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Production of HF from H_2SiF_6

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Abstract

During the reaction of phosphate ore and sulphuric acid, silicon tetrafluoride (SiF_4) and HF are formed as byproducts. These gases are usually scrubbed with water, forming fluorosilicic acid, H_2SiF_6 (FSA) as a waste stream. Until recent years, FSA was mostly used for drinking water fluorination and for the production of Aluminium Fluoride (AlF_3) or, in most cases, was neutralised or disposed to sea or ponds. Research and pilot work for the industrialization of a process to produce hydrofluoric acid (HF) and anhydrous hydrofluoric acid (AHF) from FSA has been conducted for nearly six decades without having developed a process that was found suitable to be built on industrial scale. Buss ChemTech has scaled the process from pilot scale (800 t/a) in one step to full scale industrial plant. Since 2008, three plants with capacities of 12,000 and 20,000 tons (two plants) of AHF per year were erected and are in operation.

Keywords: Anhydrous Hydrogen Fluoride, Fluorosilicic Acid, Environment Protection

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1. Introduction

The majority of fluorochemicals are produced by starting from fluorspar. From the early 1930ies, fluorspar is mixed with sulphuric acid and fed to a rotating kiln. The HF produced is cleaned, condensed and purified. With AHF as a base product and raw material, other chemicals are manufactured.

With the growing demand for fertilizers and thus more and more production facilities starting up, the need to

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dispose of the FSA by-product grows. Gases containing fluorine will form in various places within the production of phosphoric acid [1]. So far, FSA is either sold for drinking water fluorination, manufacture of aluminium fluoride of low bulk density, cryolite, silicon tetrafluoride and other fluorosilicates [7]. However, annual production of phosphoric acid now exceeds 58 million tons per year [3]. Therefore, more than two million tons of FSA (reported as 100% FSA) need to be disposed of. In reality, the volume of FSA is significantly higher, by a factor of four to five, depending on the concentration. Changing legislation in many countries for the disposal of liquid waste are challenging the manufacturers to comply with environmental protection laws and reduce neutralisation or disposal costs.

Manufacturing of AHF from FSA opens the door to phosphoric acid producers to new markets such as organic fluorochemicals or aluminium fluoride as a bulk chemical.

BUSS ChemTech AG (BCT) has optimised the process developed by Lubon in 1977 [2] and scaled this up in one step to a capacity of 20,000 tons per year (t/a). Three plants of 12,000 t/a and 20,000 t/a (two plants) are now operating successfully in China. The quality of the AHF and the simplification in the purification of the acid is one of the advantages that allows this process to be compared favourably to the fluorspar route of AHF production regarding economics.

Nomenclature

FSA	Hexafluorosilicic Acid (H_2SiF_6)
AHF	Anhydrous Hydrogen Fluoride
STF	Silicon Tetrafluoride (SiF_4)
SSF	Sodium Silico Fluoride (Na_2SiF_6)
SBF	Sodium Bifluoride ($NaHF_2$)
SF	Sodium Fluoride (NaF)
AF	Ammonium Fluoride (NH_4F)
IEX	Ion Exchange Resin, Ion Exchange Filter

2. Chemistry

2.1. AHF from Fluorspar

The production of AHF from fluorspar is based on the main reaction of fluorspar with sulphuric acid according to

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \tag{1}$$

2.2. AHF from FSA by direct reaction with sulphuric acid

The main reactions for the production of AHF from FSA are

$$H_2SiF_6 \xrightarrow{Heat} 2\,HF + SiF_4 \tag{2}$$

$$3\,SiF_4 + 2\,H_2O \rightarrow 2\,H_2SiF_6 + SiO_{2(s)} \tag{3}$$

and simplified

$$H2SiF6 + 2\,H_2O \rightarrow 6\,HF + SiO_{2(s)} \tag{4}$$

Reaction (2) needs energy, coming from the sulphuric acid as dehydration chemical.

2.3. AHF from FSA by precipitation of a salt or Ion Exchange process

The chemistry of the processes involves a larger number of reactions that will not be shown in full detail. A short explanation is given. In general, the FSA is precipitated to a salt. This salt is to be reacted either with sulphuric acid or heated to split HF. The other reaction byproducts can be recycled to other process steps and thus form a closed loop.

Ion Exchange filters are operated in batch mode. First, the unloaded resin is loaded with ions that replace the counterions that are attached to the functional group of the resin. In this case, the silicofluoride ion will be attached to the resin.

In the regeneration step, the loaded ion exchange resin will be washed and then contacted with a regeneration chemical, leading to a high concentrated solution of the ion that was removed from the solution to be treated. This solution can then be further processed.

3. AHF from FSA – Process overview

Numerous processes have been proposed by a number of researchers and authors. This was summarised by Dreveton [7].

Theoretically, FSA can be used in two ways to produce AHF. One is by using an intermediate salt that can be transported elsewhere for processing to HF, the other is by the reaction in the liquid phase and separating the silica from the concentrated FSA as given in equation (3). Processes involving ion exchange exist, too and are summarised later. Other processes with direct reaction of FSA with chemicals exist but are not directly related to the production of HF.

3.1. Production of AHF by direct contact with sulphuric acid

This process was scaled up and optimised by BCT for the production of AHF in industrial scale. FSA is fed to a concentration step that raises the acid concentration by absorption of SiF_4 from approx. 18% to 24%-wt to levels of >45%-wt. Silica is precipitated and will be filtered from the concentrated acid solution. This is according to the reaction equation (3).

The FSA is then pumped to a reactor where it is contacted with sulphuric acid. According to reaction (2) HF and SiF_4 form and are separated. The crude HF is condensed and purified, the SiF_4 flows to the concentration step and concentrates the FSA. The diluted sulphuric acid is stripped of residual HF in a stripping column with steam and air and is then recycled back to the phosphoric acid plant. The AHF production plant has to be attached to a phosphoric acid plant to close the loop of sulphuric acid and water. This is shown as a block diagram in figure 1.

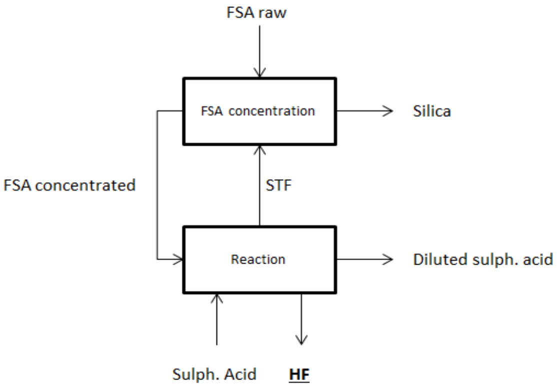

Fig. 1. Process block diagram for the production of HF from FSA by direct reaction with sulphuric acid

Compared to the salt processes the direct reaction has the advantage of being a process that is largely liquid gas operations only, with one filtration step for the silica. As solids handling involves higher maintenance than the liquid gas operation plant, the latter will therefore be lower in operation and maintenance costs.

3.2. Production of AHF by precipitation of an intermediate salt

In numerous patents and process proposals, the production of HF by an intermediate precipitation step of the FSA is described. Examples are given in [7] and [4]. The resulting salts are e.g. SSF, SBF, SF or AF. Please note that this list is not complete, other variations of Ammonia and sodium salts are possible.

These intermediates will react to HF and another salt that can be recirculated such that waste by-products can be minimised. The reactions can be used in a production process mainly by applying heat or mixing with sulphuric acid. The precipitation can be done with sodium carbonate, sulphate or chloride or ammonia salt solutions or ammonia solutions. Figure 2 a gives a process according to [5], figure 2 b shows a highly integrated process described by [7].

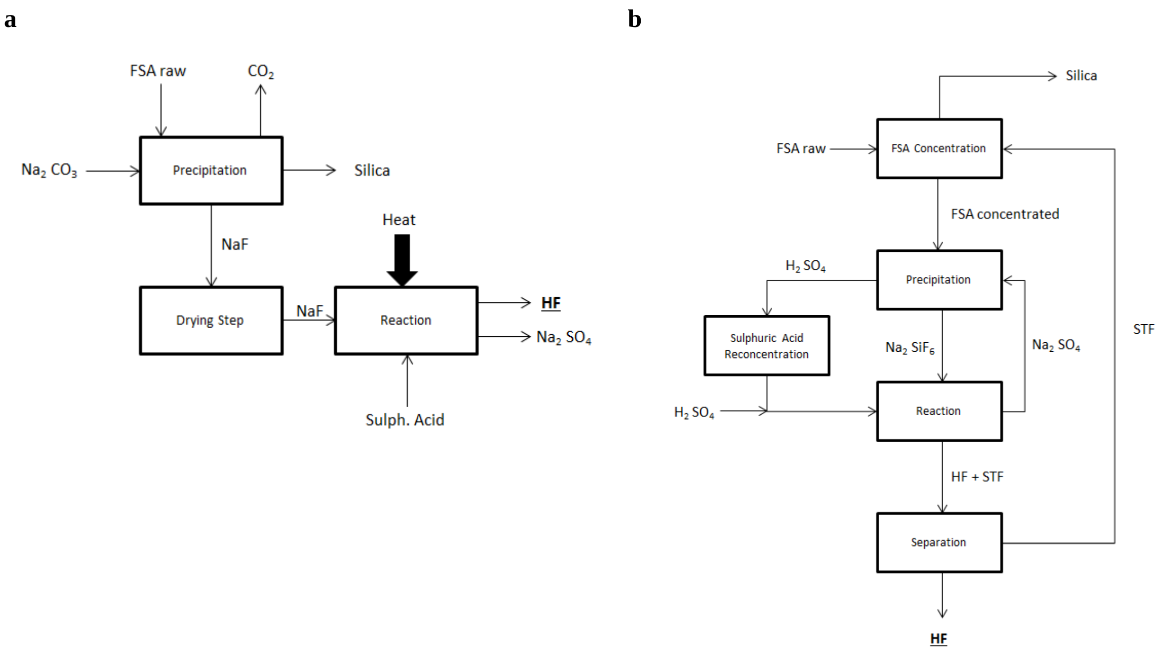

Fig 2. (a) AHF from FSA by precipitation with Sodium Carbonate (b) AHF from FSA by precipitation with Sodium Sulphate (integrated process)

Sarawade et al. [5] use a sodium carbonate precipitation step to create a high quality silica. However, this is also a complicated process in an industrial scale as it is incorporating a large number of unit operations, including filtrations, drying and reaction steps. A scale up of such a process would be a semi batch process with many equipment to be used. Until now, the processes that use an intermediate salt have not been designed or built on an industrial basis despite their theoretical advantages such as lower volumes of acid being used or easier transport of a solid as an intermediate. Further, the precipitation step of the FSA with a salt solution to silica and the fluorine salt results in a defined silica quality with regards to the active surface area. This would theoretically create another valuable product for a plant owner as one can match different consumers specifications of silica.

Figure 2 (b) depicts a highly integrated process that recirculates all solid intermediates, thus creating fewer byproducts. The sulphuric acid that is formed during the precipitation step dilutes with water contained in the concentrated FSA. This acid can either be neutralised or recycled by concentrating the acid to a level where it can be fed to the process again.

Even with lower volumes of sulphuric acid being used, a re-concentration of sulphuric acid to higher levels of 85% is technically feasible but limited to the size of the equipment and their materials of construction when it comes to fluorine impurities in the acid [9]. Compared to the sulphuric acid plant sizes, a re-concentration unit can only handle a small amount (approx. 10%) of acid produced in a small size industrial sulphuric acid plant of 500 t/d. Investment costs for such a re-concentration plant add significantly to the already high capital cost of the process. An economic evaluation including the comparison of transportation costs for liquid and solids has not been published to date.

3.3. Ion Exchange Process for Fluorine Recovery

The case of treatment of FSA of a concentration of up to 2 %-wt from cooling ponds or barometric condensers in the US has been piloted and patented by Berry[6]. In this case, the FSA or the water to be treated will be contacted with a strong base anion exchange resin which is commercially available. The resin takes up silicofluoride ions and later phosphate ions. When the resin is loaded, regeneration is performed with an Ammonia solution in two steps such that on the first hand, the fluorides are recovered, then in a next step the phosphates. Resulting treated water concentrations are claimed to be in the range of 100 ppm for the fluoride ions. With the resulting ammonium-fluoride, HF could be manufactured.

The ion exchange filters are installed such that they can be operated in a continuous way, allowing regeneration of loaded filters while loading the freshly regenerated filters. This was done by installing the filters on a rotating setup, the advanced separation device (ASD) with several filters installed. A pilot unit has been built and was in operation for several years. It is claimed that economics are good and the advantages are high when resolving the environmental problem and creating value for the phosphate producer at the same time. However, [5] has stated that the process of using Ammonia is not economical for making AHF. The approach of this process differs from the other processes shown within this paper. The ion exchange process focuses on the recovery of the fluoride after being dumped or diluted in condensers. The processes that precipitate higher concentrated FSA or directly react with sulphuric acid have the focus on the prevention of waste streams by using the higher concentrated, smaller volume flows coming directly from production. Hence, a direct comparison cannot be made. The use of ion exchange resins on higher concentrated effluents is not a feasible option. Figure 3 shows the uptake and regeneration cycle when an ion exchange resin is used for fluorine recovery. The phosphate uptake and regeneration cycle has been omitted.

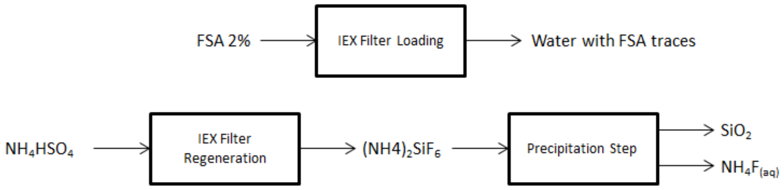

Fig.3. FSA recovery by ion exchange

4. Process scale-up and optimization of the direct reaction process

The base of the process was the production plant of the Polish company Lubon. This production plant had a capacity of 800 t/a and could make HF of up to 70%-wt. BCT has analysed the existing process with two main goals:

- Increase the capacity to 20,000 t/a of AHF
- Manufacture AHF instead of only 70%-wt HF

4.1. Process Analysis

The production process as it was built in Poland, had to be re-calculated and a mass and heat balance was created to identify potential for optimization. The majority of the columns and absorption towers within the existing plant could be directly scaled up with good engineering practice. Size limitations did not apply for any of this equipment. However, the mass and heat balance revealed that the HF generation section could be optimized with regards to the recovery of HF. Further, a liquefaction and purification section had to be designed to suit the process and achieve the required concentrations of HF and impurities levels.

4.2. As built plant and changes in the optimized design

In figure 4, the small scale plant is shown as a process flow diagram (simplified). Three columns, C1, C2 and C3 are used to separate STF from HF, dry and pre-purify HF and to dry off gases from the second desorber. The loaded sulphuric acid from the reactor is desorbed in two stages, in the first by applying heat, in the second by stripping. This column setup brings certain disadvantages for the downstream processes and the product quality. The off gas stream from C2 and the following condensation is directed to the concentration section for the FSA. This is correct but will dilute the STF feed to the concentration section, reducing the efficiency. Further, the off gas from column C3 with its higher air content from the second desorber is also mixed with the condensed product from column C2. This will create the problem of a higher impurities level due to any particles and liquids entrained in the gas stream, despite the usage of demisters after the column C2.

BCT has changed the process path in the new designed plant. The small scale plant feeds sulpuric acid directly to the columns C1, C2 and C3 as shown in figure 4. This will decrease the fluorine recovery and was therefore changed. In the new design, sulphuric acid is fed to the columns equivalent to C1 and C3 and is then further used in all downstream columns. In this way, the fluorine recovery was improved.

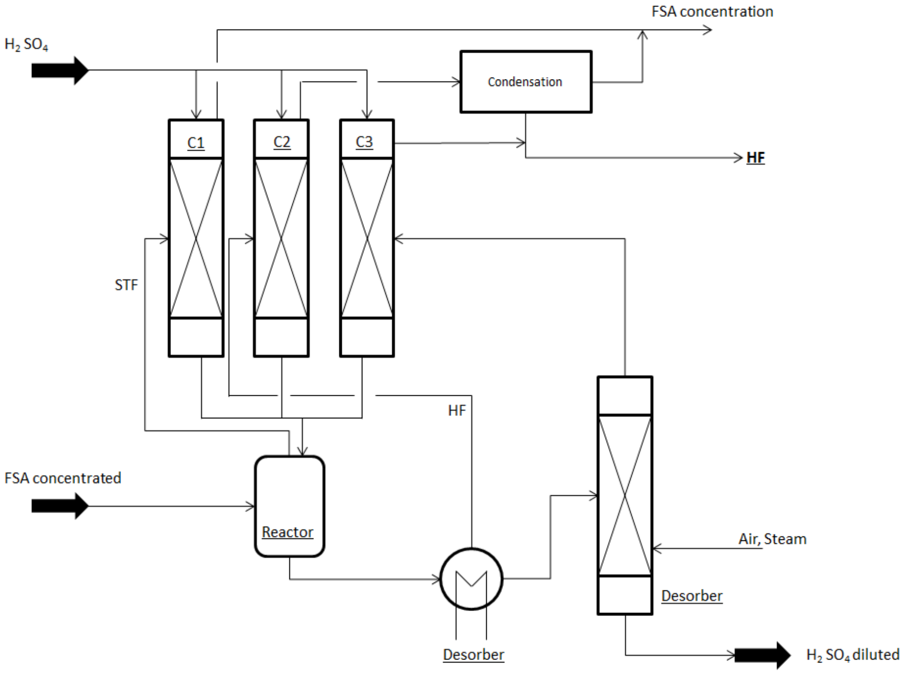

Fig. 4 Process Flow Diagram of small scale plant

As BCT has a long term experience in purification and liquefaction of AHF, an entirely new designed purification section was added. The crude HF gas coming from the HF generation column C2 flows to a purification section where the acid is liquefied and purified to >99.9%-wt. The non condensable gases flow to a washing stage where FSA is pre-concentrated and then flows to the main concentration section. Thus, STF losses are minimized and dilution effects in the concentration stage can be avoided.

4.3. Construction changes

BCT's long history in designing columns for purification of HF could be used to design the purification section for the new plants. The new process showed differences to the traditional route to AHF from Fluorspar. Usually the difficulty of sulphur components blocking packings and pumps arose. As the reaction temperatures are lower than in a rotating HF kiln and the reaction involves no solids or gases in the reactor, the fouling potential of the entire system is low. Thus, the traditional approach of removing heavy boilers could be altered and adapted to the conditions of the different raw material source. Hydraulic conditions could be changed and high performance packing used. The change in design brings advantages for the product quality because

- The packing in the column can be entirely used for the separation process. There is no need to allow a desulphurization section
- Without the sulphur, high performance packing can be used
- Maintenance cycles of the equipment are longer, less maintenance and operational costs, no regular shutdowns and exchange of packing necessary, maintenance mostly consists of a packing inspection only

The changes in the HF generation were implemented based on the results of the mass and heat balance analysis. Construction showed no challenges as these are standard absorption columns; long term experience with HF could avoid any material issues due to the corrosive nature of the process.

4.4. Limitations

While the process “HF from FSA” was scaled up in one step and with a factor of 25, there are limitations that make it difficult to build single line plants with capacities higher than 30,000 t/a. The reason is mainly due to difficulty of applying the material of construction for larger sizes of a few key equipment..Some equipment that is used in the process have to be custom made from special materials. Building these as large single piece of equipment is expensive and increases the manufacturing time. This prevents the construction of plants with capacities comparable to large single line AHF plants (with fluorspar as raw material) of 53,000 t/a. Figure 5 shows a possible block type layout for a production plant with higher capacity, 54,000 t/a. The HF reaction plant section and the FSA concentration section are doubled for some parts where the size is getting too large for the used materials of construction. Especially lined columns and heat exchangers do have maximum sizes that prevent larger single line plants. Maintenance and purchasing costs would be too large when a single production line of this size would be built. The purification section on the other hand, could be built in a single line. BCT has experience with purification and condensation of AHF of that size. The same is for the storage tanks. This depends on the customers' requirements on safety and storage capacity.

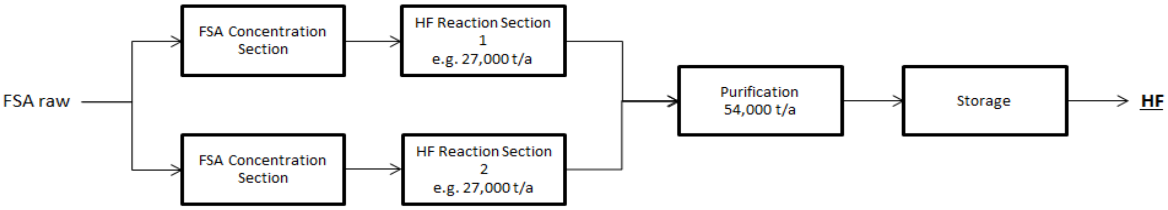

Fig. 5. Block type plant layout for larger production capacities

4.5. Process evaluation

The influence of the changes described in the previous two sections were measured in the second plant with a capacity of 12,000 t/a. It was found that the BCT condensing section with two distillation columns was performing well above the designed intent. Due to the quality of the raw materials the quality was reached without using the second distillation column within any reference for AHF. This column, to reduce lights, was shut down and isolated. It is kept as standby column should the raw material require light boiler removal. In table 1, reference HF parameters are shown, compared to the values achieved in the full scale plant. With regards to the output of the plant, the design capacity was reached and during a two week observation, the output was 105% of the designed 12,000 t/a.

Table 1. AHF Quality of the 12,000 t/a production plant with optimized purification section compared to a reference acid

Parameter	Unit	AHF Standard	Optimised Large Plant
HF, min.	%-wt	99.95	99.98
Water, max.	ppm	200	31
H_2SO_4, max.	ppm	100	34
FSA, max.	ppm	100	28
SO_2, max.	ppm	50	not detectable

The optimized process flows within the HF and STF generation section brought improvements in the overall fluorine recovery from the columns. In addition, the efficiency of the FSA concentration section was increased and the loss of STF to the off gas scrubber could be minimized. Table 2 summarizes the results.

Table 2. Improvements in Fluorine recovery and STF losses of small scale plant and the large plant

Parameter	Unit	Small scale Plant	Optimised Large Plant
F recovery	%	60	90
STF losses	%	Not given	0.5

One other important factor is the operability of the plant. With a commissioning time of only six weeks, the plant reached design capacity. This is mostly due to the robust process design and the limited number of critical unit operations such as solids handling steps or the sulphuric acid reconcentration unit. For operating the plant, only a few persons in the field are required. The control system handles the operational scenarios such as shutdowns or load changes.

5. Conclusion

The first attempts to develop a process that directly reacts FSA with sulphuric acid has been researched and many patents have been filed [4], [8], [2]. The production of AHF from FSA has now been commercialized and since 2008, plants are operating.

With the commercialization of the process and optimizing the product acid quality and the overall fluorine recovery, BCT has shown that the direct scale up in one step from 800 t/a to 20,000 t/a is possible and was successfully implemented. Despite the disadvantage of the AHF plant being restricted to be build next to the phosphoric acid production complex, AHF can be produced economically and with very good quality.

With changing legislations and the need to build essentially waste water free plants, this process can help phosphoric acid producers to create a situation in which they can increase the profitability with the need to dispose of a liquid waste stream. A combination of the AHF plant and high value downstream processes such as organic and inorganic fluorides, STF purification and silica purification and sale can create value in addition to a phosphate producers core business.

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