Improvements in the field of AlF₃ and HF technologies

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Improvements of AlF₃ and HF production technologies, using fluorspar as a raw material, are highlighted in terms of productivity, yield, maintenance and product quality. This article focuses on the fluorspar pre-reaction, conversion rate, importance of the feed acid composition and the preheating of raw materials which are necessary to obtain the optimum conditions for a good pre-reaction using a special “co-kneader”. The opportunities to increase capacities and efficiencies of HF reactors, indirectly heated rotary kilns and AlF₃ reactors, and fluid bed reactors are explained.

The process technologies to produce aluminium fluoride (high density AlF₃) and anhydrous hydrofluoric acid (AHF) from fluorspar are based on the same unit operations to generate the crude gaseous hydrofluoric acid. This reaction is preferably carried out in a two-stage reaction system: a pre-reactor unit and an HF reactor (an indirectly heated rotary kiln). After scrubbing with sulphuric acid the gaseous hydrofluoric acid is either condensed and purified to produce the AHF or is reacted with alumina trihydrate in a fluid bed reactor to produce aluminium fluoride.

The fluorspar pre-reaction
In the late 1950s, the company Buss AG (presently known as Kvaerner Process Technology (Switzerland) AG) introduced a new pre-reaction step using its special co-kneader, the pre-reactor unit, as pre-mixer for the reaction between sulphuric acid and fluorspar in the manufacture of anhydrous hydrofluoric acid and manufacture of aluminium fluoride.

The pre-reactor unit consisting of a monoshaft screw-type designed for heavy duty conditions is used for the initial reaction between dried, finely divided fluorspar and sulphuric acid. Its interrupted-flight screw which rotates and reciprocates at the same time, interacts with the stationary teeth in the barrel to provide intensive kneading action. This barrel is heated. The temperature, feed acid composition and residence time in the pre-reactor unit are selected to ensure thorough treatment of the plastic-like corrosive phase as the reactants advance through the unit. After about 60% conversion of the CaF₂ has taken place in the pre-reactor unit, the product, now crumbly material, enters as a free-flowing reaction mass in the rotary kiln.

The localisation of the most corrosive and unwieldy phase (the plastic-like material is very sticky) to a relatively small piece of equipment made of special materials prolongs the lifetime of the rotary kiln drum considerably. Moreover, the use of special materials in construction reduces the corrosion rate to a minimum. Furthermore, the localisation of the plastic-like material in the pre-reactor unit and proper feed conditions will avoid a crust build-up on the heated wall surface of the rotary kiln which would reduce production capacity considerably.

The chemical reactions taking place in the entire process section to generate the gaseous hydrofluoric acid including acid feed, fluorspar pre-reaction, HF reaction, water neutralisation, and crude HF gas scrubbing are described as follows:

- The water contained in the sulphuric acid and the water condensed in the pre-scrubber are neutralised with oleum according to reaction (5) under such conditions that the extent of reaction (4), reaction of HF with SO₃ will be limited or totally avoided.
- The sulphuric acid mixture is reacting with fluorspar according to a two-step reaction producing first the acid calcium sulphate and later the calcium sulphate described by reactions (1) and (2). The overall reaction is highly endothermic. Most of the acid calcium sulphate is formed during the fluorspar pre-reaction.
- The presence of traces of water in the reaction system either contained in the feed acid or produced by side-reactions of impurities (6) (7) and (8) with the acid will suppress the formation of fluosulfonic acid (3) especially under high temperature and will catalyse later the decomposition of the acid calcium sulphate to calcium hydrogenosulphate (4). Finally the solid particles will be covered by a layer of sulphates resulting in the non sticking material.

An excess of water will decompose the acid calcium sulphate. A liquid phase containing the sulphuric acid not bound will be formed. Water, hydrofluoric acid, fluosulfonic acid will remain soluble in the liquid phase created. Due to the reaction of hydrofluoric acid with sulphuric acid and the low vapour pressure of hydrofluoric acid in this highly non-ideal mixture, less HF gas will be developed. The water obviously is playing an important role.

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1) \( \text{CaF}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Ca(HSO}_4)_2 + 2 \text{HF} \)
2) \( \text{Ca(HSO}_4)_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{SO}_4 \)
3) \( \text{H}_2\text{SO}_4 + \text{HF} \leftrightarrow \text{HFSO}_3 + \text{H}_2\text{O} \)
4) \( \text{SO}_3 + \text{HF} \rightarrow \text{HFSO}_3 \)
5) \( \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \)
6) \( \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \)
7) \( \text{SiO}_2 + 4 \text{HF} \rightarrow \text{SiF}_4 + 2 \text{H}_2\text{O} \)
8) \( \text{Me}_2\text{O}_3 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Me}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{O} \quad (\text{Me} = \text{Metal}) \)

In fact traces of water and traces of fluorine in the feed acid are playing an important role. In industrial plants, the fluorspar is reacted in the pre-reactor unit with a mixture of sulphuric acid, oleum including the spent scrubbing acid recycled from the pre-scrubber containing water and fluorine. The feed acid composition of 100% H\text{SO}_4 can only be approached and cannot be reached exactly. The return of the spent scrubbing acid to the pre-reaction system will be a determinant factor and will influence considerably the quality of the pre-reaction. This recycle cannot be avoided as the pre-scrubbing system is essential to the technology.

The duty of the pre-scrubbing system is to cool down the crude HF gas, remove condensable components evaporated during the course of the HF reaction (water, fluorosulfonic acid, sulphur trioxide, etc.) and remove the dusts entrained with the crude hydrofluoric acid gas. In AHF plants, the pre-scrubber is also used to desorb the HF recovered in sulphuric acid fed from the absorption system after the condensation step where HF contained in the inert gas leaving the condensers is absorbed into sulphuric acid. The recycle of sulphuric acid containing the hydrofluoric acid and any additional make-up use of fresh sulphuric acid added to the pre-scrubber will influence the conversion rate and the material consistency after pre-reaction. It will affect the pre-scrubbing efficiency, improve the removal of dusts and sometimes the removal of sulphur from the crude HF gas evolving from the HF reactor.

The main target of the pre-reaction is to obtain a crumbly material at the pre-reactor unit outlet together with a significant conversion rate. A slightly wet crumbly material is found to provide better transport characteristics for the solids in the HF reactor. When the conversion rate is above approximately 50% the material consistency will be satisfactory.

**Influences on pre-reaction**

Many parameters influence the pre-reaction and are discussed in the following sections:

**Feed acid composition**

In order to achieve the optimum conditions for the pre-reaction, the feed acid shall have the following composition: H\text{SO}_4 98.0-98.5% min., HF 0.5-1.0% max., H\text{O}_2 0.0-0.5% max.

The concentration of H\text{H}_2\text{SO}_4 in the feed acid must be as high as possible. If the strength in H\text{H}_2\text{SO}_4 decreases by 2% only, the conversion rate will be decreased by 10-15% approximately. The water shall be present as traces only to get the positive effects explained above. Excess of water will produce an adverse effect.

Sulphuric acid reacts with hydrofluoric acid to produce fluosulfonic acid according to reaction (3). It can also be produced under certain conditions according to reaction (4). If the feed acid contains a high concentration of fluosulfonic acid, say a few percent, it will be impossible to obtain the consistency required for the reaction mass. The reaction mass will be a slurry. The fluosulfonic acid has the tendency to build up in the reaction system if the feed conditions are not met and the temperature of the pre-reaction is not high enough. The fluosulfonic acid can only be destroyed by the presence of water according to the reversible reaction (3). This process is relatively slow.

The presence of hydrofluoric acid and fluosulfonic acid in excessively high concentration in the feed acid will result in additional corrosion at the feed acid inlet part of the pre-reactor unit. It can also result in abnormal corrosion of the feed end section of the HF reactor.

**Temperature of raw materials**

The higher the inlet temperature of the reactants (feed acid and fluorspar), the higher will be the conversion rate of the pre-reaction stage. The acid mixture containing sulphuric acid, oleum and the recycled spent scrubbing acid is heated up to 150-160 C. The fluorspar is heated up to 150-200 C. If the fluorspar is preheated, the generation of HF gas will be more spontaneous and the reactivity will be better. This will help the reaction where fluorspar of low reactivity is used.

The average temperature of the raw materials fed to the pre-reactor unit should be around 150 C or more in order to reach a conversion rate between 50 and 70%. Preheating of the feed acid will increase, the generation of HF gas will be more spontaneous and the reactivity will be better. This will help the reaction where fluorspar of low reactivity is used.

Additional heat input to the system can be introduced by heat of reaction or heat of mixing. The typical example to illustrate this method is given by the processes using gaseous sulphur trioxide and steam or sulphur trioxide, steam and sulphuric acid as reactants.

**Residence time**

The residence time of the reaction mass in the pre-reactor unit should be as long as possible. In practice, the optimum residence time is a few minutes based on experience and for economical reasons.

**Intensity of mixing**

The mixing intensity plays also an important role. This is demonstrated by the results obtained using a specific type of

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**Table 1. Conversion rate of acidspar pre-reaction**

<table>
<thead>
<tr>
<th>Fluorspar temperature (°C)</th>
<th>Sulphuric acid mixture temperature (°C)</th>
<th>Spent scrubbing acid recycle</th>
<th>Average raw materials temperature (°C)</th>
<th>Residence time (min.)</th>
<th>Average conversion rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>140</td>
<td>yes</td>
<td>110</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>yes</td>
<td>110</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>yes</td>
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<td>150</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>150</td>
<td>160</td>
<td>yes</td>
<td>150</td>
<td>3</td>
<td>65</td>
</tr>
<tr>
<td>200</td>
<td>160</td>
<td>yes</td>
<td>175</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>200</td>
<td>160</td>
<td>yes</td>
<td>175</td>
<td>2</td>
<td>70</td>
</tr>
<tr>
<td>200</td>
<td>220 (1)</td>
<td>no</td>
<td>200</td>
<td>3</td>
<td>75</td>
</tr>
</tbody>
</table>

Note (1): using sulphuric acid only or SO₃, steam and sulphuric acid.
pre-reactor. The pre-reactor unit is an efficient mixer and a high conversion rate is possible.

**Excess of calcium**
An excess of calcium or ratio Ca/CaF₂ is also an important parameter to adjust to obtain the right consistency. The excess of calcium will react or bind with the sulphuric acid to produce acid calcium sulphate \((\text{Ca(HSO}_4\text{)}_2 = \text{CaSO}_4\cdot\text{H}_2\text{SO}_4)\). This excess of calcium is either present in the fluorspar as CaCO₃ or can be added as CaCO₃, CaSO₄, CaO or can be recycled as CaSO₄. This is the principle used by HF reactors having an internal recirculation screw to recycle anhydrite. This effect is also well known from fluorspar having a high content in calcium carbonate. In addition to the above positive effect, the carbonates will produce water, heat of reaction and liberate CO₂ that will help to desorb HF from the reaction mass.

**Excess of sulphuric acid**
An excess of sulphuric acid above the stoichiometric amount also helps the reaction. Nevertheless it is preferable to operate with a stoichiometric feed rate and approximately stoichiometric feed conditions in the pre-reaction in order to avoid additional severe corrosion of the HF reactor. The method of addition of the acid has an influence too.

**Quality of acid-grade fluorspar**
This subject is well known. It was treated and discussed many times in the past. The main points to remember are outlined below:

- **Granulometry:** average particle size (25% to 55% particles less than 45 microns), homogeneous distribution of the particle sizes (to get an homogeneous reaction and avoid some particle segregation in the HF reactor), specific surface area, method of milling, etc.
- **Impurities:** CaCO₃, SiO₂, Fe₂O₃ + Al₂O₃, S, organics

**Optimising acidspar pre-reaction**
It is well known that the acidspar pre-reaction is strongly influenced by temperature and feed acid composition. A better knowledge of these influences allows us to optimise the design of the pre-reaction stage and plants. The effect of residence time and temperature on pre-reaction is shown in Figure 1 and Table 1.

With better preheating of the feed acid and fluorspar, allowing an efficient input of heat directly to the reaction mass with small heat losses, and with better control of the feed acid composition by removing most of the HF and HFSO₃ from the recycled spent scrubbing acid by adding a new desorption system, it is possible with a pre-reactor unit as described above to reach a conversion rate of 60% or more. These are the essential improvements to optimise the acidspar pre-reaction.

The main problems generally encountered are corrosion, crustling and low reactivity, which can be avoided by implementing a more intensive pre-reaction.

**The HF reaction**
The HF reaction is completed in a second stage. The HF reactor is an indirectly heated rotary kiln using hot combustion gas as heating medium. The reaction is controlled by a diffusion process through the calcium sulphate layer covering the particles. According to the size of particles, the residence time to complete the reaction can be estimated to be 90 minutes minimum and preferably a few hours are considered in practice. The HF reactor systems which have an internal screw to recirculate anhydrite have lower residence times, basically a half or a third of the residence time of HF reactors having no recirculation screw. The systems using an internal recirculation screw are limited with respect to capacity by the residence time.

Having the optimum process conditions to perform the pre-reaction, the traces of water will catalyse the decomposition of the acid calcium sulphate as explained above and the thermal decomposition of the latter will not be experienced. The heat transferred to the reaction mass is used efficiently for the progress of the reaction and a minimum of energy is consumed for the evaporation of side-products.

Looking at the heat required to complete the reaction, approximately 70% of the total heat of reaction is transferred from the hot gas to the reaction mass by radiation and convection. The overall heat transfer coefficient by radiation depends on the hot gas temperature only. As the maximum hot gas temperature will be limited by the material of construction used, the optimum temperature is easily defined. The heat transfer coefficients by convection between the hot gas and the shell and convection between the shell and the solids can be increased to optimum values by considering the following improvements:
The velocity of the hot gas in the heating jacket is increased to obtain a significantly higher outside gas heat transfer coefficient by convection. For this purpose, a design considering a counter-current flow is preferred. This also improves the temperature profile for the reaction along the kiln.

The rotary speed of the kiln’s shell is increased to improve the mixing within the reaction mass, to reduce segregation phenomena of particles and to increase the inside heat transfer coefficient by convection between the solid bed and wall surface.

The new design gives higher output for the HF reactor and plant as shown in Table 2. The power required to recirculate the hot gas is practically unchanged. The heat is transferred more efficiently to the reaction mass while the heat losses are kept constant. This provides additional energy cost savings. The experience shows that the corrosion is even reduced and is practically insignificant on the hot wall surfaces. Generally the capacity of most of the existing HF reactors could be increased significantly. At present, Kvaerner Process Technology has no limitation in the design of large HF reactors, capacity over 200 tpd.

The yield of the reaction can be improved to produce anhydrite (anhydrous calcined gypsum) of high quality containing 1% CaF₂, 0.1% H₂SO₄ before neutralisation (conversion rate of fluorspar up to 98% approx.). A good quality of anhydrite is a decisive criteria for selling it at a reasonable price to the building industry, especially for floor levelling applications.

The selectivity of the reaction can be modified to minimise the quantity of silica converted to SiF₄ by reaction (7). This is an appreciable advantage for the production of aluminium fluoride via the gaseous hydrofluoric acid to obtain low silica aluminium fluoride.

Using an acid-grade fluorspar with a typical content in silica of 0.7%, a typical fluorine yield of 95% to 97% maximum can be achieved for AIF₃ plants corresponding to 2,100 kg of aluminium fluoride per tonne of 96% maximum can be achieved for AlF₃ plants corresponding to 2,100 kg of acid-grade fluorspar (97% CaF₂) per tonne AHF.

The correct selection of process parameters including raw materials; conditions such as residence times, temperatures, and chemical compositions; and the correct selection of equipment and materials of construction; ensures the most economical conditions such as residence times, temperatures, and chemical compositions; and the correct selection of equipment and materials of construction; ensures the most economical solution for the production of hydrofluoric acid and provides a significant opportunity to increase the capacity of operating plants.

Table 2. Productivity of HF reactors

<table>
<thead>
<tr>
<th>Hot gas temperature</th>
<th>Rotation speed</th>
<th>Productivity factor</th>
<th>Energy consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>480-500 °C</td>
<td>Large size rotary kiln</td>
<td>%</td>
<td>factor per tonne %</td>
</tr>
<tr>
<td>Cross flow</td>
<td>1.2-1.4</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Counter-current flow</td>
<td>1.6-1.8</td>
<td>140</td>
<td>77</td>
</tr>
<tr>
<td>Counter-current flow</td>
<td>1.8-2.0</td>
<td>160</td>
<td>70</td>
</tr>
</tbody>
</table>

♦ The knowledge of the process chemistry involved in the production of aluminium fluoride and anhydrous hydrofluoric acid is still developing. A better understanding of many mechanisms is helping Kvaerner Process Technology AG to provide customers with the best expertise and process technology with all the associated competitive advantages. It is also helping the producers to define new improvements they may need.

The AlF₃ reaction

High density aluminium fluoride can be produced by process technologies using a dry process or gas phase process only. A product of high density (bulk density: 1,400-1,600 kg/m³ (loose material)) having high flowability properties is also produced and is the preferred material of aluminium smelters using point feeders.

For economic reasons the gaseous hydrofluoric acid produced from the previous HF reaction system is used directly after scrubbing. The HF gas is reacted with alumina trihydrate in a three-stage reaction system: the bottom bed and top bed of the fluid bed reactor and in cyclones. The main reaction stage is the top bed where the alumina trihydrate is dehydrated (9) producing in-situ activated alumina which will react spontaneously with HF gas (10).

The capacity of the system is only limited in its ability to separate and recirculate the dusts efficiently in order to obtain a high conversion rate for the fine particles. The capacity of existing aluminium fluoride reactors can be increased.

By carefully controlling the process operating parameters of the top bed of the aluminium fluoride reactor it is possible to avoid the precipitation of silica (11) while obtaining a yield of 98-99% based on HF entering the aluminium fluoride reaction.

By improving the scrubbing efficiency of the crude hydrofluoric acid gas in the pre-scrubber, by modifying the operating conditions and by recirculating more pre-scrubbing acid to the desorption system it is possible change the concentration of the species of the fluophosphonic acid equilibrium represented by the reactions (12-15). As a result of this modification the PO₄³⁻ content of the aluminium fluoride produced can be influenced without having to condense and purify the hydrofluoric acid. An aluminium fluoride product of low PO₄³⁻ content less than 200 ppm corresponding to Grade F can be produced from most of the acid-grade fluorspar commercially available.

The process technology to produce aluminium fluoride directly from gaseous hydrofluoric acid without the need to liquefy the HF is available now for all quality grades of aluminium fluoride in a more economical way.Using an acid-grade fluorspar with a typical silica content of 0.7%, a typical fluorine yield of 94% to 96% maximum can be achieved for AIF₃ plants corresponding to 1,380 kg maximum of acid-grade fluorspar (97% CaF₂) per tonne of 90% AlF₃.

In summary

The knowledge of the process chemistry involved in the production of aluminium fluoride and anhydrous hydrofluoric acid is still developing. A better understanding of many mechanisms is helping Kvaerner Process Technology AG to provide customers with the best expertise and process technology with all the associated competitive advantages. It is also helping the producers to define new improvements they may need.