FORGING A NEW PATH

Thomas Dahlke,
BUSS ChemTech AG, Switzerland,
explains a more sustainable process for producing hydrofluoric acid.

The production of phosphoric acid (H_3PO_4) and phosphate fertilizers creates silicon tetrafluoride (SiF_4), an off-gas which is toxic for human beings and their anthroposphere. Currently, this problem is resolved by absorbing SiF_4 in water and disposing the formed fluorosilicic acid (FSA) into the sea, storing it in ponds or through neutralisation. With growing awareness of environmental issues however, the pressure on producers to take measures to reduce waste disposal is increasing. As FSA byproducts are large waste streams, their disposal generates considerable costs for producers and minimises overall profit.

Although there is a technology available on the market which can convert FSA to silicon dioxide (SiO_2) and hydrofluoric acid (HF) – the latter a valuable chemical component produced from the mineral fluorspar (CaF_2) – fertilizer and phosphoric acid producers are reluctant to valourise the fluorine in the FSA stream. The focus of the Chinese government on environmental protection in recent years has boosted attention on this technology in the country. Besides the environmental aspects, producers are obliged to extend their value chain. Converting FSA into HF creates added value from phosphate rock, the raw material for H_3PO_4, and removes the costly neutralisation.

Since the 1960s, several patents and ideas have been developed to recover the fluoride from FSA. In 1973, a Polish company patented a process to manufacture HF from FSA and constructed a pilot plant with a capacity of 800 tpy of 70 wt% HF. The plant was operational until

2010 but never intended to be further developed to commercial scale or to promote the process to other phosphoric acid producers.

Traditionally, HF is produced by reacting CaF_2 with sulfuric acid, which creates the byproduct anhydrite ($CaSO_4$). The FSA process needs the sulfuric acid as well but as a 'catalyst' and drying agent only, before being sent back to the phosphoric acid plant. This makes the overall economics of the process more attractive in terms of OPEX. With the current sharp price increase of CaF_2, the payback period for a traditional HF plant may exceed 10 years. By switching to the FSA route it can be reduced to 4 to 5 years or less. Operation and maintenance are simpler and the investment costs (CAPEX) are similar for both processes.

Commercialisation

In 2000, Buss ChemTech AG (BCT) decided to commercialise this process. It was decided, based on market demands, to start with a capacity of 20 000 tpy of HF – a capacity 25 times that of the pilot unit.

This target created questions and unknowns that had to be solved and answered.

The technology transfer from the pilot and understanding the shortcomings of this unit was one crucial step towards a scale-up. It was necessary to obtain an in-depth understanding of the chemistry of the FSA, and the thermodynamic properties and specialities of the phase diagrams and reaction conditions. It quickly became clear that copying the process flow of the pilot plant and enlarging the equipment was not feasible. In laboratory and pilot facilities, numerous experiments were carried out to reproduce the reaction yield under certain conditions. With this practical, laboratory scale work, several of the initial questions could be answered, yet others were generated as a result. Valuable data was created for the later design of the process and equipment.

Several visits of the pilot plant by teams of process, mechanical and automation engineers helped to develop a new FSA process based on the old ideas.

Combating scaling

One of the challenges that had to be overcome was the equipment design for the reaction of dilute FSA with SiF_4 to generate a concentrated aqueous solution with a concentration of more than 45 wt% FSA. This reaction is difficult to handle due to the fact that silica (SiO_2) will form and precipitate. The tendency of scaling was a key issue to be resolved. Standard equipment for gas liquid contacting in absorption towers did not work as they were blocked by SiO_2 crusts within a short operating time. A special rotating contactor device was chosen to overcome the problem. Low concentrated FSA (18 – 22 wt%) is sucked through the device and sprayed evenly within a contactor vessel.

Figure 1. 20 000 tpy HF plant commissioned in 2016.

The droplets react with the SiF_4 and form the layer of SiO_2. Managed by the forced circulation and the flow pattern in the contactor vessel this layer is destroyed permanently. Therefore absorption is not stopped while fine SiO_2 forms and collects at the bottom of the contactor. It is filtered off and can be used in downstream processes.

In order to optimise the contactors for usage with higher gas and liquid flows, full scale experiments were performed in cooperation with a university. The results were compared with computational fluid dynamics (CFD) calculations. Throughput, pressure loss and spray pattern were adapted. Efficiency was enhanced and the design basics were laid out and documented for the scale-up.

In parallel to the experimental work, the process was analysed and optimised by using process simulation software. All these calculations had to be compared with the laboratory results, thermodynamic models for phase equilibrium and other physical properties available for these reactions. The data received and created was used to develop the full mass and heat balance for the process, reflecting BCT's aim to increase the fluorine recovery, and minimise energy consumption and gaseous, solid and liquid byproducts. The mass and heat balance was refined until the calculations aligned with the plant data from the pilot plant. This development work was necessary to assure the scale-up for an optimised plant design to produce HF with a capacity of 20 000 tpy in one step.

In February 2006, a contract to supply the first industrial plant to the Chinese phosphate producer Wengfu (Group) Co. Ltd was signed. The engineering started in mid-2006 and commissioning concluded in mid-2008. Following this, regular exchange between the two companies ensured that new developments were implemented into the process design, the selected material of construction or the operation of the plant. Wengfu operates four plants, with a fifth under construction and due to start operation in late 2019.

Customers outside China have become attentive to this new process and BCT was subsequently awarded a contract to design a plant. The customer had special requirements for byproducts and the reuse of its own sections. A tailored solution was therefore developed where wastewater prevention and high quality HF ($LiPF_6$ specification) were the main drivers. Additionally existing equipment had to be implemented into the design in order to reduce CAPEX.

The work included onsite assessments, as well as reviews of existing equipment, feasibility studies and the basic engineering phase. The feasibility study was completed after three months, and the basic engineering was completed within six months with the handing over of the final basic engineering package.

Conclusion

The FSA process has opened a new route to producing HF. The resources for a cheap and large source of F, the phosphate rock, exceed the resources for CaF_2 and theoretically can replace it as a main source for HF production. When looking at the total world production of HF, only approximately 5% of the amount is produced using the FSA route. The potential for production is, based on the current ore consumption of fertilizer/phosphoric acid producers, higher than the total production of HF worldwide.

With legislation asking for no effluent plants, combined with external pressure for a sustainable and environmentally friendly production, producers are being forced to act. The growing interest of producers in this process show that the environmental issues are being taken seriously. **WF**