# Indian Minerals Yearbook 2022

## (Part- III : Mineral Reviews)

## 61th Edition

## CRYOLITE

### (ADVANCE RELEASE)

**GOVERNMENT OF INDIA**
**MINISTRY OF MINES**
**INDIAN BUREAU OF MINES**

Indira Bhavan, Civil Lines,
NAGPUR – 440 001

PHONE/FAX NO. (0712) 2565471
PBX : (0712) 2562649, 2560544, 2560648
E-MAIL :cme@ibm.gov.in
Website: www.ibm.gov.in

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# 8 Cryolite

Cryolite is a double fluoride of sodium and aluminium and has a stoichiometry very near the formula $Na_3AIf_6$ and a melting point of about 1,010 $^0$C. It was found to occur in substantial quantities in Ivigtut, Greenland, and was mined extensively there in the early twentieth century, but the mine is now essentially exhausted. Synthetic cryolite can be produced by reacting hydrofluoric acid with an alkaline sodium aluminate solution.

It is usually colourless to white, brownish, reddish, brick red colour having vitreous to greasy lusture. cryolite normally found to occur in coarsely granular masses form having no cleavage. It has a specific gravity of about 2.5 to 3. It has a low index of refraction close to that of water. Synthetic cryolite is used as an electrolyte in the reduction of alumina to aluminium due to non-availability of natural cryolite. Composition and properties of synthetic cryolite are the same as that of natural cryolite, but synthetic cryolite is often deficient in sodium fluoride.

## INDUSTRY

Synthetic cryolites are obtained by adopting several processes. The selection of the process depends upon the availability and cost of raw materials.The simplest and most common method of obtaining synthetic cryolite is by reacting hydrofluoric acid with soda ash and alumina hydrate. Hydrofluoric acid is produced by reacting acid-grade fluorspar with sulphuric acid and this process also yields gypsum as by-product. In the secondary reaction between hydrofluoric acid and sodium chloride brine, sodium fluoride and hydrochloric acid are produced. In the primary reaction, dry aluminium hydroxide reacts with hydrofluoric acid to produce aluminium fluoride which reacts with sodium fluoride produced earlier and forms synthetic cryolite.

Besides fluorspar, fluorine gas produced as by-product at plants that produces phosphatic fertilizer and phosphoric acid, has emerged as an important alternative source for hydrofluoric acid and other fluorine chemicals including cryolite and aluminium fluoride. Rock phosphate usually contains 7–8% $CaF_2$. In terms of fluorine, it works out to 3–4% which is liberated at the time of acidulation of rock phosphate with sulphuric acid. Fluorine combines with silica to form silicon tetrafluoride which when scrubbed with water forms fluorosilicic acid. By recycling, 18–24% fluorosilicic acid is obtained, which serves as a raw material for manufacturing various fluoro-chemicals, including synthetic cryolite. From fluorosilicic acid, fluorine values are precipitated as sodium fluorosilicate by treating it with sodium salts. Sodium fluorosilicate becomes starting point for the production of synthetic cryolite.

For manufacture of synthetic cryolite from sodium fluorosilicate, two routes are generally adopted in the country. In the first route, sodium fluorosilicate is reacted with ammonia and in other route, sodium fluorosilicate is reacted with soda ash.

## SPECIFICATIONS

The Indian Standard Specifications of cryolite for use in Aluminium Industry defined vide IS - 5893 : 1989 (Second Revision; reaffirmed 2008) are as follows:

| Constituents (on dry basis) | Specification |
|---|---|
| F | 53% min. |
| Na | 31 to 34% |
| Al | 13 to 15% |
| $SiO_2$ | 0.20% max. |
| $Fe_2O_3$ | 0.10% max. |
| $CaF_2$ | 0.06% max. |
| $Al_2O_3$ | 1.00% max. |
| $SO_3$ | 0.50% max. |
| $P_2O_5$ | 0.01% max. |
| Loss on Ignition (LOI) | 0.50% max. |
| $NaF/AlF_3$(by mass) | 1.45 max. (ratio required to maintain in acidic region) |

***Note:*** *i) LOI is to be determined at 550 $^0$C for 60 minutes.*

*ii) Moisture should not be more than 0.20% when* *determined at 110 ± 5 °C.*

## CONSUMPTION

The consumption of cryolite is nowadays not estimated because many industries prefer the use of synthetic cryolite instead of natural cryolite. However, consumption was reported earlier in bonded abrasives as a filler, insecticides, porcelaneous glass and salts of sodium & aluminium.

## USES AND TECHNOLOGY

The commercial application of cryolite is confined mainly to aluminium metallurgy where it is used as an electrolyte in the reduction of alumina to aluminium metal by the Hall-Heroult process. Alumina is a bad conductor of electricity and its melting point is 2,348 °C. It is very expensive to carry out electrolysis at this temperature.To facilitate electrolysis, alumina is dissolved in molten cryolite as it lowers the melting point. Further, addition of certain additives, such as, aluminium fluoride improve the physical and electrical properties of the electrolyte, besides lowering the melting point. The amount that is added is, however, limited as it also causes reduction in electrical conductivity. Addition of calcium fluoride ($CaF_2$) further depresses the melting point with less adverse effect on conductivity. In contrast to this advantage, too much $CaF_2$ raises the density of the melt closer to that of liquid aluminium metal, thus inhibiting the separation of metal from electrolyte. The substituent, sodium fluoride, though is known to improve the density and conductivity, it also affects current efficiency.

A compromise made on all these factors has led to the following general composition of the bath to be in use —80–85% cryolite, 5–7% $AlF_3$, 5–7% $CaF_2$, 0–7% LiF and 2–8% $Al_2O_3$. The electrolyte bath tends to deplete $AlF_3$ content of cryolite during the process. Hence, the composition of the electrolyte has to be adjusted regularly by addition of $AlF_3$.

In aluminium refining, high density electrolyte capable of floating aluminium is required. For this purpose, barium fluoride is used to raise density. Aluminium fluoride can be used to improve current efficiency of cryolite bath.

Cryolite is obtained as a by-product during the production of phosphatic fertilizer/phosphoric acid. When utilised in the Aluminium Industry, necessary precautions are observed as even 0.01% P in the electrolyte could cause 1–1.5% reduction in current efficiency in the production process of aluminium.

Other metallurgical uses of cryolite are in aluminising steel, in compounding of welding rod coatings and as fluxes. In glass, cryolite functions as a powerful flux because of its excellent solvent power for oxides of silicon, aluminium & calcium and for its ability to reduce melt viscosity at lower melting temperatures. Cryolite is used as a filler for resin-bonded grinding wheels in Abrasive Industry to impart longer life. Sodium fluoride (NaF) or fluorosilicic acid is also used for this purpose. Cryolite is used in certain nitrocellulose-based gun propellants required in small-calibre weapons, cannons and small & large rockets.

## FOREIGN TRADE

### Exports

In 2021-22, exports of cryolite and chiolite decreased marginally by 15% to 126 tonnes from 149 tonnes in the previous year. USA (60%), Turkey (19%), France (8%), Saudi Arabia (7%), Iraq (3%), Indonesia (2%) and Egypt (<1%) were the main buyers from India in 2021-22 (Table-1).

### Imports

In 2021-22, imports of cryolite and chiolite decreased by 34% to 4,167 tonnes from 6,338 tonnes in the previous year. Imports were mainly from China (76%), Bahrain (10%), Mozambique (6%), Norway (3%), Germany (2%), and Belgium & South Africa (1% each) (Table-2).

**Table – 1 : Exports of Cryolite and Chiolite (By Countries)**

| Country | 2020-21 (R) | | 2021-22(P) | |
|---|---|---|---|---|
| | Qty (t) | Value (₹'000) | Qty (t) | Value (₹'000) |
| **All Countries** | **149** | **8467** | **126** | **12127** |
| USA | 20 | 1206 | 75 | 8086 |
| Turkey | 81 | 2536 | 24 | 1305 |
| France | 10 | 761 | 10 | 840 |
| Indonesia | 4 | 894 | 3 | 812 |
| Saudi Arabia | 21 | 1271 | 9 | 688 |
| Egypt | 1 | 100 | 1 | 226 |
| Iraq | - | - | 4 | 82 |
| Brazil | 1 | 203 | ++ | 36 |
| Australia | - | - | ++ | 32 |
| UAE | 9 | 1097 | ++ | 20 |
| Other countries | 2 | 399 | - | - |

*Figures rounded off*

**Table – 2 : Imports of Cryolite and Chiolite (By Countries)**

| Country | 2020-21(R) | | 2021-22 (P) | |
|---|---|---|---|---|
| | Qty (t) | Value (₹'000) | Qty (t) | Value (₹'000) |
| **All Countries** | **6338** | **174382** | **4167** | **152877** |
| China | 2419 | 104486 | 3162 | 122288 |
| Germany | 148 | 15986 | 78 | 9012 |
| Bahrain | 2404 | 33317 | 404 | 6050 |
| Belgium | 42 | 2814 | 42 | 4852 |
| Mozambique | 396 | 5680 | 245 | 3507 |
| Netherlands | - | - | 21 | 3266 |
| Taiwan | - | - | 29 | 1770 |
| Norway | - | - | 130 | 1004 |
| South Africa | 50 | 548 | 52 | 569 |
| Hungary | 2 | 495 | 4 | 557 |
| Other countries | 877 | 11056 | ++ | 2 |

*Figures rounded off*

## FUTURE OUTLOOK

The future of cryolite is dependent upon its use in the Aluminium Industry. Increased usage of aluminium and high performance fluoropolymers in automobiles will drive growth in inorganic and specially fluorochemicals segments. It is learnt that some US firms have registered success in their research and pilot plant tests for the production of aluminium directly from the mineral bauxite without the intermediate process of reduction cell. Viability of this may probably eliminate the use of cryolite in the near future.