Chap 4-5

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HYDROFLUORIC ACID
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Hydrofluoric acid manufacture

A special premixer gives this process important advantages over conventional HF processes.

Anhydrous hydrofluoric acid or hydrogen fluoride was only a laboratory curiosity 30 years ago. Since 1931, however, when it was produced for the first time industrially, it has become an important chemical product. The main uses for HF are in the manufacture of fluorinated hydrocarbons (type Freon), in the manufacture of fluorcarbons and their polymers (type Teflon or Kel-F), as catalyst and reaction medium for alkylation of olefins nd isoparaffins, as fluorinating agent or organic and inorganic fluorides, as eagent in the extraction of uranium nd beryllium, as chemical agent in he separation of zirconium from hafium, of tantalum from columbium nd many others.

HF is a colorless, fuming, extremely orrosive chemical compound. It is one of the few chemicals which react with glass. It has the same specific gravity as water and a boiling point of about 67°F.

Hydrofluoric acid was prepared for the first time almost 200 years ago, by treating fluorspar (calcium fluoride) with concentrated sulfuric acid, according to the endothermic reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2\ HF + CaSO_4 \qquad (1)$$

The reaction is believed to take place in a sequence of steps:

$$CaF_2 + H_2SO_4 \rightarrow Ca\ (HSO_4 \cdot F \cdot HF) \rightarrow$$
$$Ca\ (HSO_4 \cdot F) + HF \rightarrow CaSO_4 + 2\ HF \qquad (2)$$

The byproduct calcium sulfate or anhydrite is recoverable.

The modern type of HF generator is either a long rotary or stationary reactor in which the HF and $CaSO_4$ are produced and removed continuously.

The process to be described was originally developed by the Swiss Engineering Company Buss and is presently used at the Paulsboro, N. J. plant of Dixon Chemical Industries. The reaction takes place in an externally heated rotary kiln, 55-ft. long and 8 ft. in diameter.

The HF formed in the reaction is passed through a series of condensers, absorption towers, and distillation columns for the removal of impurities, while the calcium sulfate or anhydrite obtained as by-product is processed in a subsequent operation into a marketable material of construction.

As distinguished from most conventional HF processes the design and the operating conditions of the plant are such that almost the entire amount of HF is produced as anhydrous acid, rather than various concentrations of aqueous acid.

Raw materials

The raw materials used in the HF process – particularly the fluorspar –

all view of the Paulsboro, New Jersey, hydrofluoric acid manufacturing plant of the Dixon Chemical Co.

must meet rigid specifications with regard to chemical composition and physical structure, to make the reaction as efficient as possible and to keep the side reactions at a minimum. The most undesirable impurities are silica, sulfur compounds, moisture, and calcium carbonate. They lead to side reactions resulting in lower yields and process complications such as:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \quad (3)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (4)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad (5)$$

$$CaS + H_2SO_4 \rightarrow H_2S + CaSO_4 \quad (6)$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \quad (7)$$

It is easy to calculate from reactions 3 and 4 that for each % of SiO_2 present in the spar more than 4% of HF is lost as H_2SiF_6. Moisture formed in reactions 3, 5, and 7 contributes heavily to corrosion; which in any HF process is a problem anyhow, sulfur formed in reactions 6 and 7 plugs up lines and equipment, and CO_2 formed in reaction 5, acting as a non-condensable gas, makes the condensation of HF more difficult. It also consumes additional amounts of H_2SO_4 thus lowering the over-all yields.

Crude fluorspar, as it comes from the mine, varies in calcium fluoride content from about 50 to 90%. To be suitable for HF production the mineral must be upgraded. This is usually done by flotation processes and results in so called "acid-grade" fluorspar, containing about 98% CaF_2, maximum 1% SiO_2, maximum 0.03% sulfur, maximum 1% $CaCO_3$ and maximum 0.1% moisture. Ninety-seven percent or more should pass a 170 mesh screen. This acid grade spar is the raw material used in the HF manufacturing process.

The spar arrives at the plant having the desired chemical purity but being in form of a cake containing about 10% H_2O. It also has a larger particle size than desired.

The first operation at the plant site is the milling and drying of spar, Figure 1. The cake of spar is fed into a flash dryer (1), where the spar is dried to a moisture content of 0.03% by means of direct combustion gases generated in an oil burner unit (2). The dried spar is taken to a ball mill (3) and to a centrifugal classifier (4), and finally to a storage silo (5).

A dust collecting system removes the extremely fine particles from all the units. The recovery of spar is well over 99%.

The second raw material in the process is sulfuric acid. The concentration of sulfuric acid as well as the ratio sulfuric acid/spar are a function of economic and technical considerations that may vary from case to case. Sulfuric acid as low as 93% or as high as 99% can be employed. The more dilute the acid, the more fluid is the reacting mass and the greater the ease with which the liberation of HF takes place; but at the same time the corrosion rate is much higher and an additional amount of water must be disposed of. On the other hand sulfuric acid stronger than 99% has a higher vapor pressure and large amounts of SO_3 will leave the reactor without reacting with spar and contaminate the HF with fluosulfonic acid, the formation of which is more appreciable at higher concentrations. In this process 99% sulfuric acid is used.

The ratio H_2SO_4-spar is usually determined by the relative cost of the two raw materials (spar is more expensive than sulfuric acid) but also by the chemical composition required to assure the quality of the by-product anhydrite.

Due to the fact that the mixture of sulfuric acid and spar has a tendency to form lumps and therefore it is very difficult to obtain homogeneous mix-

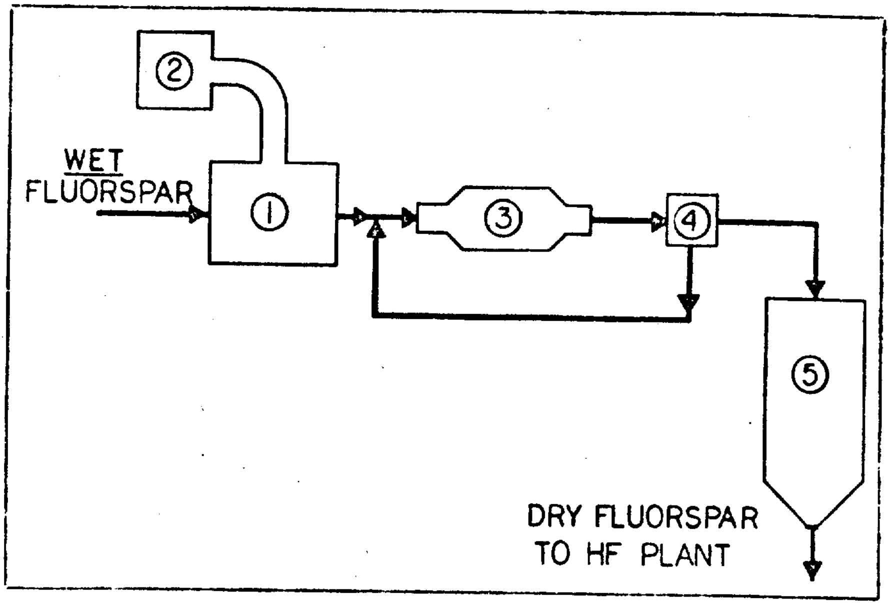

Figure 1. Flowsheet for the milling and drying of spar.

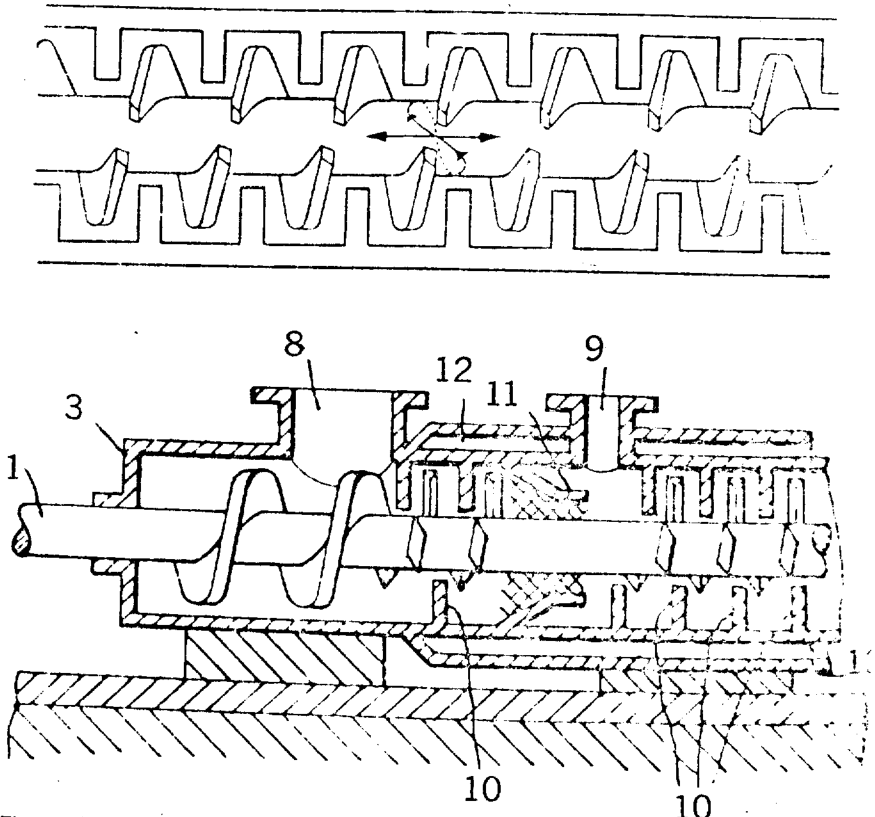

Figure 2. Cross section of the Ko-kneader premixer.

ing of the two materials, most commercial processes use an excess of sulfuric acid up to 10 to 15% over the amount theoretically required. This excess of sulfuric acid is disadvantageous from a corrosion point of view and it also contaminates the HF formed in the reaction. It further makes almost impossible the recovery of anhydrite.

Special premixer

One of the special features of this process is the use of a premixer called Ko-kneader in which the initial reaction between fluorspar and sulfuric acid takes place, Figure 2.

The Ko-kneader was developed by the Buss Co. of Basle, Switzerland. It consists of an interrupted screw conveyor (1) which performs both a rotating and reciprocating movement. There are a number of stationary kneading teeth corresponding to the gaps cut in the screw blade.

The spar and the preheated sulfuric acid fed into the Ko-kneader through inlets (8 and 9) respectively are advanced by the screw and steadily moved forward until the mixture comes against a kneading tooth. The mixture is returned to the previous flight of the screw and moved in form of loops. In this manner, a positive exchange of materials occurs in every direction of the entire length of the casing as shown in the upper portion of Figure 2. This results in an intimate mixing and kneading of the individual particles. Each kneading tooth is therefore, in combination with the relative screw flight, a small mixer, and because there are a large number of these teeth, it is possible to achieve a high degree of mixing even with a relatively short retention time.

The incorporation of the Ko-kneader provides a series of important advantages over conventional HF processes, namely:

1. By conducting the first, most corrosive portion of the reaction in a relatively small piece of equipment (about 6-ft. long by 1 ft. in diameter as compared with the 55 by 8 ft. reaction kiln), the initial investment and replacement cost of corrosion-resistant-alloy parts is kept low and the parts are physically easy to replace.
2. The thorough mixing of sulfuric acid and spar accelerates the subsequent reaction in the kiln, increasing plant capacity as much as 30% for a given kiln size.
3. A much smaller excess (or even stoichiometric amounts) of sulfuric acid can be used, since separation of the two components is no longer possible after leaving the Ko-kneader and a local shortage of sulfuric acid is avoided. This results in better quality HF and in an anhydrite quality suitable for further processing.
4. Due to the perfectly homogeneous mixture of sulfuric acid and spar substantially lower temperatures can be employed in the kiln, whereby: (a) the sulfuric acid has a lower vapor pressure and contaminates the HF stream to a lesser extent and (b) the kiln is subjected to much less chemical attack.

Table 1. Hydrofluoric acid analyses.

Impurities	Before distillation	After distillation
H_2O	0.4%	0.02%
H_2SO_4	0.02%	0.003%
SO_2	0.4%	0.005%
SiF_4	0.01%	0.005%

Table 2. Anhydrite quality specifications.

pH	min. 7
$CaSO_4$	min. 92%
R_2O_3	max. 2%
Fineness, 20% retained	on 170 mesh
H_2O requirement	max. 30%
Setting time, min.	
start	120
end	160
Compressive strength, lb./sq. in.	
3-day	3,500
7-day	4,500

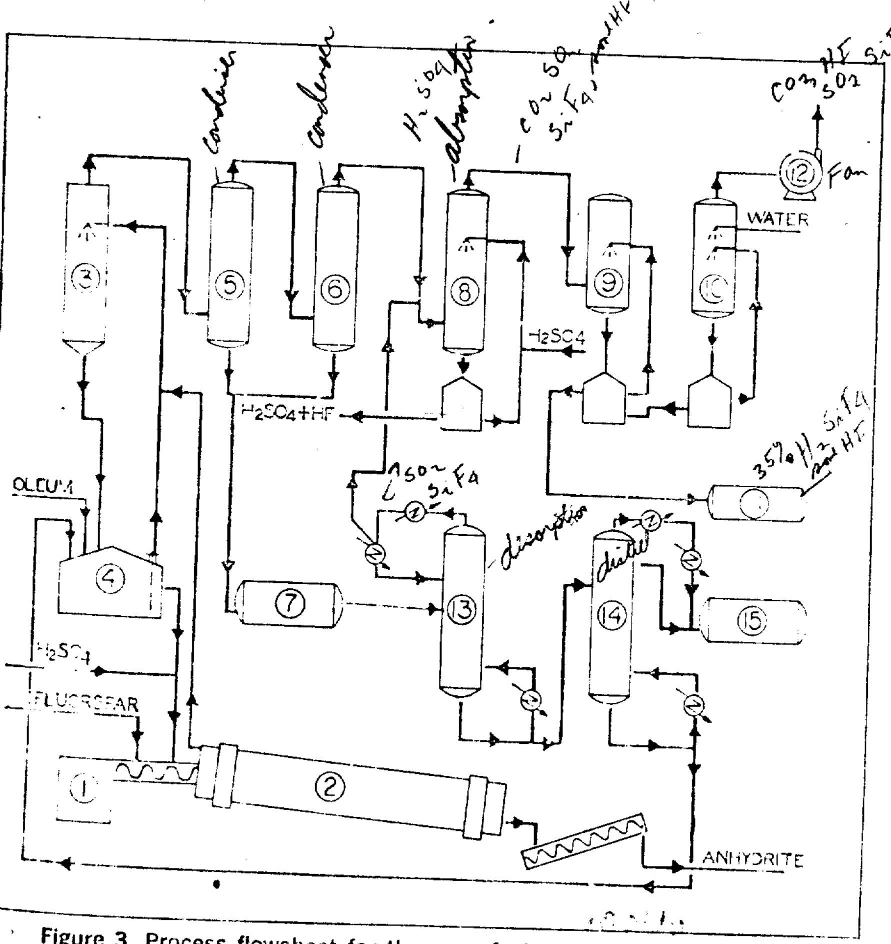

Figure 3. Process flowsheet for the manufacture of hydrofluoric acid.

Process flowsheet

A flowsheet of the entire process is shown in Figure 3. From the Ko-kneader (1) the mixture passes to an externally heated rotary kiln (2). The calcium sulfate leaves the opposite end of the kiln through a seal screw and enters the anhydrite section of the plant, which will be described later.

The HF gases containing all the by-products formed in the side reactions, *i.e.* H_2O, SO_2, SiF_4, S, CO_2 as well as small amounts of unreacted spar and sulfuric acid, and calcium sulfate, leave the feed end of the kiln and enter the lower part of a tube and shell precondenser (3) where the gases are freed from solids (spar, anhydrite, sulfur) by cyclone action plus washing with liquid condensing from the upper tube-and-shell section. The washing effect is supplemented by liquid continuously circulated to the scrubbing section of the precondenser from an intermediate tank (4).

The upper section of the precondenser (3) is a water cooled tube-and-shell heat exchanger, the function of which is to condense water and sulfuric acid out of the HF stream. A certain percentage of HF is condensed together with the liquid impurities and this is the solution used for the removal of solids.

The condensed stream from the pre-

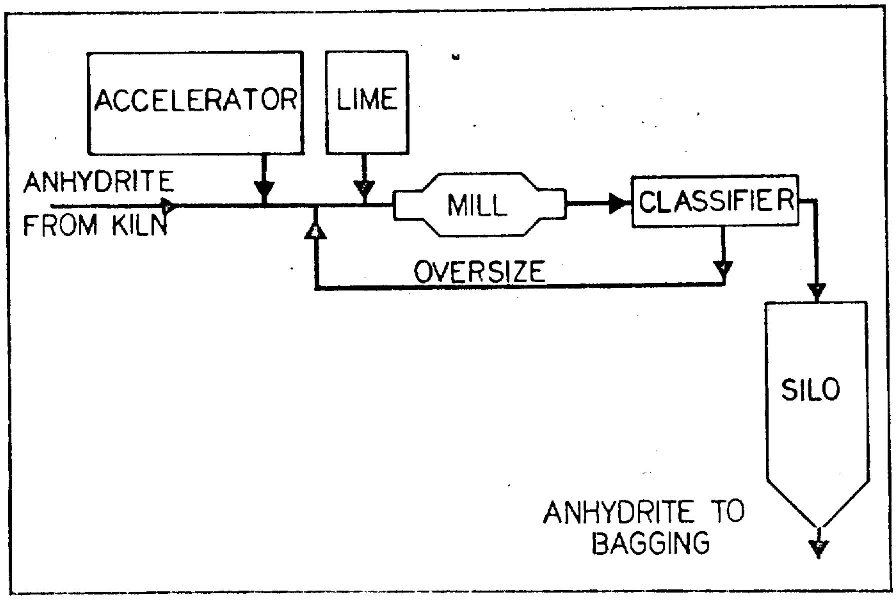

Figure 4. Anhydrite recovery flowsheet.

condenser enters the intermediate tank (4) to which a measured amount of 20% oleum is added to combine the water in the system.

The HF vapors, from which most of the H_2O and H_2SO_4 has been removed are subsequently condensed in two tube-and-shell condensers (5 and 6) installed in series. The crude condensed hydrofluoric acid represents almost 98% of the production. It flows by gravity into intermediate storage tanks (7) and is later distilled.

Absorption and distillation

The uncondensed gases from condensers (5 and 6) enter an absorption tower (8) where they are washed with fresh sulfuric acid. The absorption acid is circulated by means of submerged pumps and enriched up to an HF content of about 25%. The HF is subsequently desorbed and recovered as anhydrous acid while the sulfuric acid is used for absorption of additional amounts of HF.

The gas stream leaving the sulfuric acid absorption tower (8) contains small amounts of HF, and practically the entire amount of SiF_4 present in the process, as well as the rest of noncondensable gases including SO_2 and CO_2. It enters the first of two packed absorption towers installed in series (9 and 10). Measured amounts of water are fed to the second of the two towers and after circulating through the two towers by means of submerged pumps, the "weak" acid leaves the first tower and flows by gravity into a lined storage tank (11). It contains 30 to 35% fluosilicic acid and small amounts of HF, and is subsequently used as raw material for other products. The limited amount of HF is of SiO_2 and plugging of lines, according to the reaction:

$$3SiF_4 + (x+2)H_2O \rightarrow 2H_2SiF_6 + SiO_2 \cdot x\,H_2O \qquad (8)$$

The gases leaving the top of the last absorption tower contain CO_2, as well as traces of HF, SO_2 and SiF_4. They are vented through a stack, after passing an exhaust fan (12) which creates a slight vacuum throughout the system.

The crude HF obtained from the two condensers is distilled in two distillation columns to a purity of 99.98% or better.

The low boiling impurities, *i.e.*, SO_2 and SiF_4 are removed in a packed desorption column (13). These overhead gases (also containing small amounts of HF) are returned to the HF absorption tower (8) where the HF is recovered. The sump product of the first column is sent to the second distillation column (14) which is a rectifying packed tower working under partial reflux. The condensed boil off is the pure HF. The uncondensed vent gases are returned to the HF absorption towers for recovery of HF, and the H_2SO_4, H_2O and HF-containing-sump is pumped to the intermediate receiver tank (4) for recovery of HF and the use of the H_2SO_4 in the process. Thus, the process operates in closed circuit, with full recovery of all materials, with the exception of insignificant amounts of HF leaving the process stack.

Table 1 shows the typical analyses of HF prior to distillation and after distillation.

The amount of impurities can be lowered appreciably just by slightly varying some of the operating conditions, *e.g.* the temperatures in the kiln, precondenser, condensers, distillation columns, the reflux ratio in the distillation column, the ratio sulfuric acid/oleum, etc.

Anhydrite by-product

As mentioned before there is an important by-product obtained in this hydrofluoric acid process, namely calcium sulfate or anhydrite. This material, which in most HF plants is a waste product presenting many problems connected with its disposal, affects very favorably the economic balance of the plant, because it commands a growing market as a high strength building material. It constitutes another attractive feature of the process. Its continuous production is made possible, among other possible variables, by the use of the Ko-kneader.

As shown in Figure 4, the anhydrite leaves the kiln through a seal screw. It contains a small, well established, percentage of unreacted sulfuric acid. After proper amounts of lime for neutralization and an accelerator have been added, the anhydrite is conveyed to a ball mill, where it is ground to the standard commercial fineness. A classifier separates the fines from the coarse material, the latter being returned to the mill. The fines are sent to a storage silo and from there to the bagging section.

The physical and chemical characteristics of the final anhydrite are shown in the Table 2.

Materials of construction

The various pieces of equipment in the entire spar milling and drying section, as well as in the anhydrite section, are made of carbon steel. Also ma carbon steel are the rotary kiln, the HF condensers, and parts of the distillation column. The scrubbing sect of the precondenser, the intermedi receiving tank, the sulfuric acid p heater, and the bottom of the se distillation column, in other words units where corrosive mixtures of HF, H_2SO_4 and H_2O are handled and t temperatures are around 200°F higher, are made of Hastelloy, M or equivalent alloys. The Ko-knead is made of Maustinox XD, a Ger Ni-Cr-Mo Alloy. Lead, carbon plastics such as PVC, Saran and Te