28 Cryolite

Cryolite is a double fluoride of sodium and aluminium with the chemical composition (Na_3AlF_6). Cryolite, an uncommon mineral of very limited natural distribution was only found in large quantities on west coast of Greenland. This natural deposit was exhausted in 1987. It is an important raw material for extraction of aluminium from alumina. It has a low index of refraction close to that of water. Notable occurrences include Ivigtut area of Greenland and also at the foot of Pikes Peak at Creede, Colorado, USA, Mont Saint-Hilaire and Francon Quarry, Montreal, Quebec, Canada and at Miask, Russia. Synthetic cryolite is used as electrolyte in the reduction of alumina to aluminium due to non-availability of natural cryolite all over the world. 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 $5NaF.3AlF_3$.

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 aluminium 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 producing aluminium fluoride which reacts with sodium fluoride produced earlier and forms synthetic cryolite.

Besides fluorspar, by-product fluorine gas emanating from plants of 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 the manufacture of synthetic cryolite from sodium fluorosilicate, two routes are being followed in the country. In one route, sodium fluorosilicate is reacted with ammonia and in other route, sodium fluorosilicate is reacted with soda ash. Fertilizers & Chemicals Travancore Ltd (FACT), Udyogmandal, Cochin, Kerala, follow the ammonia route whereas Dharamsi Morarjee Chemicals Co. Ltd Ambarnath, Maharashtra, follow the soda ash route.

Important known units producing synthetic cryolite with their installed capacities are given below. The production data for these units are not available:

1. Navin Fluorine Industries, Bhestan, Surat, Gujarat.
2. Tanfac Industries Ltd (formerly Tamil Nadu Fluorine and Allied Chemicals Ltd) Kudikadu, Cuddalore, South Arcot, Tamil Nadu (3,000 tpy).

3. Dharamsi Morarjee Chemicals Co. Ltd, Ambarnath, Thane, Maharashtra (1,500 tpy).
4. Adarsh Chemical & Fertilizer Ltd, Udhana, Surat, Gujarat (540 tpy).
5. Premier Fertilizers Ltd, Chennai, Tamil Nadu (540 tpy).

The total installed capacity of aluminium fluoride in organised sector was 27,210 tonnes in 2006-07. Production of aluminium fluoride was 20,083 tonnes and 20,303 tonnes in 2005-06 and 2006-07.

SPECIFICATIONS

The Indian Standard Specifications of cryolite for use in aluminium industry defined vide IS - 5893 : 1989 (Second Revision; reaffirmed 2003) are as follows:

Constituent (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°C for 60 minutes.*

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

When cryolite obtained as a by-product of phosphate manufacture is to be used in aluminium industry, it is important to note that even 0.01% P in the electrolyte causes 1-1.5% reduction in current efficiency in the aluminium production.

CONSUMPTION

The reported consumption of cryolite in 2007-08 was 18,000 tonnes, almost all of which was in aluminium metal extraction industry. Insignificant consumption was reported by abrasive, electrical and electrode industries (Table-1).

Table - 1 : Reported Consumption of Cryolite 2005-06 to 2007-08 (By Industries)

(In tonnes)

Industry	2005-06	2006-07(R)	2007-08(p)
All Industries	**15000**	**18000**	**18000**
Aluminium	15000 (6)	18000 (6)	18000 (6)
Others (abrasive, electrical and electrode)	++ (4)	++ (4)	++ (4)

Figures rounded off. Data collected on non-statutory basis.

Figures in parentheses denote the number of units in organised sector reporting consumption.

USES AND TECHNOLOGY

The commercial application of cryolite is confined mainly to aluminium metallurgy where it is used as electro type in the reduction of alumina to aluminium metal by the Hall process. Alumina is a bad conductor of electricity and its melting point is 2348°C. It is very expensive to carry out the electrolysis at this temperature. Therefore, alumina is dissolved in molten cryolite for

electrolysis as it lowers the melting point. Further, certain additives improve physical and electrical properties of the electrolyte; e.g., aluminium fluoride lowers the melting point. The amount that can be added is, however, limited because it also reduces electrical conductivity. Fluorite (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 melt closer to that of liquid aluminium metal, thus inhibiting the separation of metal from electrolyte. Sodium fluoride improves density and conductivity but reduces current efficiency. A compromise made on all these factors has led to the following general composition of 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. Hence, composition of 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 can also be used to raise density. Aluminium fluoride can be used to improve current efficiency of cryolite bath.

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 and calcium and ability to reduce melt viscosity at lower melting temperatures. Cryolite is used as a filler for resin-bonded grinding wheels in abrasive industry to give longer life. Sodium fluoride (NaF) or fluorosilicic acid may also be used for this purpose. Cryolite is used in certain nitrocellulose-based gun propellants required in small-calibre weapons, cannons and small and large rockets.

The future of cryolite, it seems, is entirely dependent upon its use in the aluminium industry. It is learnt that some US firms are doing research and pilot plant tests have been carried out with success for the production of aluminium directly from the mineral bauxite without the intermediate process of reduction cell, whereby it will be possible to completely eliminate the use of cryolite.

FOREIGN TRADE

Exports

In 2007-08, exports of cryolite (artificial) increased to 401 tonnes from 79 tonnes in the previous year. Iran was the main buyer in 2007-08 (Table - 2).

Imports

Imports of cryolite (artificial) in 2007-08 decreased to 9,194 tonnes from 14,600 tonnes in the previous year. Canada (48%), Australia (21%), New Zealand (13%) and UK (6%) were the main suppliers (Table - 3).

Table - 2 : Exports of Cryolite (Artificial) (By Countries)

Country	2006-07		2007-08	
	Qty (t)	Value (Rs.'000)	Qty (t)	Value (Rs.'000)
All Countries	**79**	**3697**	**401**	**17934**
Iran	–	–	326	15325
Peru	–	–	24	938
UAE	–	–	21	788
Spain	72	3381	18	645
Nepal	–	–	10	236
Oman	5	226	2	92
Zambia	2	90	–	–

Table - 3 : Imports of Cryolite (Artificial)
(By Countries)

Country	2006-07		2007-08	
	Qty (t)	Value (Rs.'000)	Qty (t)	Value (Rs.'000)
All Countries	**14600**	**289381**	**9194**	**169837**
Canada	1486	27210	4456	84206
Australia	1816	32051	1886	31552
New Zealand	3834	68471	1212	20026
UK	360	7716	560	9737
South Africa	628	8438	491	8981
Mozambique	2788	50045	311	5507
China	377	13864	112	4431
Japan	1739	51705	100	3119
Iceland	301	5448	–	–
UAE	1176	21570	–	–
Other countries	95	2863	66	2278