

Synthetic Cryolite*

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The mineral cryolite, chemically called sodium aluminum fluoride ($\text{AlF}_3 \cdot 3\text{NaF}$), is found in commercial quantities only at Ivigtut, on the southwest coast of Greenland. In 1865, mining operations began in the form of a 75-year concession from the Danish government to two distributing companies, namely the Pennsylvania Salt Company of Philadelphia which has the exclusive selling rights in North America, and the Oresund Company of Copenhagen with selling rights for the rest of the world. This monopoly is of serious concern to the countries possessing a domestic aluminum industry during economic and political crises. For example, several years ago as a result of an advancement in the price of cryolite, graphite electrodes, and power, the Japanese Electrochemical A-G was forced to operate at a loss. The factors of a price monopoly, the widely distributed sources of fluorine such as fluorspar and fluorapatite, and the trend towards economic independence obviously led to the search for a synthetic product.

To obtain a clearer picture of the entire situation, a brief analysis of the distribution and uses of natural cryolite will be discussed. Gibbs¹ in his article, "Cryolite as a Chemical Raw Material," gave an excellent review of this topic. During 1925-1934,² the annual production of cryolite varied from 10,000 to 35,000 tons with approximately one-third of it going to the Pennsylvania Salt Company.

The chief outlet for cryolite is in the electrolytic reduction of aluminum of which Germany, United States, France, Canada, Norway, U. S. S. R., Italy and Great Britain produce approximately 90 per cent of the world supply. The entire world production of aluminum for 1934 was 170,000 metric tons.³ In the production of aluminum, cryolite is used as a solvent for alumina; the molten bath contains only about two to five per cent of alumina.⁴ In other metallurgical processes, also, cryolite finds use as a flux. The ceramic industry is a large user particularly in the manufacture of enamels, glass, and glazes. In the case of enamels, it has a double value, namely, as a flux and as a secondary opacifying agent. Here the quantity of cryolite used varies from four to sixteen per cent. The glass industry uses it chiefly as an opacifying agent although its fluxing action is important also. The degree of opacity is determined by the amount of cryolite and period of heating. With glazes, cryolite is essentially a solvent although it also is an opacifier. It is used also as a binder for abrasive materials, and as a promoter of particular types of crystal growth in ceramic bodies.

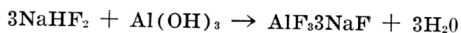
A very recent development in the utilization of cryolite is in the insecticide industry. It has been known for a long time that cryolite dust was effective in destroying the potato bug. More recently it has been found to be an effective stomach poison for chewing insects. In order to be effective, the particle size must be five microns or less (approximately 1/5000 inch). Not until fairly recently was it possible to grind natural cryolite to this fineness.

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The appearance of synthetic cryolite on the market is not surprising, because of the importance of the mineral in our industrial age. The fact that the natural material is also under the control of a monopoly enhanced the entree of the synthetic product. The sources of fluorine for the manufacture of this product are widely distributed and readily available to the major aluminum producing nations. Fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$) occurring in immense deposits and fluorspar in more localized areas are the two main mineral sources of fluorine. In the case of fluorapatite, if it is used in the manufacture of superphosphate fertilizer, the fluorine is evolved as silicon tetrafluoride and is almost a valueless by-product. Fluoroapatite contains about 3.7 per cent fluorine.⁵ Reynolds and Jacobs state that in a normal year 20,000 tons of fluorine can be obtained as a by-product from superphosphate manufacture in the United States. This amount of fluorine is equivalent to more cryolite than has ever been mined at Ivigtut in a single year, and more than three times the annual requirement for the United States.

The other fluorine mineral, fluorspar, is the chief source the world over of hydrofluoric acid and its derivatives. The industrial technology of hydrofluoric acid is very well understood and can be obtained in unlimited quantities. The price of fluorspar is from one-fourth to one-half of that of the natural cryolite. In short, these fluorine-containing minerals are the answer to the national economic independence of this valuable industrial product.

Berzelius⁶ in 1824 probably prepared the first synthetic cryolite in the laboratory by the reaction of a NaHF_2 solution with $\text{Al}(\text{OH})_3$.

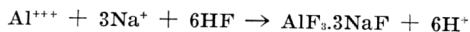


However, the initial commercial production of synthetic cryolite is obscure but it appears that Germany and France were the first in the field and their product has been on the American market for some time. France⁷ is capable of supplying its own domestic needs. Italy⁸ is importing synthetic cryolite and projecting plants⁹ of her own. Japan¹⁰ is already producing about one-half of its cryolite needs. Russia¹¹ projected a production of 25,000 metric tons annually beginning with 1936. The Aluminum Company of America and the Grasselli Chemical Company hold the American patents. Statistics are not available for the United States although it is known that a domestic synthetic product is available for insecticidal purposes. The Aluminum Company¹² has a plant for the production of "its own cryolite using fluorspar" at East St. Louis, Illinois.

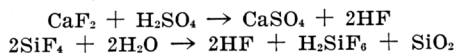
Industrially, synthetic cryolite is prepared by two methods depending upon the available raw material. Briefly, they may be called (1) the silicofluoride method, and (2) the hydrofluoric acid method. The silicofluoride method is essentially the reaction of a silicofluoride with alumina in the presence of an additional sodium salt. The silica is removed by appropriate means, and the process can be represented as follows:



The hydrofluoric acid method involves the treatment of alumina or an aluminum salt in the presence of sodium ions with hydrofluoric acid:



the hydrofluoric acid having been obtained from fluorspar or silicon tetrafluoride as follows:



Japan appears to be the only country using the silicofluoride by-product of the phosphate industry, whereas the other countries most likely use fluorspar.

The future for synthetic cryolite is very promising. The raw materials are readily available, it is being successfully manufactured, it is competing with the natural product on the open market, and a great deal of industrial research is in progress to lower its cost still more.

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