

ALUMINUM FLUORIDE SYNTHESIS IN CIRCULATING FLUIDBEDS

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The aluminum fluoride synthesis according to the Lurgi process is operated in two stages with circulating fluidbeds in the reactor with recycling cyclone and in the subsequent Venturi reactor. Liquid HF and partly dehydrated $\text{Al}(\text{OH})_3$ are used as feed materials. The flow sheet and operation experiences of a 30 tpd plant are discussed.

Circulating fluidbeds are characterised by uniform gas-solids distribution, a good radial gas mixing and an intensive gas-solids contact. These favourable reaction conditions and the high specific gas throughputs of highly expanded fluidbeds make this system very efficient.

By partial dehydration the specific surface of the hydrate is increased and thus results in even better conditions for a high conversion during AlF_3 synthesis. The direct injection of liquid HF into the fluidbed yields advantages regarding reliability of operation and control.

There are two routes to produce aluminumtrifluoride: A new wet process (1) starting from aluminumtrihydrate and fluorosilic acid - a byproduct of the fluorine recovery in fertiliser plants - and the classical process starting from aluminumtrihydrate and hydrofluoric acid. In the classical route the dry processes are more and more replacing the wet processes because the corrosion problems are much smaller. The dry processes utilise a number of reaction stages - generally fluidized beds - arranged in series either one above or beside each other (2,3,). Several reaction stages in series form a counter-current flow, thus realizing a good yield of hydrofluoric acid at a high aluminum-fluoride content in the product. The Lurgi process achieves this result in only two stages with highly expanded fluidbeds in a reactor with recycling cyclone and a subsequent Venturi reactor.

Advantages of the circulating fluidbed system

The principle of highly expanded fluidbeds and its advantages in relation to conventional fluidized beds have been described in detail in several publications (4-6). This paper will discuss mainly those characteristics of this fluidbed type, which are of special importance for the reaction of fine particles with the fluidizing gas.

Figure 1 shows the highly expanded fluidbed system: the reactor, equipped with a nozzle grid and completely filled with gas-solids suspension, and the cyclone precipitator. The solids concentration decreases continuously in direction of the flow. Part of the solids are discharged at the reactor top, so that a corresponding amount of solids has to be permanently fed in order to maintain a stable fluidbed. This is assured by recycling the solids precipitated in the cyclone directly to the reactor. That is why this system is called a circulating fluidbed. Fresh solids are fed to the reactor while a corresponding amount of product is being withdrawn from the recycle or alternatively from an outlet at the reactor bottom.

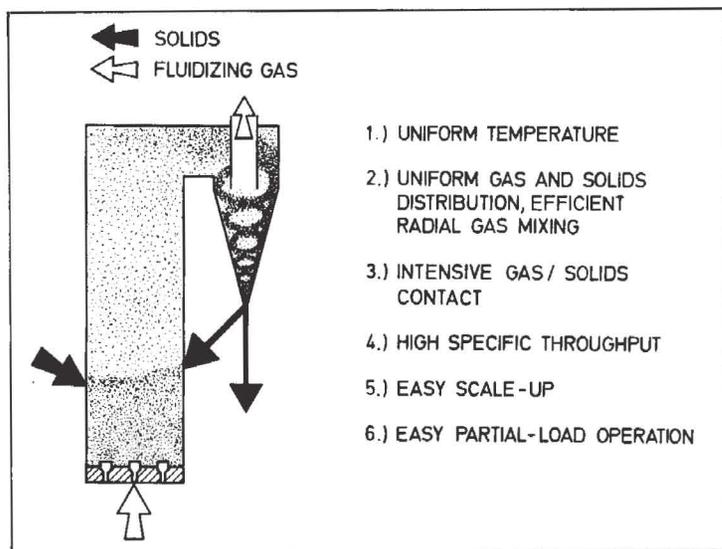


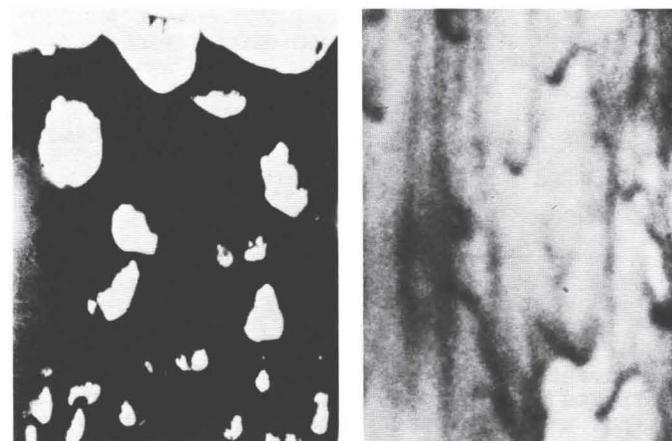
Figure 1: Advantages of the highly expanded fluidbed system

The advantages of the circulating fluidbed principle are listed in figure 1, items 2 and 3 being most important for the development and yield of heterogeneous gas-solids reactions. In processes like drying or calcining, where solids are only heat-treated, the product quality at a given temperature is mainly determined by the uniformity of temperature in the system and by the solids' retention time. The efficiency of gas-solids reactions however, depends on both gas and solids retention time, respectively on the duration and intensity of the contact between the two reaction components.

A uniform gas-solids distribution in radial direction at all levels of the reactor, a good radial gas mixing and an excellent gas-solids contact create very favourable conditions for a rapid development and good conversion of heterogeneous reactions in circulating fluidbeds. If, in addition, the gas-solids reactions are very fast - as for example the synthesis of aluminumtrifluoride - the short gas retention time of some seconds only is sufficient for a good reaction yield in fluidized beds.

The aforementioned advantages of circulating fluidbeds (items 2 and 3 in figure 1) in relation to conventional fluidized beds may be demonstrated by the different flow mechanism of these two fluidbeds (figure 2).

The conventional fluidized bed on the left is characterised by a defined bed surface and by gas bubbles which, on the whole, rise along preferred lines. These bubbles cause part of the gas to by-pass the bed without having been in intimate contact with the solids. Moreover, the radial gas mixing is insufficient. Therefore, the use of conventional bubbling fluidbeds requires a number of reaction stages to achieve the desired high reaction yield.



BUBBLING FLUIDIZED BED

EXPANDED FLUID BED

Figure 2: Mechanism of flow in (different) fluidized beds

The photo on the right showing the structure of the highly expanded fluidbed was taken from a plexi-glass model at the City College of New York (7). It shows clearly the uniform distribution of gas and solids as well as the intensive gas-solids contact. The dense solids' clouds visible in the photo are permanently broken up and formed anew, so that each solids particle is in intimate contact with the fluidizing gas. Expanded fluidbeds have no defined bed surface, the entire reactor is filled with solids and the whole reactor volume is utilised for the reaction whereas in conventional fluidbeds the reaction is limited to the bed volume itself.

The other advantages of circulating fluidbeds listed in figure 1, such as uniform temperature, high specific throughput because of gas velocities which are ten times higher than the velocity applicable to conventional fluidbeds, easy scale-up and easy partial-load operation, have been reported in detail in papers about the Lurgi/VAW fluidbed calciner at former AIME-meetings (8,9).

The influence of different alumina-types

Two types of alumina may principally be used in this process, either dry hydrate - that means a loss of 34,6% on ignition - or preferably a hydrate predried to about 15 to 20% L.O.I. To study the influence of grain size, the plant was operated with two dry hydrates. Figure 3 shows the grain size distributions. The coarser material corresponds approximately with the granulometry of an American type alumina, while the finer material comes closer to what is considered a European alumina type.

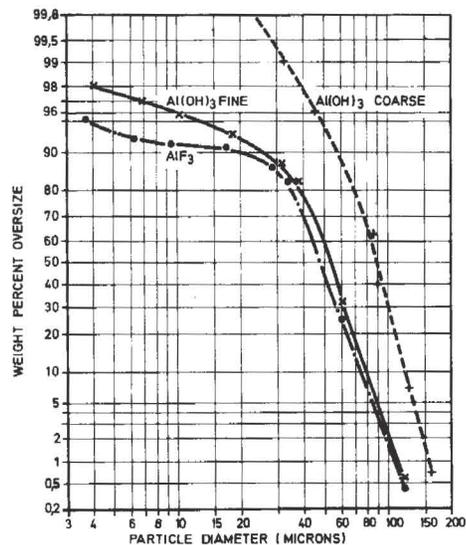


Figure 3: Grain size distributions of $Al(OH)_3$ and AlF_3

At constant product quality the hydrofluoric acid yield is slightly higher for the finer hydrate. This is due to the increase of specific surface area with decreasing grain size.

The indicated grain size distribution for the aluminumfluoride refers to the finer hydrate as primary material. As can be seen from the very similar scope of the curves, particle breakdown in the system is practically negligible.

Apart from the outer surface area as determined by the particle diameter the total surface of the hydrate is greatly dependent on that part of the inner surface area which is produced by evaporating the crystal water during the calcining process. Figure 4 shows specific surface area and loss on ignition of heated $Al(OH)_3$ (10,11). The sharp increase of the specific surface area in the temperature range between 200 and 400 degree C. is especially important for the realization of the process because it creates highly favourable conditions for a fast gas solids reaction.

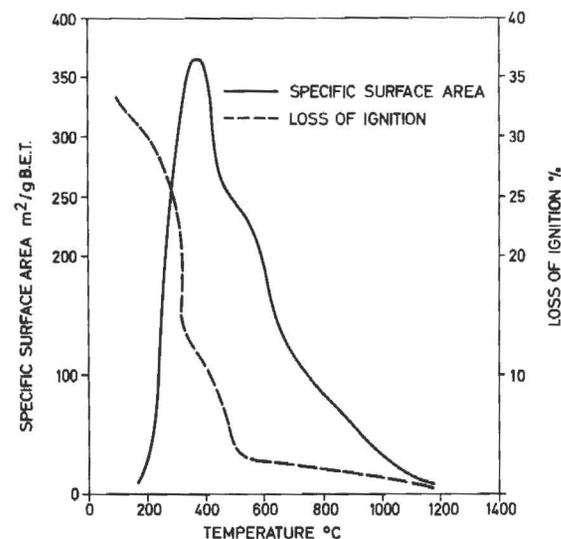
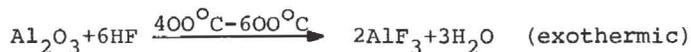
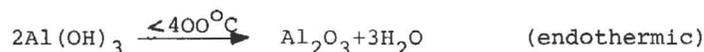


Figure 4: Specific surface area and loss on ignition of heated $Al(OH)_3$

Reaction equation, advantages of predrying



The total reaction may be split up into two steps. The first step being the endothermic evaporation of chemically bound water, the second, the exothermic reaction between the aluminum oxide and the gaseous hydrofluoric acid to form aluminumtrifluoride. The reaction in total is exothermic if the hydrofluoric acid is added as a gas. Technically, the reaction is conducted in the temperature range between 400 and 600 degree C. Above 600 degree C the pyrohydrolysis starts as a counter-reaction. Therefore the possibility of speeding the reaction up via an increase in temperature in the reactor is limited, thus suggesting the preferred range of reaction temperature between 500 and 600 degree C.

In reality the two reaction steps - dehydration and fluorization - here listed separately, take place simultaneously. Thus a partial dehydration of the hydrate before feeding it to the process, yields the following advantages for a quick development of the gas-solids reaction:

1. The evaporation of chemically bound water hinders the fluorization because the hydrofluoric acid must be transported by diffusion to the particle surface against the outgoing water vapour stream.
2. The specific surface area of the predried hydrate feed is much larger right from the beginning which gives better conditions for mass transfer.
3. Additional heat requirements in the form of hot fluidization gas is smaller, thus enriching the concentration of HF-gases in the reactor. Additional heat supply is necessary to cover heat losses and the heat of evaporation of the hydrofluoric acid.

In total these advantages result in an improved hydrofluoric acid yield, when partially dehydrated hydrate is used.

Process description

The layout and the construction of the plant with a daily capacity of 30 t AlF_3 is based on the aforementioned concept.

- to utilise the excellent hydro- and thermodynamic conditions for gas-solids reactions with fine particles in the circulating fluidbed
- to improve the reaction conditions on the solids side by predrying the hydrate

As indicated on the flowsheet in Figure 5, the Lurgi process is operated in two stages with expanded fluidbeds in both the reactor with recycling cyclone and in the subsequent Venturi reactor, thus realizing a counter-current flow of gas and solids. During construction special attention was paid to automation, simple control, easy start-up and shutdown of the plant and a high security level in handling the highly corrosive and highly toxic hydrofluoric acid. The dry or partial dehydrated hydrate is fed via a weigh belt system to the Venturi, where it forms an expanded fluidbed together with the hot gas stream coming from the recycling cyclone. At temperatures in the range of 300 to 400 degree C the hydrate is dehydrated with the sensitive heat of the hot gas stream and simultaneously reacts with hydrofluoric acid contained therein.

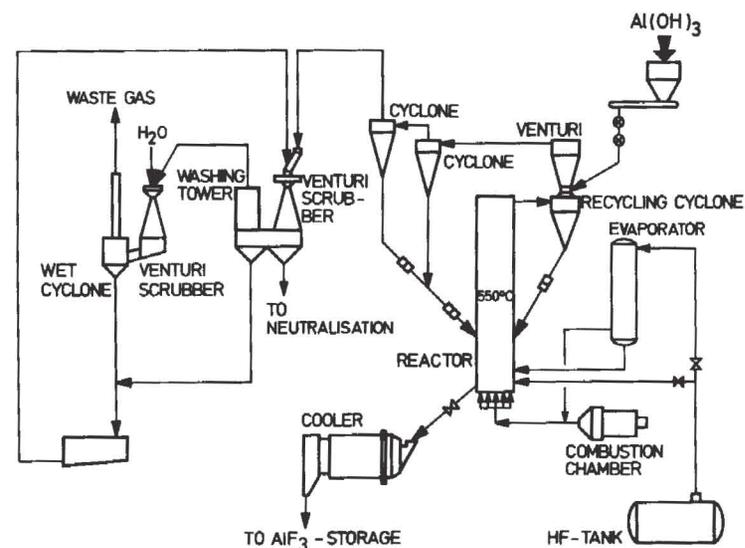


Figure 5: AlF_3 -synthesis in a circulating fluidbed

The mainly dehydrated and partly fluorated solids are entrained together with the waste gas, precipitated in a series of two cyclones and fed to the reactor.

In this circulating fluidbed the main reaction takes place at about 550 degree C. Solids entrained from the reactor, are returned to the reactor via the recycling cyclone, the product leaves the reactor at the bottom, is cooled in a drum cooler and then pneumatically conveyed to an AlF_3 silo.

Hydrofluoric acid is pumped from a storage tank and injected directly into the fluidbed by lances. The liquid injection of the HF yields the following advantages when compared with a pre-evaporation of the HF:

1. Simplicity of the system
2. Easy start-up and shut-down of the plant
3. Easy regulation and control of plant operation
4. Reduced corrosion.

Hot fluidization gases are produced in a separate combustion chamber and fed to the reactor via a nozzle grid.

The HF-evaporator, indicated on the flowsheet, demonstrates the second possible means of operating the plant. This is applicable in the case of lack of, or insufficient dehydration of the hydrate before being fed to the plant. In this case the heat deficiency is covered by partial evaporation of the hydrofluoric acid at the expense of both the above-mentioned advantages of liquid HF-injection and partial dehydration of the hydrate.

Figure 6 shows a photo of the AlF_3 -plant. Reactor, recycling cyclone and precipitation cyclones are easily detectable, also the combustion chamber, the washer and the drum cooler for the product.

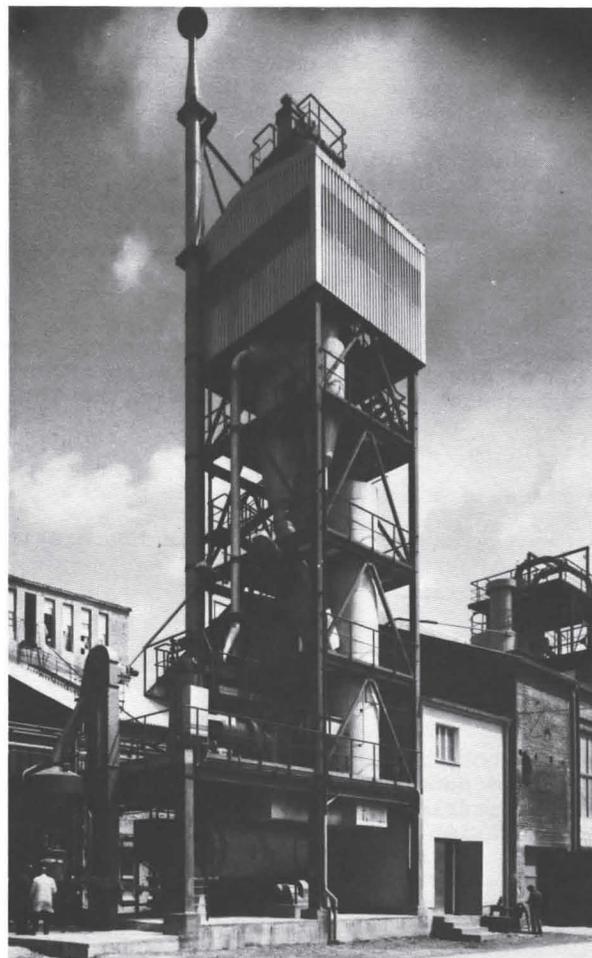


Figure 6:
View of
the AlF_3 -
plant

The use of a separate combustion chamber to adjust the heat balance dilutes the HF-concentration in the reactor, but this disadvantage is not significant because of the excellent reaction conditions in the expanded fluidbed. This is demonstrated by the comparison of achieved AlF_3 -contents and HF-yields with other fluidbed processes, even if the stage from which the product is discharged, is fluidized by concentrated hydrofluoric acid.

The method of operation, described above, results in a number of important operational advantages, such as:

- simple filling and emptying of the reactor without HF-injection;
- the possibility of keeping the plant in operation with small amounts of fuel and air but with HF-injection turned off. The reactor remains fluidized, it is not necessary to shut down the plant when the HF is lacking - as would be necessary if fluidized by pure HF;
- simple regulation of reactor temperature by adjusting the amount of fuel, only possible otherwise by varying the HF temperature or the degree of pre-dehydration of the hydrate.

A wet scrubber cleans the waste gas of dust and unreacted hydrofluoric acid. Figure 7 shows a photo of the scrubber, which consists of a two-stage Venturi washer with intermediate washing tower.

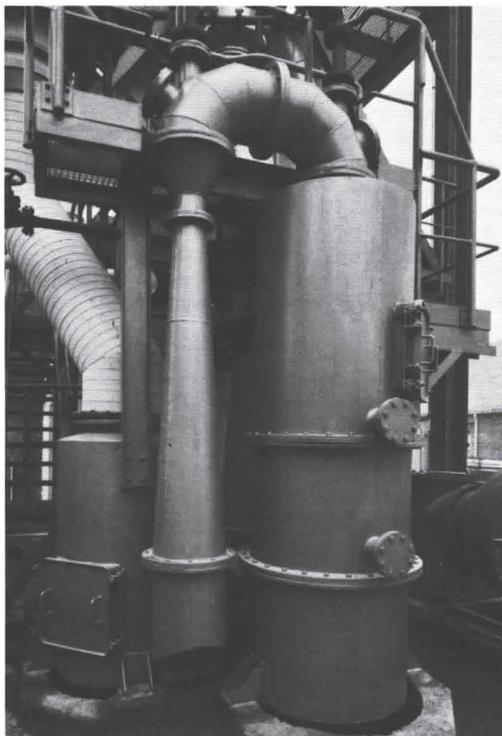


Figure 7:
Three-stage
wet scrubber

Operation results

As expected, the scrubber assures clean gas contents of less than 10 mg/Nm³ HF and 50 mg/Nm³ AlF₃ dust.

At a quality of 90-92 % AlF₃ in the product, the hydrofluoric acid yield reaches 97 %. The three percent loss covers both fluorine in the waste gas as HF and in the AlF₃-dust. The fact that these figures have been arrived at in only two reaction stages despite the HF-dilution in the reactor, demonstrates the advantage of using dehydrated hydrate and the circulating fluidbed system.

The pressure drop is about 3500 mm WG, measured between the entrance of the combustion chamber and the exit of the clean gas stack.

If necessary, the plant can be operated at partial load down to 30-40 % of the full capacity without impairing the product quality and hydrofluoric acid yield.

One man per shift is sufficient for the operation and daily service of the plant.

The average availability, measured over a three year period from 1974 to 1976, exceeded 85 %. Over the same period repair and maintenance costs were about 6,5 % from the plant investment costs, which is a good figure for a process working with highly corrosive hydrofluoric acid.

All reaction stages, cyclones and connecting tubes are made of a high chrome-nickel alloy which does not show any corrosion after more than a four year period of operation.

The operation of the plant has shown that the specific throughput of the plant can be further increased without losses in product quality and HF yield.

The aluminumfluoride plant is owned by the Vereinigte Aluminium-Werke AG, Bonn, Germany and was erected at the VAW Flußspat Chemie GmbH, Stulln/Nabburg.

Acknowledgements

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Recommended Reading

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