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## FLUORINE ABSORPTION AND INDIRECT CONDENSATION IN WET PROCESS PHOSPHORIC ACID CONCENTRATION

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Wet-process phosphoric acid, produced by digestion of rock phosphate with sulphuric acid, contains 28-32%  $P_2O_5$  by weight, 1-2%  $H_2SiF_6$ , 2-4%  $H_2SO_4$  and other contaminants.

A common process for concentration of phosphoric acid to 50-54% is by flash evaporation under vacuum. The solution is circulated, through a heat exchanger, to the flash chamber where under the prevailing vacuum intensive boiling takes place and water vapors, accompanied by HF and  $SiF_4$  gases, are removed.

In the concentration units, which were previously at work in F & C, the water vapors were conventionally condensed, in barometric condensers, in direct contact with water.

The main disadvantages of these units were the consumption of large amounts of potable water used for vapor condensation and then discarded to sewer, thus causing pollution of the environment by fluorine compounds involving costly disposal treatment.

The principal aim of the project, carried out at F & C premises, was to develop a unit that would condense the vapors indirectly, without contaminating the cooling water.

In order to minimize the heat transfer area, the vapors from the flash chamber had to be saturated by a scrubber which at the same time absorbed the fluorine values.

A one-stage phosphoric acid concentration unit at F & C, with a capacity of 20 tons  $P_2O_5$  per day, was converted to operate as a pilot plant which employed a vapor scrubbing apparatus and a surface condenser, designed by the new method.

After the successful operation of the pilot plant for over two years, a one-stage concentration unit, with a capacity of 65 tons  $P_2O_5$  per day, designed in accordance with the new technique developed and erected by the local engineering staff, started its smooth operation in April 1978.

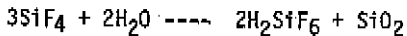
### THE PROCESS

The main principle in the process is to maintain the HF/ $SiF_4$  molar ratio at a desired level throughout the unit, in order to avoid silica precipitation.

It is known that above 50%  $P_2O_5$  in the phosphoric acid circulated, the vapors evolving from the flash chamber contain fluorine compounds with an HF/SiF<sub>4</sub> ratio of 2 or above, so forming fluosilicic acid, H<sub>2</sub>SiF<sub>6</sub> :



At a phosphoric acid concentration less than 50% the ratio falls below 2, the excess SiF<sub>4</sub> forming SiO<sub>2</sub> precipitate when coming in contact with water:



Silica precipitate, especially in the condenser, may lead to a rapid clogging of the tubes and consequently cause a shut-down of the concentration unit. Indirect condensation has not previously been used, mainly for the reason that any SiF<sub>4</sub> not removed during scrubbing is likely to block the condenser tubes. However, no precipitation will occur if the right conditions are retained throughout the process.

A flow diagram of the process is shown in Fig. 1.

This method can be employed for one-stage concentration of all kinds of phosphoric acids regardless the source of the phosphate rock and its SiO<sub>2</sub> content.

The vapors leaving the flash chamber are passed into a scrubber where fluorine is removed, by a countercurrent flow of fluosilicic acid, 18% H<sub>2</sub>SiF<sub>6</sub>, at 96% absorption efficiency. The solution itself may be concentrated up to 25%, but above 18% H<sub>2</sub>SiF<sub>6</sub>, fluorine recovery is reduced as the fluorine content increases in the scrubbing solution.

This scrubbing apparatus has a unique design in order to achieve a high absorbing efficiency and an excess of free HF in the vapors at the scrubber's exit, this accomplished by cooling the circulated fluosilicic acid.

The amount of water for the solution's make-up is introduced by partial condensation of an equivalent amount of water vapors. This maximizes the absorption efficiency, according to fluorine vapor pressure equilibrium dynamics at the prevailing conditions, where the water drop condensed, in equilibrium with the vapors, is richer in fluorine content than the vapors. The equilibrium diagram is illustrated in Fig. 2. The cooling of the scrubbing liquor also contributes to vacuum building in the equipment.

The vapors leaving the scrubber come in contact with liquid which has a considerably lower F concentration than the circulated solution. The lower the % F in the liquor, the higher is the molar ratio HF/SiF<sub>4</sub> in the vapors in equilibrium with the liquid (as indicated in Table 1), thus acting as a better safeguard against SiO<sub>2</sub> clogging in the condenser tubes.

$\frac{\text{HF}}{\text{SiF}_4}$ molar ratio in vapor	3	7	13
$\text{H}_2\text{SiF}_6$ % in solution	10	5	1

Table I.

Vapor equilibrium over  $\text{H}_2\text{SiF}_6$  solution

The most common process in industrial use for removing fluorine in phosphoric acid vacuum-concentrators is the Swift process. Both this system and the modified Swift process developed by Swenson have a reported fluorine recovery efficiency of 92-95% with product concentration of 15%  $\text{H}_2\text{SiF}_6$ . All the systems discussed above employ barometric condensers.

The vapors, being desuperheated in the scrubber, require minimum heat transfer area in the surface condenser. The condensing occurs in a shell-and-tube heat exchanger cooled by a closed circuit cooling water via a conventional tower.

The process condensate leaving the concentration unit contains only 0.2% F and can be recycled to the phosphoric acid production unit, thus totally eliminating the pollution problem and increasing the fluorine recovery.

We believe that this technique, developed at F & C, is economically preferable to systems employing closed circuit barometric condensers via acidic cooling towers or ponds. The latter systems have larger capital and maintenance costs due to more expensive building materials and sedimentation disposal, in addition to the entrainment of acidic droplets from towers. Units operating with pond water require a higher power consumption.

The new process enables F & C to save 50 m<sup>3</sup> of water per ton  $\text{P}_2\text{O}_5$  concentrated, to eliminate totally environmental pollution caused by phosphoric acid concentrators, considerably reducing effluent disposal treatment costs in the factory, and to produce 50 kg fluorine per ton  $\text{P}_2\text{O}_5$  as fluorides and fluosilicates.

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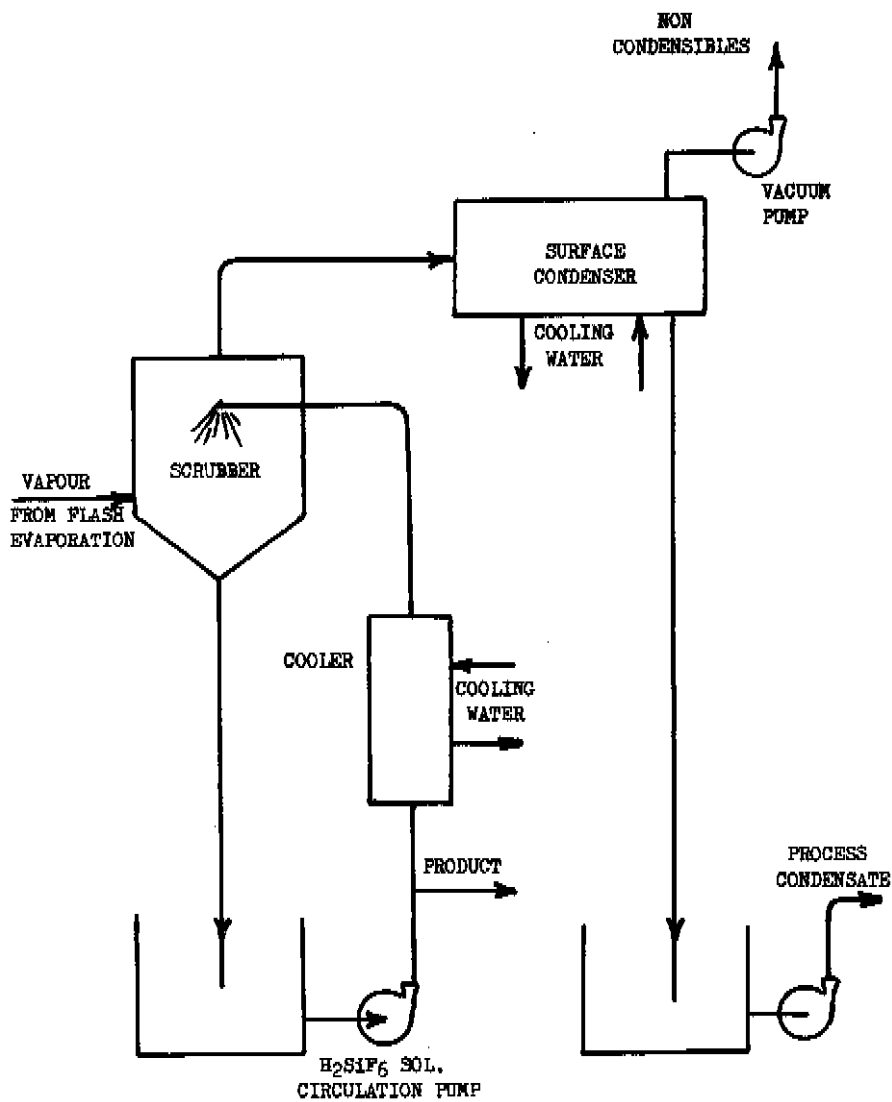


FIG. 1 - PROCESS FLOW DIAGRAM

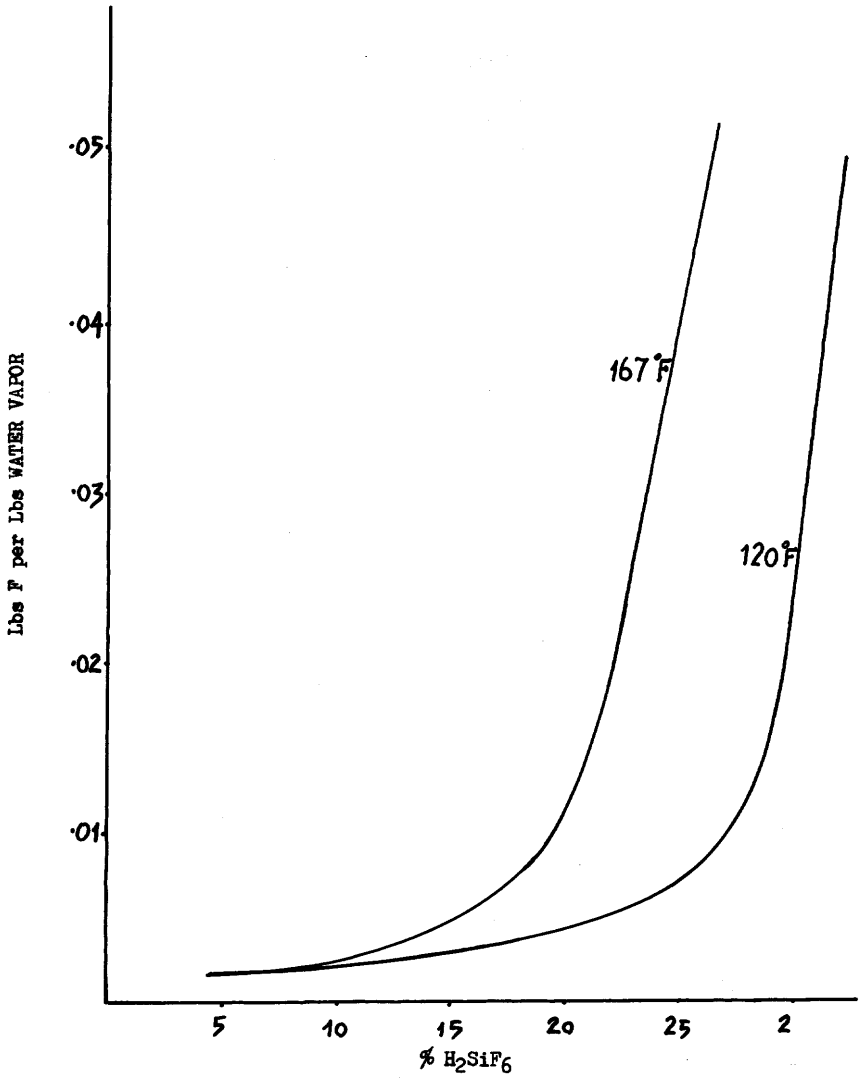


FIG. 2 - EQUILIBRIUM OF HF AND SiF<sub>4</sub> AS F  
OVER BOILING SOLUTION OF H<sub>2</sub>SiF<sub>6</sub>