Fluorochemicals are essentially produced from fluorspar (Acid Grade Fluorspar: CaF₂ > 97%). A small amount only (about 5%) is produced from phosphate rock:

- Fluosilicic acid
- Fluorsilicates
- Cryolite
- Aluminium fluoride
- Silicon tetrafluoride

Fluosilicic acid is used as water fluoridation agent of drinking water to prevent tooth decay in US, Canada, South Africa, Australia mainly. The US production of fluosilicic acid in 2010 estimated and reported by USGS is 68’000 tons (FSA as 100% H₂SiF₆) mostly used for water fluoridation and production of silicon tetrafluoride (STF = SiF₄) up to 20’000 tons as raw material for polysilicon production by MEMC an intermediate to high purity silicon for solar and chips applications. In this process, MEMC claimed that the capital cost is reduced by 50% compared to classical Siemens process and electric consumption for purification reduced by 20 folds. Other uses of FSA are in the tanning of animal skins, in ceramic and glass etching, in technical paints, in oil well acidizing, preservative of wood, hardening of masonry, remover of mould, remover of rust and stain in textiles, cleaning and sterilising agent in industry, and in electro-refining of lead, etc. Very minor quantities of FSA are produced also from fluorspar processing.

<table>
<thead>
<tr>
<th>FSA USES</th>
<th>COMPANY</th>
<th>FLUOROCHEMICAL PRODUCT</th>
<th>CAPACITY MTPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>4 Plants /Companies Reporting</td>
<td>FSA</td>
<td>&lt;&lt; 68’000</td>
</tr>
<tr>
<td>US</td>
<td>PCS Phosphate Co.</td>
<td>STF</td>
<td>23’000</td>
</tr>
<tr>
<td>UE/BE</td>
<td>Prayon</td>
<td>SSF/PSF</td>
<td>18’000 / 3’000</td>
</tr>
<tr>
<td>UE/HU</td>
<td>Bige Holdings</td>
<td>Cryolite</td>
<td>&lt;&lt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UE/PL</th>
<th>COMPANY</th>
<th>FLUOROCHEMICAL PRODUCT</th>
<th>CAPACITY MTPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>Several Plants</td>
<td>SSF/PSF/MGSF/NH₄F</td>
<td>?</td>
</tr>
<tr>
<td>CN</td>
<td>Yunnan Three Circles Chemical Industry Co.</td>
<td>SSF/PSF</td>
<td>?</td>
</tr>
<tr>
<td>UE/SE</td>
<td>Alfluor</td>
<td>AlF₃</td>
<td>23’000</td>
</tr>
<tr>
<td>JO</td>
<td>JPMC</td>
<td>AlF₃</td>
<td>20’000</td>
</tr>
<tr>
<td>ID</td>
<td>PT Petrokimiya Gresik</td>
<td>AlF₃</td>
<td>12’000</td>
</tr>
<tr>
<td>RU</td>
<td>Phosagro /Ammophos</td>
<td>AlF₃ / SSF</td>
<td>20’000</td>
</tr>
<tr>
<td>BY</td>
<td>JSC Gomel Chem. Plant</td>
<td>Cryolite / AlF₃</td>
<td>5’000/5’000</td>
</tr>
<tr>
<td>LT</td>
<td>Eurochem / Lifosa</td>
<td>AlF₃</td>
<td>17’000</td>
</tr>
<tr>
<td>CN</td>
<td>Several Producers</td>
<td>AlF₃</td>
<td>Small &lt;&lt;</td>
</tr>
<tr>
<td>IN</td>
<td>Alfluoride</td>
<td>AlF₃</td>
<td>5’000</td>
</tr>
<tr>
<td>IN</td>
<td>Hindalco</td>
<td>AlF₃</td>
<td>5’000</td>
</tr>
<tr>
<td>CN</td>
<td>Wengfu</td>
<td>AHF</td>
<td>20’000</td>
</tr>
</tbody>
</table>

Aluminium fluoride is still the major product out of FSA until now with a production <100’000 MTPA against about 800’000 MTPA produced from fluorspar in 2009 (see table below).

STF could grow significantly as its added value is higher than AlF₃ / AHF making projects even more attractive. Already five projects have been implemented in Asia (approx. 70’000 MTPA STF) using the fluorspar process although it makes more sense to start from FSA.

World and China AlF₃ production and consumption per year (kt)
There is a supply shortage of FSA for water fluoridation in US and Canada and prices of FSA have risen significantly.

China is dominating largely the fluorspar industry (59% according SRI / IHS in 2009) and China is starting to face sourcing problems at present. China has changed its policy with tighter rules. Consequently fluorspar prices are rising. Europe has included fluorspar in a list of 14 minerals classified as “critical”. This means that raw material is labelled “critical” when the risks for supply shortage and their impacts on the economy are higher compared with most of the other raw materials provided that the recoverable reserves of fluorite will fail to increase.

China is deficient in fluorite resource and demand is growing for fluorite year after year at significant pace. In 2009, the apparent consumption of fluorite in China reached 2.8 million tons, up 8.2% from a year earlier; and the figure in H1 2010 hit 1.93 million metric tons (MMT). Concerning the consumption of fluorite, China ranks first around the globe, but lags far behind the developed countries in term of downstream consumption. A case to this point is fluorine chemical industry, the demand of fluorite is 30% less in China than opposed to nearly 60% in developed countries.
As long as fluorspar was cheap, there was no need for an alternative source of fluorine like FSA. Presently the price of fluorspar is about USD 350.-/MT FOB compared to FSA 100% that can be produced very cheaply, by operating a single absorber. The theoretical price of FSA would be USD 600.-/MT if fluorine contained F is assumed at the same value of F contained in fluorspar. At this price, it makes any business for fluorine attractive and it is adding appreciable value to the phosphate business. Especially for aluminium fluoride that is a bulk chemical, easily transportable requiring large amount and competitive sources of fluorine. At the time of writing this paper, some Acid Grade Fluorspar from China has reached USD 500.-/MT back to pre-recession highs.

The world population is expected to reach 9 billions of inhabitants in 50 years and productions / capacities are forecasted to increase by more than 50% maybe 70%. In the near future, fluosilicic acid uses will increase probably bearing in mind that technical hurdles are now resolved, technical expertise is available and communication between the industrial sectors concerned is improving continuously.

The phosphate rock reserves are assumed to be sufficient for more than a century; other base reserves less attractive will be considered at the end of the century. (See below Hubbert peak for phosphorus)

<table>
<thead>
<tr>
<th>Mine production</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>26,400</td>
</tr>
<tr>
<td>Algeria</td>
<td>1,600</td>
</tr>
<tr>
<td>Australia</td>
<td>2,800</td>
</tr>
<tr>
<td>Brazil</td>
<td>6,350</td>
</tr>
<tr>
<td>Canada</td>
<td>700</td>
</tr>
<tr>
<td>China</td>
<td>62,000</td>
</tr>
<tr>
<td>Egypt</td>
<td>5,000</td>
</tr>
<tr>
<td>Israel</td>
<td>2,700</td>
</tr>
<tr>
<td>Jordan</td>
<td>5,200</td>
</tr>
<tr>
<td>Morocco and Western Sahara</td>
<td>23,000</td>
</tr>
<tr>
<td>Russia</td>
<td>10,000</td>
</tr>
<tr>
<td>Senegal</td>
<td>650</td>
</tr>
<tr>
<td>South Africa</td>
<td>2,340</td>
</tr>
<tr>
<td>Syria</td>
<td>2,470</td>
</tr>
<tr>
<td>Togo</td>
<td>850</td>
</tr>
<tr>
<td>Tunisia</td>
<td>7,400</td>
</tr>
<tr>
<td>Other countries</td>
<td>8,620</td>
</tr>
</tbody>
</table>

Phosphate rock production and reserves according to USGS

According to International Fertilizer Association (IFA), the world production of phosphate rock in 2009 was: 162 MMT phosphate rock (49.7 MMT as P2O5)

According to International Fertilizer Association (IFA), the world production of phosphoric acid was: 33.6 MMT as P2O5 (48.6 MMT as H3PO4)

Assuming that phosphate rock contains 2%-5% fluorine (average approx. 3 % F) 4.8 MMT of fluorine are available (about double of F in fluorspar)

Assuming a recovery rate of 35% as a minimum as per data below for DH & HH Phosphoric Acid processes:

1.7 MMT F can be recovered (2.0 MMT FSA 100%) corresponding to 1.4 MMT AHF about 70% of world production.

For higher accuracy of this assessment, the production of FSA should be listed if known or calculated if not known.

As explained above Fluosilicic acid finds its main application in the manufacture of aluminium fluoride being a large volume chemical mostly produced from fluorspar as high bulk density (HBD) aluminium fluoride and as well from fluosilicic acid in a small amount as low bulk density (LBD) aluminium fluoride. Hereby are disclosed new process technologies for manufacturing anhydrous hydrofluoric acid (AHF) from fluosilicic acid (FSA) from which (HBD) aluminium fluoride can be produced. Aluminium fluoride is essentially used as a flux for smelting aluminium by adding it volumetrically to the cells of aluminium smelters in order to regenerate of cryolite bath. HBD aluminium fluoride is the preferred material and it is fully produced from fluorspar; none of this material being currently produced from FSA through AHF which process technology often referred to as the Dry/FSA Process is available, feasible and proven at this time. An opportunity to invest in profitable projects does really exist. Additionally the manufacture of various downstream products of fluorine: refrigerants, fluoropolymers, etc and downstream products of silicon; silicon metal, silicon tetrafluoride, silicas may offer further interesting opportunities.
**FSA1G** LBD-Aluminium fluoride from FSA

FSA1G Technologies based on FSA of the first generation (1G) known also as wet FSA process, wet AlF3 process from FSA or HF/fluorspar wet process and cryolite process also.

The first process known for manufacturing (LBD) aluminium fluoride from fluosilicic acid was patented by Chemie-Linz, Austria about 50 years ago and many plants were built based on this technology or comparable technologies.

**Chemistry:**

\[ H_2SiF_6 + Al_2O_3 \cdot 3H_2O \rightarrow 2 AlF_3 + 3 SiO_2 + 4H_2O \]

This process uses the direct neutralization of the fluosilicic acid with alumina hydroxide in a stirred reactor. It is often referred to as the Wet/FSA Process. Although this technology tends to be abandoned due to the low density and low fluidity (flowability) of the product, the high capital cost of the plant and its environmental issues resolved partially only as neutralization of mother liquors may still be required, further developments of this process would refresh this technology being still accepted by few players only. Improvements are available from us for material of construction and cost-effective design, improved crystallisation process, product granulation, etc.

This process requires very pure FSA. Quality of the FSA is often a limitation to the use of FSA by this process.

**Plants built with this technology:** JPMC, Alufluor, Lifosa, Ammophos, Alcoa, Luzhai, Guixi, Dayukou, Wengfu, Achinsk, Péchineny Salindres, Lubon, DMCC, Alufluoride, Navin, Hindalco, Spic, PT Petrokimia Gresik, AlQaim, Gomel, Trepca. (usual name)
AD PROCESS STRATEGIES SARL - Manufacture of High-Bulk Density Aluminium Fluoride from Fluosilicic Acid (HBD-AIF₃ from FSA) and AHF – Page 5

FSA2G HBD-Aluminium Fluoride from FSA and AHF from FSA

FSA2G Technologies based on FSA of the second generation (2G) known also as HF from FSA or dry process for AlF₃ from FSA or fumed silica process by the fluorine route.

A process for manufacturing AHF / HF from fluosilicic acid 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 Lubon Works, 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:

\[
\begin{align*}
H_2SiF_6 + SiF_4(aq) + H_2SO_4 & \rightarrow 2 SiF_4 + 2 HF(aq) + H_2SO_4 \\
5 SiF_4 + 2 H_2O & \rightarrow 2 H_2SiF_6 + SiF_4(aq) + SiO_2(s) \\
Al_2O_3 \cdot 3H_2O & \rightarrow Al_2O_3 + 3 H_2O \\
Al_2O_3 + 6 HF & \rightarrow 2 AlF_3 + 3 H_2O
\end{align*}
\]

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. The evaporation can be with one single stage or two stages. Presently AD Process Strategies Sarl 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 normally 30 T/T AHF as 100% H₂SO₄ can be reduced to 15 T/T. Water is reduced from more than 10 T/T AHF down to 5 T/T.

The FSA2G technology is proven, resolves environmental issues, is very profitable as raw material costs are low (low cost of fluorine, no cost for sulphur or sulphuric acid), capital cost is reasonable and it offers access to promising markets like HBD aluminium fluoride and anhydrous hydrofluoric acid, both being large volume chemicals.

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

FSA2G Simplified flowsheet AHF from FSA

An optional process is a process with hydrolysis of STF 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.

FSA2G Flowsheet HBD-Aluminium Fluoride from AHF

Plants built with this technology: Lubon, Grace, Wengfu for AHF (usual name)
FSA3G HBD-Aluminium Fluoride from fluosilicates (Sodium Silicofluoride) (from SSF / FSA) and AHF

FSA3G (FSA-based technology of the third generation). This is the advanced process for stand-alone plants providing many alternatives for having not to recycle the water and sulphuric acid to the phosphoric acid plant or optional re-use of the materials available in streams in the process cycle.

When diluted sulphuric acid stream is not returned to the phosphoric acid plant or can not be re-circulated due to technical reasons or not and in particularly in the above FSA2G process, AD Process Strategies Sarl proposes a new technology for stand-alone HF plants. The proposed process uses fluosilicate as an intermediate (solid) raw material, which is transportable not like FSA and reaction of this fluosilicate with strong sulphuric acid. The silicon tetrafluoride and hydrofluoric acid obtained are treated as per the state of art in a similar manner as mentioned above using absorption and desorption of HF in sulphuric acid. The diluted sulphuric acid stream resulting from this process can be pre-concentrated and recycled to the phosphoric acid plant or used in production of fertilizers like single superphosphate SSP, dicalcium phosphate DCP, ammonium sulphate AS, etc or concentrated and recycled to the HF reaction or purified for sale.

Abbreviations:
SSF Sodium SilicoFluoride or sodium fluosilicate,
SA Sulphuric Acid,
ATH Alumina TriHydrate or Aluminium hydroxide,
STF Silicon TetraFluoride,
Rock Phosphate Rock,
DCP DiCalcium Phosphate,
MOP: Muriate of Potassium KCl
SSA Sodium Sulphate Anhydrous,
SOP Sulphate Of Potassium,
SAC Sulphuric Acid Concentration,
R- Reactor, S- Separator, A- Absorber, C- Crystallizer,

In dark (blue colour) MAIN PROCESS,
In light (blue colour) OPTIONAL PROCESS SECTION

FSA1G Wastewater to be neutralised or recycled in cooling tower water loop.
FSA2G 30 MT to 15 MT sulphuric acid and 10MT to 5 MT water per MT HF (or per 45 MT P2O5) to be recycled.
Chemistry: The process does use the same reaction of sulphuric acid / sodium fluosilicate in opposite direction under different conditions, aqueous, low temperature and anhydrous, high temperature:

**Step-1 Production of sodium fluosilicate (SFS) or silicofluoride (SSF) by one of these process route:** (reaction 2 is the usual process to manufacture SFS)

\[
H_2SiF_6(aq) + Na_2SO_4(s) → Na_2SiF_6(s) + H_2SO_4(aq)
\]

**Step-2 Decomposition of SFS by Sulphuric acid and recycle of SiF₆²⁻ to generate additional FSA and SSF.** (Reaction was tested and is working, incompleteness is not so important as the salt is recycle or can be purified as required)

\[
Na_2SiF_6(s) + H_2SO_4 → 2 HF(g) + SiF_6^{2-}(g) + Na_2SO_4(s)
\]

\[
3 SiF_6^{2-} + 2 H_2O → 2 H_2SiF_6(aq) + SiO_2(s)
\]

**Step-3 Reaction of HF with alumina trihydrate in a fluidized bed reactor (same process as fluorspar process or FSA2G)**

\[
Al_2O_3·3H_2O → Al_2O_3 + 3 H_2O
\]

\[
Al_2O_3 + 6 HF → 2 AlF_3 + 3 H_2O
\]

**Step-4 Pre-concentration of sulphuric acid (pilot unit operating since almost 10 years on concentration of sulphuric acid up to 85% in presence of fluorne) and recycle to process or reused by other consumers.**

Plants built with this technology: First Prefeasibility Study underway. Acceptance for FSA3G is higher than for FSA2G

Using the PSF Potassium Fluosilicate process instead of the SSF still needs to be investigated.

**Related productions and chemistries.**

Many possibilities are available with the aim of reducing recycling and improving benefits and economics of projects.

**Production of Dicalcium Phosphate (DCP)**

Production of DCP from HCL (and optionally from sulphuric acid and sodium chloride or sea water) for production of DCP (Feed grade) or as neutralization unit with separation of solids and recycling.

Dicalcium Phosphate dihydrate CaHPO₄·2H₂O, is produced by a wet process that comprises the following phases:

\[
Ca_3(PO_4)_2 + 4 HCl → Ca(H_2PO_4)_2 + 2 CaCl_2
\]

Ca(H₂PO₄)₂ → Ca(OH)₂ → 2 CaHPO₄·2 H₂O + 2 H₂O

Reaction of phosphoric rock with hydrochloric acid, main raw materials, a process from which a monocalcium phosphate liquor is obtained.

Purification of the remaining solution by means of the removal of the inert matter and undesirable compounds.

Production of dicalcium phosphate by means of calcium salts precipitation and product filtration.

Drying of dicalcium phosphate at moderate temperature to keep its two water molecules

**Production of Sulphate Of Potassium (SOP)**

Production of SOP by the double salt decomposition, Glaserite process. In this process sodium sulphate is reacted with potassium chloride to yield potassium sulphate.

This reaction occurs in two steps as follows:

\[
4 Na_2SO_4 + 6 KCl = Na_2SO_4·3K_2SO_4 + 3 K_2SO_4 + 6 NaCl
\]

\[
2 KCl + Na_2SO_4·3K_2SO_4 = 2 NaCl + 4 K_2SO_4
\]

This process route is cheaper than the Mannheim process and it makes sense if the sulphate is available and cheap.

**Production of Silicon Tetrafluoride (STF)**

STF is dried, purified and compressed into pressure cylinder for transportation to the polysilicon plant.

**Production of Sodium Sulphate (SSF) and Purification**

Sodium sulphate can be purified according to the crystallization process as required for the final application of SSA detergents, paper, glass, etc
Production of Silica

Byproduct silica can be used in the defluorination process of phosphoric acid or sulphuric acid, production of water glass, of precipitated silica, zeolite, of cements, as soils conditioners.

Fluorine chemistry is basically a good solution for higher added-value to the downstream products:

\[ \text{SSF} < \text{FSA} < \text{AlF}_3 < \text{AHF} < \text{STF} < \text{HFC} < \text{PTFE} < \text{NF}_3 < \text{LiPF}_6 \]

Continuation of this paper will deal with the introduction of economics of all these technologies. No doubt, economics of all these technologies are good. It is only a matter to discuss how good they are? What are the options to be selected?

Presently as costs of raw materials are escalating, expertise is available, technologies are affordable and of course through us, the barriers between various industries are not anymore a brake between fluorine and other industrial sectors, like fertilizers, aluminium, cement, solar and silicon, etc, great opportunities for cooperation are in front of us. We hope that all of you will cooperate with us regarding technology and other business matters.

All these technologies are offering high flexibility and can be implemented with confidence in a cost effective manner. They are real innovations for the fertilizer industry and surely they will be implemented progressively. More and more projects are under study and hopefully some projects may be executed in the near future....

The ammonia route to HF / AlF$_3$ is not discussed in this paper as it is not significant yet.

This article was first presented at Sympos, First symposium on Innovation and Technology in the Phosphate Industry, held from May 9th to 13th, 2011 in Marrakech and sponsored by OCP.

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The author has written several papers and given several presentations on the topic of fluorine technologies. He was working previously with Buss AG and Fluorsid SpA. He has over 25 years of experience with fluorine, process intensification of the fluorspar process including about 20 years experience with FSA2G, projects, process engineering, process development of the technology HF from FSA, etc...