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Recovery and valorization of fluosilicic acid from phosphoric acid plant for the production of concentrated hydrochloric acid

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Abstract: Fluosilicic acid is the main fluoride waste water on phosphoric acid production. This effluent is simply discharged into the sea from phosphoric acid plant in Senegal. The disposal of this effluent is an ever more serious environmental problem for phosphoric acid manufacturers. In fact large amount of fluosilicic acid is discharged into the sea. Therefore our attention has been focused on developing process for working-up this fluorine waste by producing hydrochloric acid. Through laboratory research, we have been able to use a water treatment plant containing fluosilicic acid in a 25% solution in order to produce hydrochloride acid in a 33% solution.

Keywords: fluosilicic acid, hydrochloric acid, phosphoric acid, production

Recuperation et valorisation de l'acide fluosilicique dans la production de l'acide phosphorique pour la production d'acide chlorhydrique concentre

Résumé: L'acide fluosilicique est le plus important déchet fluoré dans la production d'acide phosphorique. Cet effluent est simplement déchargé en mer au Sénégal. L'élimination de cet effluent est un souci environnemental pour les usines de superphosphates. En effet des qualités importantes d'acide fluosilicique sont déchargées dans la mer. Pour cette raison, notre attention a été attirée par la mise en place d'un procédé de traitement de ce déchet fluoré en produisant de l'acide chlorhydrique. À partir de recherche de laboratoire, nous avons pu utiliser une solution aqueuse traitée d'acide fluosilicique à 25% pour produire une solution d'acide chlorhydrique à 33%.

Mots clés : acide fluosilicique, acide chlorhydrique, acide phosphorique, production

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1. Introduction:

The only economic alternative way to produce phosphoric acid is “wet process”. When sulfuric acid is used to attack phosphate rock which contents calcium fluoride, it results polluting streams such as silicon tetrafluoride and hydrogen fluoride[1]. The combination of these gaseous and the absorption of silicon tetrafluoride by water generates fluosilicic acid solution[2]. In Senegal, fluosilicic acid (as a by-product of phosphoric acid production) is discharged into the sea in large quantities[3]. Elsewhere fluosilicic acid is an interesting raw material for manufacturing a range of chemicals. In fact several different articles relate working-up fluosilicic acid solution[4], manufacturing processes of sodium fluosilicate[5], hydrochloric acid[6] and sodium hydroxide[7]. From fluosilicic acid, which is only adverse by-product of phosphoric acid production[8], it is possible to produce mixture of fluorine compounds and amorphous silica[9] or calcium silicate and calcium fluoride usable in cement industry[10].

2. Theory

Hydrochloric acid is a versatile chemical used in a variety of chemical processes. The open world market size is estimated at 5 mt/year[11]. The main process which is used to produce hydrochloric acid is the absorption of hydrogen chloride. It is known that hydrogen chloride is produced by the combination of hydrogen and chloride. The absorption of hydrogen chloride generates hydrochloric acid in a 37% aqueous solution[12]. Hydrochloric acid may be manufactured by the reaction of metallic chlorides, as a byproduct of chlorination, the thermal decomposition of the hydrated heavy-metal chlorides, and the incineration of chlorinated organic waste[13].

In this work, fluosilicic acid attacks sodium chloride to produce hydrochloride acid approximately in an azeotropic composition. Azeotropic distillation is then used for obtaining the product in a 30%-33% solution. The proposed method of distillation includes a phase of absorption which uses sulfuric acid.

3. Methodology

3.1. Recovery of fluosilicic acid

The fluosilicic acid in a 25% solution is recovered from the production of a phosphoric acid industry in Senegal. During the production of phosphoric acid from fluorapatite and sulfuric acid, the calcium fluoride present in the rock is converted, by reaction with the silica also present, into fluosilicic acid according to the following equations:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4.2H_2O + 6H_3PO_4 + 2HF$$ **(Reaction 1)**

$$3CaF_2 + 3H_2SO_4 + 4H_2O + SiO_2 \rightarrow 3CaSO_4.2H_2O + H_2SiF_6$$ **(Reaction 2)**

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

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$ **(Reaction 4)**

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$ **(Reaction 5)**

$$3SiF_4 + 6HF \rightarrow 3H_2SiF_6$$ **(Reaction 6)**

During reaction of the phosphate rock with sulphuric acid, hydrogen fluoride evolves and reacts with the silica contained in the phosphates and forms gaseous silicon-tetrafluoride (SiF_4) and fluoslicic acid (H_2SiF_6). The fluorous gases are withdrawn into a ventilation pipe to an absorption unit and are utilized for making fluosilcic acid.

3.2. Tranformation of fluosilicic acid

Fluosilicic acid is transformed into hydrochloric acid according to **Reaction 7:**

$$H_2SiF_6 + 2NaCl \rightarrow 2HCl + Na_2SiF_6$$ (**Reaction 7**)

Experiments were carried out in a batch reactor (250 mL) where 35 g of technical-grade sodium chloride (90%) were attacked by 125 mL of fluosilicic acid in a 25% solution. The hydrochloride acid in 18% aqueous solution near to its azeotropic composition (20%) and the sodium fluosilicate were separated by filtration using a diaphragm pump. The cake which mainly composed of sodium fluosilicate was washed with water and dried in a MEMMERT furnace at 100 °C and was used to produce caustic soda[6, 10].

3.3. Azeotropic distillation of hydrochloric acid

Sulfuric acid was used to crack the azeotropic compound produced by **Reaction 7**. The gaseous compound of hydrochloric acid was absorbed by an aqueous hydrochloric acid solution. **Figure 1** is the schematic which illustrate the process of producing concentrated HCl. Several experiments were carried out to investigate the

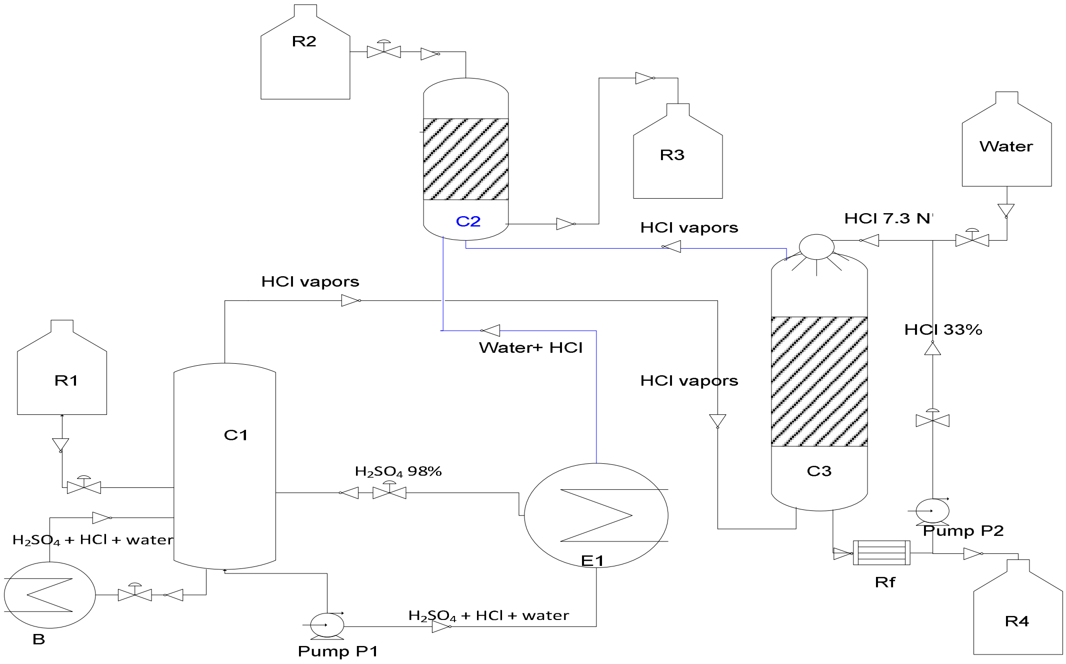

Fig. 1: Schematic showing the process of producing concentred HCl

Table I : Operational parameters

Samples	Volume of diluted HCl (mL)	Volume of H_2SO_4 (mL)	Volume of absorbing HCl (mL)
Sample 1	80	30	80
Sample 2	80	60	80
Sample 3	80	90	80

operational conditions as quantity of H_2SO_4 and recycled HCl.
Experiments were carried out with a fixed volume of HCl (18%), variable volumes of H_2SO_4 (98%) and an absorption with of HCl 7.3 N. These compounds were produced from PANREACT QUIMICA (Barcelona, Spain). Table 1 shows the operational parameters.

4. Results and discussions

4.1. Determination of the mass transfer coefficient

The macroscopic balance of sodium chloride in the absence of reaction can be written by the following equation:

$$\frac{VdC_s}{dt} = K_c a N(C_s^* - C_s) \qquad \textbf{(Eq. 1)}$$

where :
V is the volume of the aqueous solution;
C_s is the concentration of sodium chloride;
T is the time of the mass transfer;
K_c is the mass transfer coefficient;
a is the interfacial area of the spherical particle of sodium chloride ;
N is the number of particles of sodium chloride;
C_s^* is the concentration at the saturation of sodium chloride (at 25°C) $C_S^* = 360$ g/L;

C_s is the concentration at the saturation of sodium chloride.
Equation 1 can be written as:

$$\frac{dC_s}{dt} = \frac{3m_s K_c}{V r_0 \rho_s}(C_s^* - C_s)r^2 \qquad \textbf{(Eq.2)}$$

Where: $C_s = \frac{m_s - m_r}{V}$ **(Eq. 3)**

(m_s- m_r : the mass of sodium chloride which is dissolved)

Then: $C_s = \frac{4\pi r_0^3 N \rho_s}{3V}\left[1 - \left(\frac{r}{r_0}\right)^2\right]$ **(Eq. 4)**

Also: $C_s = \frac{m_s}{V}\left(1 - \frac{r^3}{r_0^3}\right)$ **(Eq. 5)**

The obtained relationships are

$$\begin{cases} \frac{dC_s}{dt} = \frac{3m_s K_c}{V r_0^3 \rho_s}(C_s^* - C_s)r^2 \\ \frac{dr}{dt} = -\frac{K_c}{\rho_s}(C_s^* - C_s) \end{cases} \qquad \textbf{(Eq. 6)}$$

Then:

$$\left(1 - \frac{C_s}{C_s^*}\right)^{-\frac{2}{3}} - 1 = \frac{2K_c C_s^*}{\rho_s r_0} t \qquad \textbf{(Eq. 7)}$$

The determination of the mass transfer coefficient during the dissolution of sodium

chloride in the aqueous solution requires the following graph (**Fig. 2**).
The obtained coefficient (K_c=2.2.10^{-6} m.s^{-1}) corresponds to the kinetic of transfer during the first steps of the dissolution what really reflects the exchange of material observed at the level of the reactor. Indeed the dissolution is so fast that if we exceeded the very first moments of the operation the coefficient of transfer would be practically unimportant because there would not be exchange anymore of material.

4.2. Duration of the mass transfer

The reaction between the fluosilicic acid and the sodium chloride was in a physical scheme.
The main phenomenon was the mass transfer of the sodium chloride into the aqueous solution. The equation of the instantaneous mass transfer is:

$$\frac{dm_s}{dt} = -K_c A C_S^* \quad \textbf{(Eq. 8)}$$

Also: $\frac{\rho_s d(NV_p)}{dt} = -K_c a N C_S^*$ **(Eq. 9)**

Then: $\rho_s a dr = -K_c a C_S^* dt$ **(Eq. 10)**

The time of the mass transfer is $t = \frac{r_0 \rho_s}{K_c C_S^*}$ **(Eq. 11)**

With the following parameters:
Sodium chloride density $\rho_s = 2165$ kg/m^3
Sodium chloride size r_0 = 0,25 mm
Concentration at the saturation of sodium chloride (at 25°C) C_S^* = 360 g/L
Mass transfer coefficient of sodium chloride K_C = 2.2.10^{-6} m/s
The value of the mass transfer duration (t = 11,24 min) confirms the speed of the reaction as we have already suggested it through the hypotheses of an immediate reaction which generates hydrochloric acid in a 18% aqueous solution. This aqueous solution is concentrated by an azeotropic distillation by using sulfuric acid to obtain hydrochloric acid in 30%-33% solution.

4.3. Optimization of the hydrochloric/sulfuric acid ratio

Table 2 shows the influence of the quantity of sulfuric acid on the azeotropic distillation. The optimization highlights a volume ratio of 1.33 which is more favorable for the azeotropic distillation considering the produced hydrochloric acid (30.9%) and the yield of production (59.5%). However, there were some lost quantities of hydrochloric acid which were caused by a low anchorage rate in the absorption column C2 (Fig. 1).

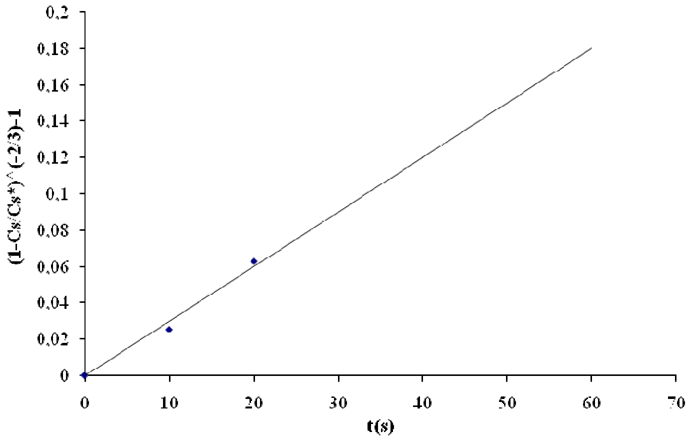

Fig. 2: schematic showing the evolution of [$(1 - \frac{C_S}{C_S^*})^{-2/3} - 1$] with the time when sodium chloride is dissolving in water

Table II: Influence of the quantity of sulfuric acid on the azeotropic distillation

Samples	Volume of HCl (mL)	Density of HCl (kg/m^3)	Yield of HCl (%)	Percentage of HCl (%)
Sample 1	85	1140	53.7	28.1
Sample 2	80	1149	59.5	30.9
Sample 3	75	1143	48.5	31.1

5. Conclusion

According to this study, it is possible to recovery and to work-up fluosilicic acid from phosphoric acid plant for the production of a wide variety of chemicals. The production of a concentrated solution of hydrochloric acid is confirmed through laboratory experiments which lead to a yield of about 60%. This production consists on transforming fluosilicic acid in a 25% solution into hydrochloric acid in a 18% solution and is completed by the concentration of the solution of hydrochloric acid with an azeotropic distillation which use sulfuric acid. However it is necessary to refine the obtained results with a continued process on a pilot installation. Indeed the industrial valorization of fluosilicic acid will require a continued process which is more efficient.

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