

CRYOLITE



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CRYOLITE

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

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8 Cryolite

Cryolite (Na_3AlF_6) is a double fluoride of sodium and aluminium which in terms of chemical composition is referred to as sodium hexafluoroaluminate. Cryolite, an uncommon mineral of very limited natural distribution was once found in large quantities on the west coast of Greenland. It is colourless to white but occurs in other shades too, for instance brown, red and some times black. It has a specific gravity of 2.5 to 3. This natural deposit was declared exhausted in 1987. 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 those of natural cryolite, but synthetic cryolite is often deficient in sodium fluoride. Chiolite is another sodium aluminium fluoride mineral having the chemical composition $\text{Na}_5\text{Al}_3\text{F}_{14}$.

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 by-product gypsum is obtained in this process. 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 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 fluorochemicals, 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.

Important known units producing synthetic cryolite are highlighted below:

1. Navin Fluorine International Ltd, Udhana-Navasari Road, Surat, Gujarat-395 023.
2. Navin Fluorine International Ltd, Agra-Mumbai Road, Dewas, Madhya Pradesh-455 002.
3. Tanfac Industries Ltd, Kudikadu, Cuddalore, Tamil Nadu-607005.
4. Harshil Industries Sarigam, Vapi, Gujarat-396195.
5. Triveni Interchem Pvt Ltd GIDC, Vapi, Gujarat.
6. S.B. Chemicals, GIDC, Vapi, Gujarat-396195.

NFIL produced 9878 tonnes of synthetic cryolite in the year compared to 9234 tonnes in 2015-16.

Navin Fluorine International Ltd is one of the largest manufacturers of speciality fluorochemicals comprising of synthetic cryolite during 2015-16. NFIL produced 9,234 tonnes of synthetic cryolite, Aluminium Fluoride & Fluorocarbon gases.

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Also, it is understood that Triveni Chemicals, S.B. Chemicals, Jay Intermediates & Chemicals (Vapi, Gujarat), Madras Fluorine Pvt. Ltd (Manali, Chennai, Tamil Nadu) and Tarun Fluo-Chem Pvt Ltd, (Delhi) manufactures synthetic cryolite besides, other fluorine chemicals. They also manufacture potassium cryolite (K_3AlF_6) which is a foundry flux and used in welding, chemicals and explosives.

The total installed capacity of aluminium fluoride in organised sector was about 25,600 tonnes per annum.

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 ₂ O ₃	0.10% max.
CaF ₂	0.06% max.
Al ₂ O ₃	1.00% max.
SO ₃	0.50% max.
P ₂ O 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:**
- LOI is to be determined at 550 °C for 60 minutes.
 - 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, porcelainous glass and salts of sodium and 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 (CaF₂) further depresses the melting point with less adverse effect on conductivity. In contrast to this advantage, too much CaF₂ 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% AlF₃, 5-7% CaF₂, 0-7% LiF and 2-8% Al₂O₃. The electrolyte bath tends to deplete AlF₃ content of cryolite during the process. Hence, the composition of the electrolyte has to be adjusted regularly by addition of AlF₃.

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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 selectrolyte could cause 1-1.5% reduction in current efficiency in the production process of aluminium.

Other metallurgical uses of cryolite are in aluminizing 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 2016-17, the export of Sodium Hexafluoroaluminate was 123 tonnes. In 2015-16, exports of cryolite & chiolite decreased marginally by 16% to 38 tonnes from 45 tonnes in the previous year. Turkey (63%) and Indonesia (15%) and Sweden (13%) were the main buyers from India in 2015-16 (Tables-1 & 2).

Imports

In 2016-17, the import of Sodium Hexafluoroaluminate was 29793 tonnes. Imports of cryolite & chiolite in 2015-16, dropped drastically by 55% to 16,497 tonnes from 37,061 tonnes in the

previous year. Norway (32%) UAE (25%), South Africa (12%), Canada (10%) China (8%) were the main suppliers to India (Tables-3 & 4).

Table-1: Exports of Sodium Hexafluoroaluminate (By Countries) 2016-17 (P)

Country	Qty (t)	Value (₹'000)
All Countries	123	6057
Indonesia	++	++
Turkey	19	1168
Iran	40	2784
Kenya	2	184
Saudi Arabia	30	1696
Nepal	15	039
Uganda	17	186

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

Country	2014-15		2015-16 (P)	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	45	4029	38	2621
Turkey	-	-	24	1393
Indonesia	2	191	6	469
Sweden	17	1531	5	458
Saudi Arabia	++	38	2	187
Iran	22	1528	1	55
Kenya	-	-	++	31
Germany	++	6	++	25
Brazil	++	5	++	2
Malaysia	1	384	-	-
Bangladesh	1	151	-	-
Other countries	2	195	++	1

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Table-3: Imports of Sodium Hexafluoroaluminate (By Countries) 2016-17 (P)

Country	Qty (t)	Value (₹'000)
All Countries	29793	442663
Argentina	3003	47736
Australia	542	8948
Brazil	964	12651
Canada	8589	110531
China	892	56337
Germany	297	20343
Hungary	3	374
Iceland	2373	22322
Mozambique	413	542
Netherlands	427	6915
Norway	581	6938
Oman	1969	23791
Qatar	351	3757
Saudi Arabia	8388	105337
UAE	1001	16141

Table – 4 : Imports of Cryolite and Chiolite (By Countries)

Country	2014-15		2015-16 (P)	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	370618	16746	16497	448796
Norway	5632	107400	5310	132750
UAE	2802	74220	4079	106872
China	1557	82424	1395	80768
Canada	3499	90737	1667	44671
South Africa	5563	75040	1925	25744
Australia	647	16872	651	17491
Argentina	1001	24964	498	13657
Brazil	-	-	518	11411
Germany	84	12344	105	7026
New Zealand	3741	92708	299	6595
Other countries	12535	240037	50	1811

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. 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.