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CRYOLITE

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12 Cryolite

Cryolite is a double fluoride of sodium and aluminium with 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. Synthetic cryolite is used as an 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 $Na_5Al_3F_{14}$.

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 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 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 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. Adarsh Chemical & Fertilizer Ltd, Udhana, Surat, Gujarat.
4. Premier Fertilizers Ltd, Chennai, Tamil Nadu (540 tpy).

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 are in the manufacture of 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 27,000 tonnes per annum. Production of aluminium fluoride was 11,550 tonnes in 2012-13.

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°C for 60 minutes.*
ii) Moisture should not be more than 0.20% when determined at 110 ± 5°C.

CONSUMPTION

The consumption of cryolite remained same to 17,700 tonnes for the last two years i.e. 2011-12, 2012-13- almost all of which was in aluminium metal extraction industry. Negligible consumption was also reported by abrasive, electrical and electrode industries (Table-1).

Table – 1 : Consumption of Cryolite 2010-11 to 2012-13 (By Industries)

(In tonnes)

Industry	2010-11	2011-12(R)	2012-13(P)
All Industries	**18200**	**17700**	**17700**
Aluminium	18200 (6)	17700 (6)	17700 (6)
Others (abrasive, electrical and electrode)	++ (4)	++ (4)	++ (4)

Figures rounded off. .
Figures in parentheses denote the number of units in organised sector reporting consumption.*
(Includes actual reported consumption and or estimates made wherever required).*

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 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 added is, however, limited as it also causes reduction in electrical conductivity. Addition of 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 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 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 can also be 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 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 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 & large rockets.

FOREIGN TRADE

Exports

In 2012-13, exports of cryolite & chiolite increased marginally to 15 tonnes from 11 tonnes in the previous year. Sweden was the main buyer in 2012-13 (Table - 2).

Imports

Imports of cryolite & chiolite (artificial) in 2012-13, increased considerably to 12,878 tonnes from 9,885 tonnes in the previous year. Canada (29%), Australia (22%), UAE(12%) and Switzerland (5%) were the main suppliers (Table -3).

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

Country	2011-12		2012-13	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	**11**	**781**	**15**	**1307**
Sweden	11	751	14	1226
Indonesia	-	-	1	54
Kenya	-	-	++	25
Ecuador	-	-	++	1
Other countries	++	30	++	1

Table – 3 : Imports of Cryolite and Chiolite (By Countries)

Country	2011-12		2012-13	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	**9885**	**236351**	**12878**	**312027**
Canada	4416	64141	3735	87618
Australia	232	5228	2805	68216
UAE	503	13897	1552	44554
Switzerland	-	-	641	19187
China	776	48836	330	18615
Mozambique	-	-	626	15642
France	-	-	491	13440
South Africa	-	-	1500	10730
Germany	238	8280	188	10480
Brazil	-	-	307	8812
Other countries	3720	95969	703	14733

FUTURE OUTLOOK

The future of cryolite is dependent upon its use in the aluminium industry. 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 near future.