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Fluosilisic acid: Recovery System and aluminum Fluoride production

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Fluosilisic acid:
Recovery System and
Aluminum Fluoride production

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1. **Introduction**

Fluosilisic acid (H_2SiF_6) is mainly produced as a by-product from the wet process of Phosphoric Acid production from fluorapatite. Phosphate rock always contains fluorine. For F/P2O5 ratios, the fluorine content in rock of sedimentary origin ranges in general from 0.10 to 0.14. Rock of igneous origin shows lower ratios, from 0.04 to 0.006. About 50kg of fluorine (as H2SiF6) per tonne of phosphoric acid (as P2O5) is evolved with the concentration of phosphoric acid in the evaporation step. Currently, most of this evolved fluorine is absorbed into the cooling pond water causing alarge environmental problem.The phosphoric and hydrofluoric acids are liberated from Phosphate rock by the action of sulfuric acid. Some of the HF in turn reacts with silicate minerals, which are an unavoidable constituent of the mineral feedstock, to give silicon tetrafluoride. Thus the formed silicon tetrafluoride reacts further with HF. The net process can be described as:

$$SiO_2 + 6\,HF \leftrightarrows H_2SiF6 + 2\,H_2O$$

Neutralization of solutions of fluosilisic acid with alkali metal bases produces the corresponding alkali metal fluorosilicate salts:

$$H_2SiF_6 + 2\,NaOH \rightarrow Na_2SiF_6 + 2\,H_2O$$

The resulting salt Na2SiF6 is mainly used in water fluoridation. Also used for intsecticides, leather processing, wood preservation and etching of glass. Related ammonium and barium salts are produced similarly for other applications. With excess base, the fluorosilicate undergoes hydrolysis, so the neutralization of the fluorosilisic acid must guard against this easy hydrolysis reaction:

$$Na_2SiF_6 + 4\,NaOH \rightarrow 6\,NaF + SiO_2 + 2\,H_2O$$

2. Production of phosphoric acid

Processes with different raw materials are used in the manufacture of phosphoric acid.
The process is known as “thermal” when the raw material is elemental phosphorus. This process is rarely used because of the amount of energy which is needed.
The processes that use phosphate ores which are decomposed with an acid, are known as “wet processes” and they are the only economic alternative way to produce phosphoric acid.

There are three possible subgroups of wet processes depending on the acid that is used for the acidulation. This may be nitric, hydrochloric or sulphuric acid route since this is the process normally used in the production of fertilizers.

Generally, the more current processes are the following:-
- Dihydrate process
- Hemihydrate process
- Di-Hemihydrate process (double-stage)
- Hemi-Dihydrate process (single-stage)
- Hemi-Dihydrate process (double-stage)

Different processes are needed because of different rocks and gypsum disposal systems, processes economy, water and energy needs and the final uses of phosphoric acid.

2.1. Description of production processes

Raw Materials for Phosphoric Acid Production:
Bones used to be the principal natural source of phosphorus but phosphoric acid today is produced from phosphatic ores mined in various parts of the world. Phosphate ores are of two major geological origins:-
- Igneous as found in Kola, South Africa, Brazil, etc.
- Sedimentary as found in Morocco, Algeria, Jordan U.S.A., etc.

The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are:-

– Fluorapatite	$Ca_{10}(PO_4)_6(F,OH)_2$
– Francolite	$Ca_{10}(PO_4)_{6-x}(CO_3)_x(F, OH)_{2+x}$

Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks.

The most easily mined phosphate deposits are found in the great sedimentary basins.

These sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds. These phosphates are interposed with sedimentary strata of the waste materials interpenetrated by gangue minerals and thus sedimentary phosphate ores have differing compositions within the same source.

Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market. Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities. This gives rise to further variations in the finished ore concentrate product. Phosphoric acid technology, having to rely on raw materials of great variety, has to readapt itself constantly.

2.2. Principles of the Process

The basic chemistry of the wet process is exceedingly simple. The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulphuric acid into phosphoric acid and the insoluble salt calcium sulphate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightleftharpoons 3Ca\ SO_4.2H_2O \rightleftharpoons +2\ H_3PO_4 + \text{Heat}$$

The insoluble calcium sulphate is then separated from the phosphoric acid, most usually by filtration.

The reaction between phosphate rock and sulphuric acid is self-limiting because an insoluble layer of calcium sulphate forms on the surface of the particles of the rock. This problem is kept to a minimum by initially keeping the rock in contact with recirculated phosphoric acid to convert it as far as possible to the soluble monocalcium phosphate and then precipitating calcium sulphate with sulphuric acid.

$$Ca_3(PO_4) + 4H_3PO_4 + 3H_2O \rightleftharpoons CaH_4(PO_4)_2.H_2O$$

$$3CaH_4(PO_4)_2.H_2O + 3H_2SO_4 + 3H_2O \rightleftharpoons 3CaSO_4.2H_2O\downarrow + 6H_3PO_4$$

Calcium sulphate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature; P_2O_5concentration and free sulphate content.

3. Production Processes

Two principal processes are available.

3.1 Dihydrate process

The dihydrate process comprises four stages: grinding, reaction, filtration and concentration and these are represented in Figure 1& 2.

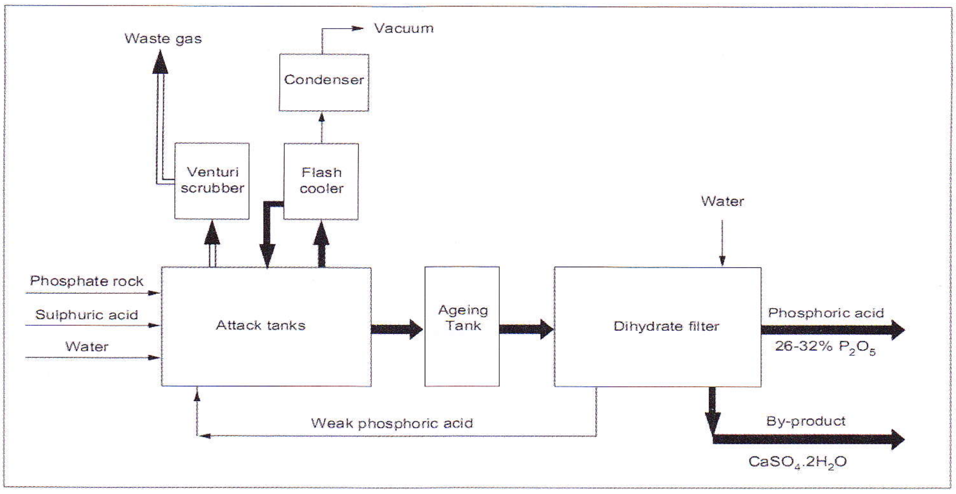


Figure 1 – Dihydrate Process.

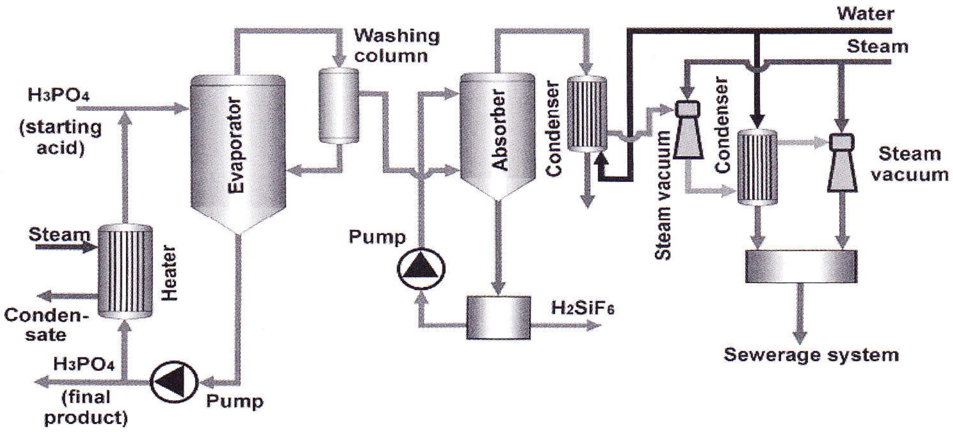


Figure 2 – Fluorine recovery system

3.2 Hemihydrate (HH) process

Operating conditions are selected in this process so that the calcium sulphate is precipitated in the hemihydrate form. It is possible to produce 40-52% P_2O_5 acid directly, with consequent valuable savings in energy requirements. Figure 3 shows a simplified flow diagram of a HH process. The stages are similar to .those of the dihydrate process but grinding may be unnecessary

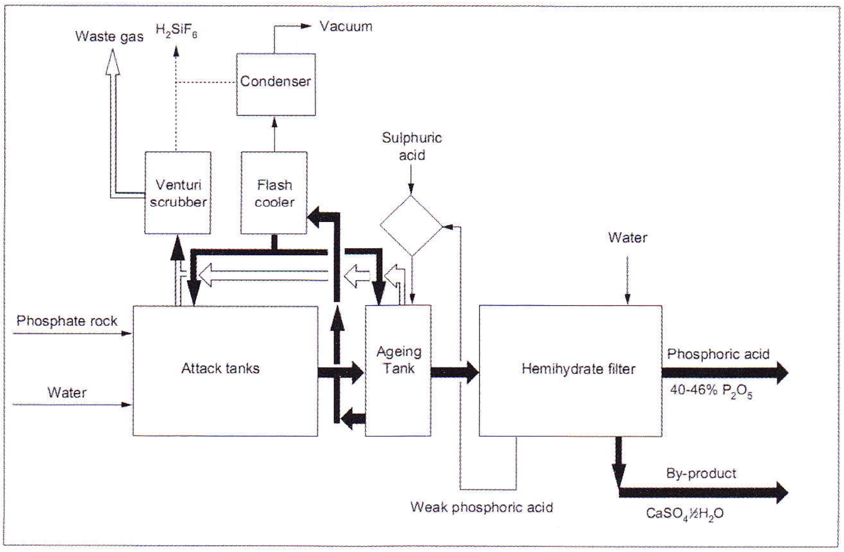


Figure 3 – Hemihydrate Process.

4. Production of fluosilicic acid (H_2SiF_6)

The gaseous and liquid effluents from all the processes need treatment to eliminate or at least to reduce, the contaminants.

Phosphate rock normally contains (2-4.4%) fluorine, it represents 10 to 14% of P_2O_5 content of the phosphate rock. About 50kg of fluorine (as H_2SiF6) per tone of phosphoric acid (as P_2O_5) is evolved with the concentration of phosphoric acid in the evaporation step. Fluorine is distributed between the product acid, the gypsum cake and the vapours evolved from the reactor and the evaporator if the acid needs to be concentrated.

The fluorine is liberated as hydrogen fluoride during the acidulation of phosphate rock. In the presence of silica this reacts readily to form fluosilicic acid via silicon tetrafluoride.

$$CaF_2 + 3H_2SO_4 + 2H_2O \rightarrow 3Ca\,SO_4.2H_2O \downarrow + 2HF_{gaz} \uparrow$$

The distribution of fluorine between the phosphoric acid, the gypsum cake and the gases, depends essentially on the following factors:

- Ratio SiO2/F phosphate rock: if silica content of phosphate is high, more fluorine is released.
- Ratio Na2O/K2O and F/F in phosphate, sodium and potassium tend to precipitate fluorine as fluosilicate or complex chemicals that end up in gypsum.
- The temperature of reaction during the phosphate attack is high, the quantity of released fluoride increases

Hydrofluoric acid reacts with the silica to form fluosilicic and silicon tetrafluoride :

$$6HF_{aq} + SiO_2 \rightleftharpoons H_2SiF_6 + 2H_2O$$
$$4HF_{aq} + SiO_2 \rightleftharpoons SiF_{4\,aq} + 2H_2O$$

This fluorosilicic acid reacts with alkaline oxide (K2O or Na2O) to give fluosilicates:

$$H_2SiF_6 + Na_2O \rightarrow Na_2SiF_6 \downarrow + 2H_2O$$

These precipitates are deposited in reactors as a hard solid. In case of a Na2O or K2O default in the phosphate, the excess of H2SiF6 is transformed into silicon tetrafluoride :

$$H_2SiF_6 \rightleftharpoons 2HF_{aq} + SiF_{4\,aq}$$

Below is shown a diagram of the reaction mechanism of transformation of fluoride during the reaction of attack of phosphate with sulfuric acid.

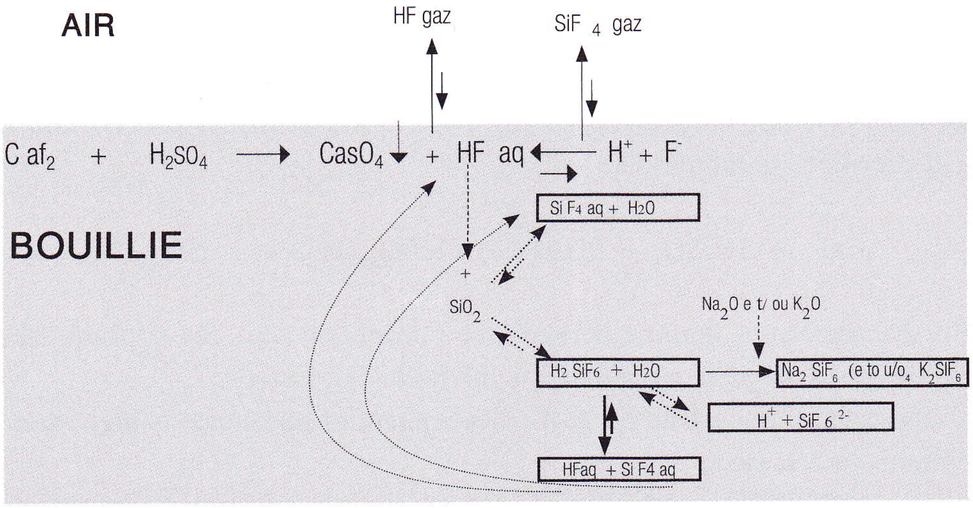


Figure 4 : Fluorine Transformation during attack phosphate rock with H2SO4

The fluosilicic acid may decompose under the influence of heat to give volatile silicon tetrafluoride and hydrogen fluoride.

$$H_2SiF_6 \longrightarrow SiF_4+2HF$$

The heat of reaction evolved during acidulation in a dihydrate process, is generally less than that required to cause this decomposition. The majority of the fluorine compounds will be evolved when weak phosphoric acid (2632%-P_2O_5) is concentrated. Conditions of higher temperature and reduced pressure exist in vacuum evaporators, thus causing the decomposition of fluosilicic acid.

Most of the fluorine is evolved during acidulation in the hemihydrate processes. Fluoride from the reaction will leave the reactor with the vacuum cooler condenser water or with the cooling air, depending on the cooling system, (flash cooler or air circulating cooler). In the first case, most of the released fluoride will be absorbed by the condenser water. In the second case, effluent gas washing must be installed.

In dihydrate processes, when flash coolers are used to control the temperature, it is usual to remove the fluoride from the gas evolved during acidulation and from the gas evolved during concentration, in separate systems. The fluoride scrubbing system is placed ahead of the condenser that follows the concentrator to avoid producing large quantities of highly contaminated water.

In hemihydrate processes, more fluoride is evolved during acidulation and may be removed from the gas from the reactor and the gas leaving the vacuum coolers that are commonly used.

4.1 Gas scrubbing systems

A number of different scrubbing systems have been used for removing fluoride. These can vary both in the scrubbing liquor and in the type of scrubber used. The most widely used scrubber is the void spray tower operating at atmospheric pressure but others, such as packed bed, cross-flow venturi and cyclonic column scrubbers have been extensively employed.

A product containing up to 22% fluosilicic acid is recovered in the fluoride recovery system at atmospheric pressure and the removal efficiency is better than 99% (90% with one absorber). Silica is removed from the acid by filtration. Fresh water, recycled pond water and dilute fluosilicic acid have all been used as scrubbing liquor.

Gas from the evaporator flash chamber is first fed through an entrainment separator if a system operating under vacuum is used. Essentially, this removes any P_2O_5 values from the gas. Only one scrubbing stage is generally used and 17-23% fluosilicic acid is obtained with a recovery efficiency of about 83-86%.

Systems operating under vacuum normally use a direct contact condenser in which most of the remaining fluoride is absorbed. An indirect condensation system has been developed to prevent the spillage of water which is contaminated with fluoride, for cases where certain phosphates are used and where a low cooling water temperature is feasible. . These two systems are shown in Figures 4 and 5. The water required for condensing is recycled in the condenser but is cooled by a heat exchanger fed from an independent water supply. These two water loops are independent and ensure that there are no fluorine compounds in the effluent.

The scrubber liquor can be disposed of after neutralisation with lime or limestone to precipitate fluorine as solid calcium fluoride, if the fluorine is not to be recovered. Often, however, the fluorine can be used and in these cases a dilute solution of fluosilicic acid is used as the scrubbing liquor. The required concentration is maintained by removing a portion of liquor, which is then filtered to remove solid contaminants.

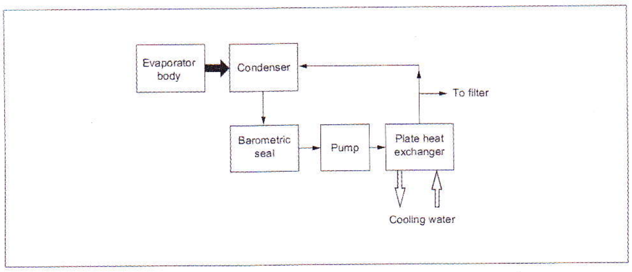


Figure 5 – Indirect Cooling Flow sheet

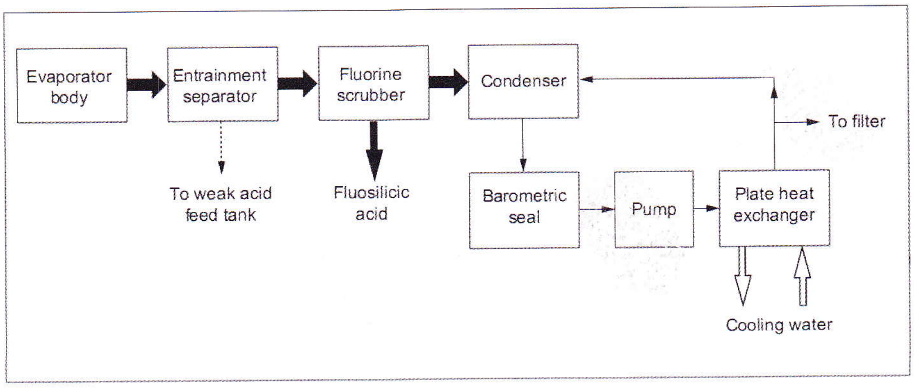


Figure 6 – Fluorine Recovery and Indirect Cooling Flow sheet.

4.2 Uses of Fluosilicic acid

Fluosilicic acid is the feedstock for "virtually all organic and inorganic fluorine-bearing chemicals". The majority of the fluosilicic acid is converted to aluminium fluoride and cryolite. These materials are central to the conversion of aluminium ore into aluminium metal. The conversion to aluminium trifluoride is described as:

$$H_2SiF_6 + Al_2O_3 \rightarrow 2\ AlF_3 + SiO_2 + H_2O$$

Fluosilicic acid is also converted to a variety of useful hexafluorosilicate salts. The potassium salt is used in the production of porceleins, the magnesium salt for hardened concretes and as an insecticide, and the barium salts for phosphors.

Fluosilicic acid is also commonly used for water fluoridation in several countries including the United States England, and Ireland. In the U.S., about 40,000 tons of fluosilicic acid is recovered from phosphoric acid plants, and then used primarily in water fluoridation, sometimes after being processed into sodium silicofluoride.

5. Production of Aluminum Fluoride from Fluosilisic

5.1 Process technologies for manufacturing AlF3

Aluminium fluoride and synthetic cryolite are components of the molten bath in the electrolytic reduction of alumina to aluminium metal. Ideally, fluorine is not consumed in this process; however substantial quantities of fluorine are lost. Fluorine losses are replaced by aluminium fluoride. . It is also used in the preparation of white enamels, as an anti-reflection coating in complex optical systems, as a constituent in welding fluxes, and in the preparation of fluorine containing glasses.

The amount of aluminium fluoride varies depending upon the technology, raw material and recycling methods used.

5.2 Aluminum fluoride quality

Aluminium fluoride produced by the dry process (with HF in the gas phase) is more suitable for the smelters using modern technologies. It is the preferred material for having the right physico-chemical properties (high-density: 1.4 – 1.6kg/l, good flowability index: less than 60sec/kg, low attrition index, and low dust content) required by feeding systems, point feeders. The new process technology for manufacturing high quality aluminium fluoride using FSA by-product as a raw material is briefly described below together with the other traditional process routes:

5.3 AlF3 from HF/FSA (dry FSA process)

This process consists of producing hydrofluoric acid from FSA and then high quality and high-density aluminium fluoride using the fluid bed process (gas phase process) of the dry fluorspar process. This route provides many advantages such as better product quality, considerably less or no waste, and the possible production of other fluorine chemicals. The process is a continuous process. The new dry FSA process is less sensitive than the wet FSA process to impurities, which may be contained in the FSA solution.

This was disclosed first by Tennessee Corp., USA maybe 50 years ago and further disclosed by Wellmann-Lord, etc and more lately by Flemmert (Nynaes Petroleum, Sweden), and Zaklady Chemiczne "LUBON" S.A., Poland, the latter operated a small pilot plant for diluted HF

In 2008 Wengfu China commissioned a first commercial plant for AHF with the technology of Buss Chemtech AG, Switzerland based on know-how from Lubon Works.

Chemistry :

$$H_2SiF_6.SiF_{4(aq)} + H_2SO_4 \longrightarrow 2\ SiF_4 + 2\ HF_{(aq)} + H_2SO_4$$

$$5\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6\ .SiF_{4\ (aq)} + SiO_{2\ (s)}$$

$$Al_2O_3.3H_2O \longrightarrow Al_2O_3 + 3\ H_2O$$

$$Al\ _2O_3 + 6\ HF \longrightarrow 2\ AlF_3 + 3\ H_2O$$

The process is based on the mixing of strong fluosilicic acid with strong sulphuric in a stirred reactor and separating silicon tetrafluoride gas and extracting the anhydrous hydrofluoric acid using sulphuric acid as dehydrating agent into separation columns as per the principle shown on the flowsheet below [ref. 6]. The evaporation can be with one single stage or two stages. Presently AD Process Strategies Sari proposes an improved process of this technology to suit the water balance of the phosphoric acid plant, DH PA Process and especially HH process not suitable to receive large amount of water. Sulphuric acid containing water that is generated from this HF plant has to be re-circulated to the phosphoric acid plant. The sulphuric acid recirculation which is normally 30 T/T AHF as 100% H_2SO_4 can be reduced to 15 T/T. Water is reduced from more than 10 T/T AHF down to 5 T/T.

This process is less sensitive to impurities contained in the FSA as an AHF purification stage is provided in the process [ref. 6].

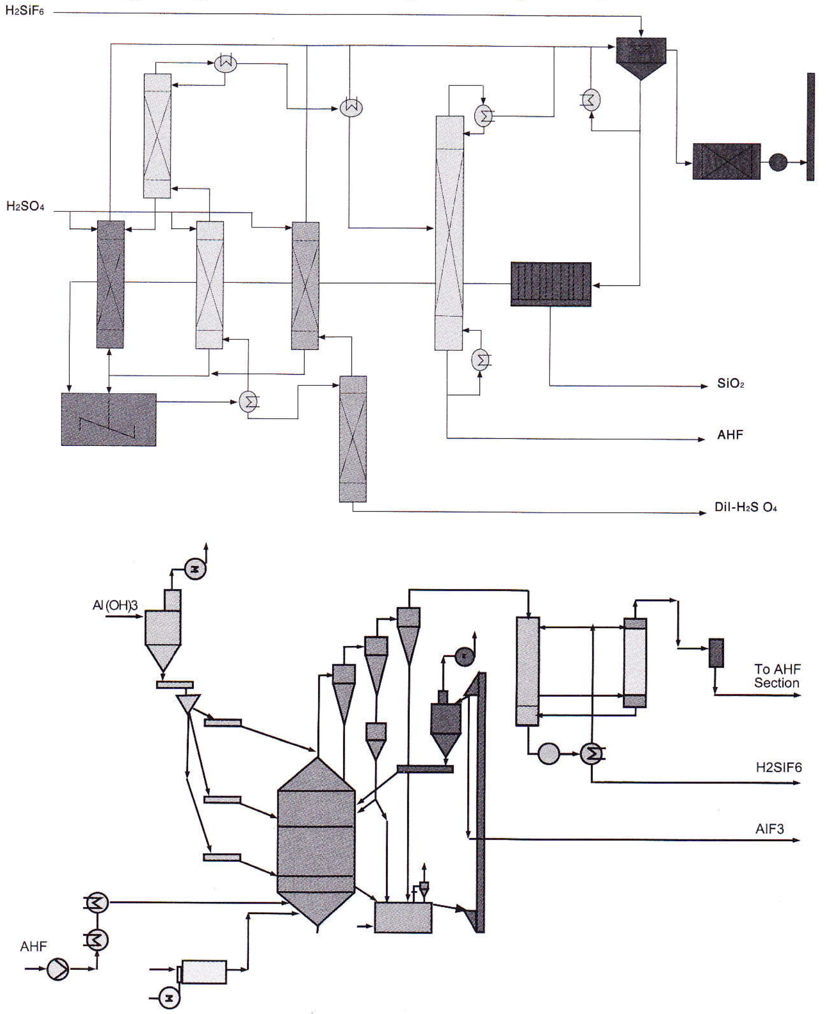


Figure 7: AlF_3 from HF/FSA (dry FSA process) [ref 6].

An optional process is a process with hydrolysis of STF ($SiF4$) in the gas phase under high temperature to produce silica, Fumed silica as per the Nynaes process or silica as per the Reed process. STF silicon tetrafluoride can be produced from this process as well.

FSA technology has the following main advantages:

- Fluorine at the fertilizer complex is an effluent and a pollutant, unless it is treated with lime or converted into H2SiF6 with absorption system. This H2SiF6 is reacted with Aluminum Hydroxide to produce Aluminum Fluoride a critical input in the production of aluminum.
- The process is considered as Import Substitution as this technology does not require any imported raw materials - as against Hydrofluoric acid route which requires Sulphur and Fluorspar to be imported.
- The process is cost effective enabling good export potential.
- This technology provides High Purity Aluminum Fluoride with less impurities as against alternate technology of Hydrofluoric acid (HF) route.
- In advanced counties, this technology is well encouraged as this helps in Conserving Critical Natural Resources like fluorspar and sulphur which are used in the HF route technology.

5.4 AlF3 from HF/CaF2 (dry fluorspar process)

Hydrofluoric acid produced by the fluorspar process is reacted with alumina trihydrate to produce high quality and high-density aluminium fluoride using a fluidized bed reactor. Some 65% of the world capacity for aluminium fluoride is currently produced using this process route.

5.5 AlF_3 from FSA (wet FSA process)

The FSA feed solution is reacted directly with the alumina trihydrate to precipitate the silica from the metastable aluminium fluoride solution. The aluminium fluoride trihydrate is then crystallized out of the solution, separated, dried and calcined. The process is operated batchwise for the reaction and crystallization operations. The aluminium fluoride product obtained is a low-density material, 0.7 to 0.8 kg/l only, having poor flowability index and containing a high amount of fine particles. Around 17% of the world capacity for aluminium fluoride is currently produced using this process route. Due to the persistent difficulties encountered to sell this quality of product, this technology will probably be abandoned in the future.

The process for production of aluminum fluoride and silica is schematically depicted in flow sheet below. The total process of fluosilicic acid interaction with aluminum hydroxide can be described by the following overall reaction:

$$H_2SiF_6 + 2\,Al(OH)_3 \rightarrow 2\,AlF_3 + SiO_2 + 4\,H_2O \qquad (I)$$

The reaction is exothermal and proceeds in several steps. It can be described by the following three reactions (Skyrlev, 1966; Dmitrevskij and Semenova, 1970):

$$3\,H_2SiF_6 + 2\,Al(OH)_3 \rightarrow Al_2(SiF_6)_3 + 6\,H_2O \qquad (II)$$

$$Al_2(SiF_6)_3 + 6\,H_2O \rightarrow 2\,AlF_3 + 3\,SiO_2 + 12\,HF \qquad (III)$$

$$12\,HF + 4\,Al(OH)_3 \rightarrow 4\,AlF_3 + 12\,H_2O \qquad (IV)$$

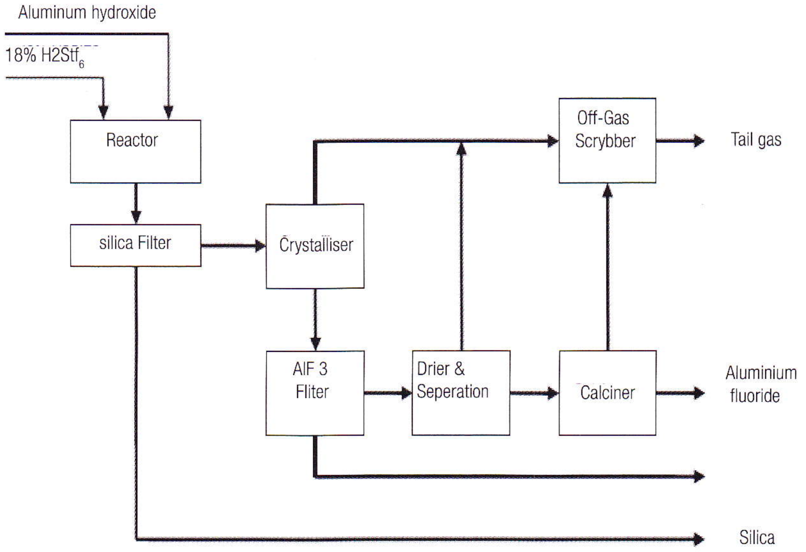


Figure 8: Simplified flow sheet Process for production of aluminum fluoride

The production of aluminum fluoride is carried out preferably between 70°C and 100°C. The concentration of fluosilicic acid can be as high as 25 wt% in a water solution. The acid concentration as well as the particle size of the aluminum hydroxide affect the rate of the reaction. The resulting aluminum fluoride solution is metastable, and the trihydrate begins to crystallize out quickly at temperatures around 90°C. Precipitated solid silica must therefore be removed as quickly as possible. The main problems in the process are firstly to carry out the reaction in such a way that the filter cake obtained by separating out the silica exhibits good filtering properties, and secondly to avoid the aluminum fluoride being contaminated with silica. This leads to the following requirement on the conditions for carrying out the reaction (Arankathu,1980):

1. The silica precipitates out in different forms, depending on the pH of the solution. At low pH values (<3) the readily filtered form of the silica predominates; with increasing pH the amount of fine and colloidal silica increases. The fine particulate form makes filtration difficult, therefore the pH should not exceed a certain value (3-4) which is determined by the method of filtration used.

2. The reaction time plus the filtering time should not be extended to the point that aluminum fluoride begins to crystallize.

3. On the other hand, to obtain a good yield and also a practically silica-free aluminum fluoride solution, it is important that the fluosilicic acid is converted as completely as possible.

5.6 AlF3 from HF/CaF2 (wet HF process)

The aqueous hydrofluoric acid feed is reacted directly with the alumina trihydrate to produce aluminium fluoride which is then calcined. The aluminium fluoride product obtained is a low-density material, 0.7 to 0.8kg/l only, having poor flowability index and containing impurities and dust particles. Some 18% of the world capacity for aluminium fluoride is currently produced using this process route. This process was used by the first generation of plants. This process is no longer economically viable and will be definitely abandoned. The fertilizer industry, the fluorine industry, and the aluminium industry will all profit from using by-product FSA as a raw material due to long term cheap availability of an economic source of fluorine and converting a hazardous waste stream to a saleable product.

5.7. AlF_3 and cryolite production from FSA in Russia:

The production is realized by two principal processes:

1. Crystallization from the solution of the reaction between aluminium hydroxide and fluosilisic acid. The trihydrate of aluminium fluoride is subjected to drying and calcining with the formation of ready product.

2. Crystallization from supersaturated solution of aluminium fluoride, ammonium fluoroaluminate with the subsequent calcining. As a result, aluminium fluoride is formed and ammonium fluoride recycled to the stage of ammonium fluoroaluminate crystallization.

In the aluminium fluoride manufacture by the first process, due to the impossibility of complete return of liquor solutions into the process, the liquor solutions can be:

- Used in cryolite production;
- Partially used for HF, SiF_4 absorption.

The flow sheet of aluminium fluoride production process by the first method and subsequent treatment of the liquor solution into cryolite is presented .

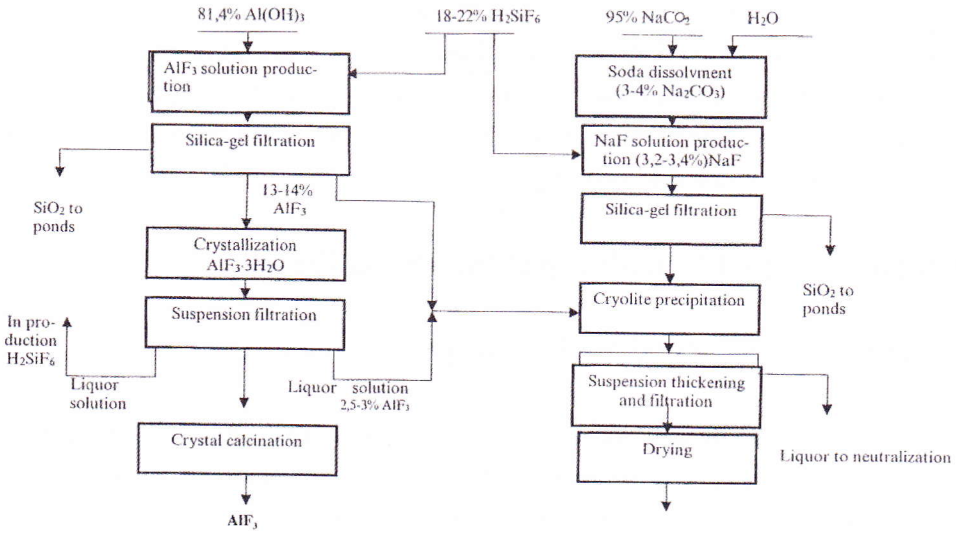


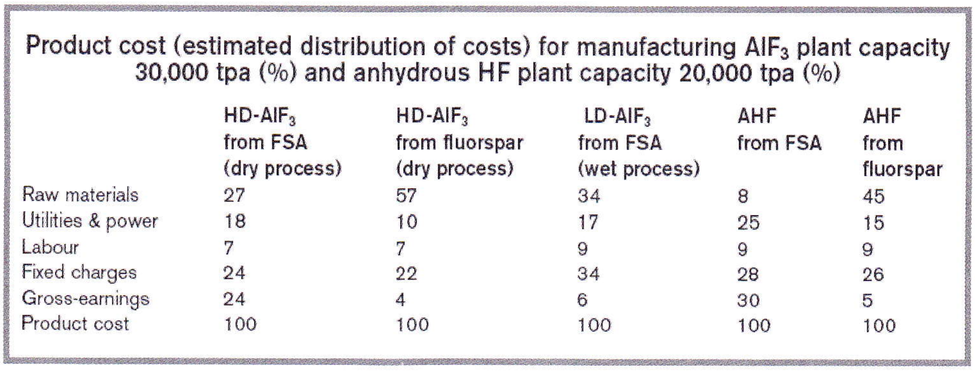
Figure 8: The principal scheme for the treatment of fluosilisic acid with the formation of aluminum fluoride and cryolite

The interaction of fluosilisic acid and aluminium hydroxide is complete within 10 minutes. Prior the aluminium hydroxide introduction, the acid is heated by steam up to 90°C. The reaction mass is filtered at the belt vacuum-filter that washes the silica-gel sediment with water with a temperature of 60-80°C. Aluminium trihydrate fluoride is crystallized within 3 hours in the presence of a seed crystal. At the beginning of crystallization, the solution is heated with steam up to 95°C. Aluminium tri-hydrate fluoride suspension is separated from the liquor solution at drum or belt vacuum-filters prior delivering materials with 50-55% humidity to the dehydration stage.

The aluminium fluoride paste calcination is conducted in drum dryers equipped special heat-exchanges, with counter current movement of heat-carrier and material, resulting in a high quality product.

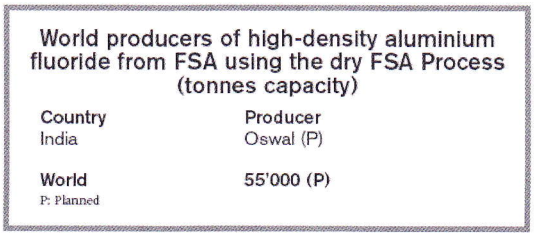
Fluosilisic acid : Recovery system and production of Aluminum Fluoride

Capacity and cost production of AlF3 from FSA and



Product cost (estimated distribution of costs) for manufacturing AlF_3 plant capacity 30,000 tpa (%) and anhydrous HF plant capacity 20,000 tpa (%)

	HD-AlF_3 from FSA (dry process)	HD-AlF_3 from fluorspar (dry process)	LD-AlF_3 from FSA (wet process)	AHF from FSA	AHF from fluorspar
Raw materials	27	57	34	8	45
Utilities & power	18	10	17	25	15
Labour	7	7	9	9	9
Fixed charges	24	22	34	28	26
Gross-earnings	24	4	6	30	5
Product cost	100	100	100	100	100



World producers of high-density aluminium fluoride from FSA using the dry FSA Process (tonnes capacity)

Country	Producer
India	Oswal (P)
World	55'000 (P)

P: Planned

- Cost advantage of FSA solely for production of AlF_3 using FSA
  FSA 20% 1.0 T/T x USD/MT 170.- = 170.-

- Cost advantage of FSA solely for production of AlF3 using CaF_2
  CaF2 97% 1.5 T/T x USD/MT 300.- = 450.-

- Cost advantage of FSA solely for production of AHF using FSA
  1.5 T/T x USD/MT 170.- = 255.-

- Cost advantage of FSA solely for production of AHF using CaF_2
  2.3 T/T x USD/MT 300.- = 690.-

- Benefit USD/MT (Gross) = 280.(AlF3 production)-

  435.(AHF production)

Gross Margin ~ 20 – 25% for cost advantage of FSA only
Return on Investment ~ 4 – 5 years for cost advantage of FSA only

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