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CRYOLITE

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GOVERNMENT OF INDIA
MINISTRY OF MINES
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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. This natural deposit was 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 $Na_5Al_3F_{14}$.

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, 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.

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

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 (formerly Tamil Nadu Fluorine and Allied Chemicals Ltd), Kudikadu, Cuddalore, Tamil Nadu .
4. Adarsh Chemical & Fertilizer Ltd, Udhana, Surat, Gujarat.
5. Premier Fertilizers Ltd, Chennai, Tamil Nadu.

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 27,000 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_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 ^oC for 60 minutes.*

ii) Moisture should not be more than 0.20% when determined at 110 $\pm$ 5 ^oC.

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 by various abrasive, electrical and electrode industries.

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^{o}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 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 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 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 2013-14, exports of cryolite & chiolite increased substantially to 93 tonnes from 15 tonnes in the previous year. Iran (54%), Sweden (23%) & Japan (22%) were the main buyers in 2013-14 (Table - 1).

Imports

Imports of cryolite & chiolite (artificial) in 2013-14, increased drastically to 24,068 tonnes from 12,877 tonnes in the previous year. South Africa (37%), China (10%), Canada (9%), Mozambique & Australia (8%) each and Norway (7%) were the main suppliers (Table -2).

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

Country	2012-13		2013-14	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	**15**	**1307**	**93**	**8124**
Iran	-	-	50	3973
Japan	-	-	20	1951
Sweden	14	1226	21	1915
Indonesia	1	54	1	151
Saudi Arabia	-	-	1	112
Kenya	++	25	++	14
Sri Lanka	-	-	++	5
Germany	-	-	++	2
Other countries	++	2	++	1

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

Country	2012-13		2013-14	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹'000)
All Countries	**12877**	**312027**	**24068**	**501163**
South Africa	1500	10730	8929	114505
China	326	18469	2390	72810
Canada	3735	87618	2236	57053
Mozambique	933	24454	2022	48256
Australia	2805	68216	1831	44022
Norway	-	-	1763	41939
Baharain	-	-	1452	30071
New Zealand	551	6664	1125	24512
Germany	240	13853	327	20225
Oman	-	-	750	19732
Other countries	2787	82023	1243	28038

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 the near future.