000	20	2,111,000	810,500
Pacific Coast States and Nevada	7,000	30,000	80,000	117,000	81,900	70	450,000	90,000	20	567,000	171,900
All other states	—	—	4,000	4,000	2,000	50	140,000	28,000	20	144,000	30,000
Alaska	—	56,000	250,000	306,000	128,500	42	2,000	400	20	308,000	128,900
Total	1,935,000	3,405,000	9,384,000	14,727,000	7,309,100	49	9,592,000	1,693,400	18	24,316,000	9,002,500

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* Based on incomplete data and believed to be conservative.

[a] Hearings before a Subcommittee of the Committee on Public Lands, U. S. Senate, Eightieth Congress, First Session, an Investigation of the Factors Affecting Minerals, Fuels, Forestry, and Reclamation Projects, May 15, 16, and 20, 1947.

Table 20.—Phosphate Rock Mined in the United States and Superphosphates (Acid Phosphate) Produced in the United States, 1928–1945[a]
(In net tons)

Year	Rock phosphate mined	Super-phosphates produced
1928	3,946,159	([b])
1929	4,241,726	([b])
1930	4,520,541	4,102,764
1931	2,986,490	2,744,528
1932	1,901,926	1,765,971
1933	2,642,791	2,694,870
1934	3,246,027	2,868,016
1935	3,538,447	2,954,130
1936	3,878,377	3,412,486
1937	4,772,786	4,429,767
1938	4,323,723	3,575,588
1939	4,466,526	3,801,194
1940	4,556,346	3,898,641
1941	5,412,845	4,326,402
1942	5,396,211	5,144,484
1943	6,014,363	6,292,955
1944	5,824,002	6,692,368
1945	6,047,708	7,372,104

[a] U. S. Bureau of Mines, Minerals Yearbooks.

[b] Not available before 1930.

Table 21.—Reserves of Phosphate Rock in the United States as of 1943, by States[a]
(In net tons)

State	Measured	Indicated	Inferred	B.P.L. percent
Florida	2,305,613,000	1,374,408,000	2,012,000,000	50–74
Idaho[b]	—	—	6,424,000,000	70+
Utah[b]	—	—	1,950,000,000	40+–70
Montana[b]	—	—	438,000,000	70+
Wyoming[b]	—	—	130,000,000	70+
Tennessee	105,056,000	—	—	35+
Arkansas[b]	—	—	222,000,000	—
South Carolina[b]	—	—	10,000,000	—
Kentucky[b]	—	—	1,000,000	—
Total	2,410,669,000	1,374,408,000	10,987,000,000	—

[a] Hearings before a Subcommittee of the Committee on Public Lands, U. S. Senate, Eightieth Congress, First Session, an Investigation of the Factors Affecting Minerals, Fuels, Forestry, and Reclamation Projects, May 15, 16, and 20, 1947.

[b] Measured and indicated included in inferred.

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