



Processes for working-up an aqueous fluosilicic acid solution

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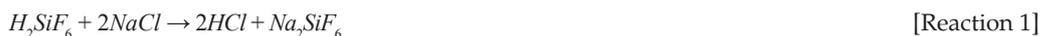
Aqueous fluosilicic acid solutions were once considered to be only adverse by-products of phosphoric acid production, which required treatment to prevent ecosystem destruction when discharged into the sea. However, a range of chemicals can be generated by the transformation of this industrial waste product. Through experiments undertaken in the laboratory, we have shown the possibility of caustic soda production. Volumetric analysis showed caustic soda to be present as a 6% – 7% solution with yields of about 70% – 80% by weight. Two processes were investigated for the caustification of sodium fluoride, using different precipitates: sodium chloride and ethanol and are described by modelling caustification curves. The activation energies of precipitation determined by semi-empirical correlations showed that precipitation by ethanol ($E_A = 933.536$ J/mol) was more successful than precipitation by sodium chloride ($E_A = 7452.405$ J/mol). Analyses performed on the precipitates highlighted compositions that are essential and useful constituents in the cement industry.

Introduction

In Senegal, fluosilicic acid (as a by-product of phosphoric acid production) is discharged into the sea. In order to avoid maritime ecosystem destruction, the fluosilicic acid must be treated beforehand. In this study, we aimed to work-up an aqueous fluosilicic acid for the production of caustic soda in an 8% solution and a mixture of calcium fluoride and silica by using sodium fluosilicate. This fluosilicate is attacked by lime to produce caustic soda and a precipitated mixture which can be useful in the production of white cement. Several articles describe the manufacturing processes of sodium fluoride,¹ sodium hydroxide,² hydrochloric acid,³ aluminium fluoride and mixtures of calcium fluoride and silica usable in the cement industry.⁴

Theory

The treatment of fluosilicic acid occurs via several processes. Fluosilicic acid (H_2SiF_6) is converted into sodium fluosilicate (Na_2SiF_6) as shown by [Reaction 1]:



The most popular process of sodium hydroxide (NaOH) synthesis from sodium fluosilicate is known as the Kiflu process.⁵ The process of the synthesis of sodium fluoride (NaF) from sodium fluosilicate was proposed by Stevenson⁶. These processes can be problematic because of the energy consumed and the pollution produced, so we have developed an alternative method of sodium fluoride synthesis. This proposed method involves the reaction of sodium fluosilicate with calcium hydroxide ($Ca(OH)_2$) according to [Reaction 2]:



Because of sodium fluoride's low solubility in water⁷ after caustification, a non-significant concentration of sodium hydroxide is produced. In this study, two methods of sodium fluoride precipitation were investigated. The first method consisted of adding sodium chloride (NaCl) as it is more soluble in water than is sodium fluoride.^{8,9} The second method includes the addition of ethanol into the solution as sodium fluoride is insoluble in alcohols.¹⁰ The precipitate of sodium fluoride is separated by filtration of the suspension. It can then be transformed into sodium hydroxide by lime as shown by [Reaction 3]:



For these processes to be effective, the quantity of the precipitants and the temperature at which the reaction occurs must be optimised.

Material and methods

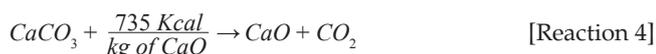
Experimental set-up

Experiments were carried out in a batch reactor (250 mL) agitated by a magnetic stirrer with a heater (Magnetic N from P Spectra, manufactured by JP Selecta S.A., Barcelona, Spain). The products were separated by filtration using a diaphragm pump (Vacuubrand GMBH + CO, Wertheim, Germany).

Compound synthesis of caustic soda

Sodium fluosilicate was produced from fluosilicic acid (25% H_2SiF_6 recovered from a phosphoric acid plant) and technical-grade sodium chloride according to [Reaction 1]. The cake which was produced was mainly composed of sodium fluosilicate and was washed with water and dried in a Memmert furnace (Fisher, Illkirch, France) at 100 °C.

The limestone (57.5% of CaO) utilised in this study was extracted from a mine in the west of Senegal. The quick lime was produced by decomposing limestone at 900 °C for 2 h in a Carbolite OAF 11/1 furnace (Fisher, Illkirch, France) according to [Reaction 4]:



This lime is then hydrated to obtain calcium hydroxide by [Reaction 5]:



Experimental methods

Caustification of sodium fluoride precipitated by sodium chloride

An aqueous solution of sodium fluoride was obtained by reacting 21 g \pm 0.001 g of sodium fluosilicate (90%) and 17 g \pm 0.001 g of calcium hydroxide (96%) in 200 mL \pm 0.2 mL of water, as illustrated in Figure 1.

The main parameter optimised in this process was the amount of sodium chloride introduced to the aqueous solution of sodium fluoride: 14 g, 28 g, 42 g, 56 g and 70 g (\pm 0.001 g). Other variables included temperature and reaction time. Precipitation was carried out in 200 mL \pm 0.2 mL of sodium fluoride. The precipitate was then treated by 7.5 g \pm 0.001 g of calcium hydroxide in 100 mL \pm 0.2 mL of water. Figure 2 shows the experimental procedure that was used for this caustification process.

Caustification of sodium fluoride precipitated by ethanol

The volume of ethanol (ranging from 100 mL to 500 mL in increments of 100 mL \pm 0.2 mL) was the essential parameter optimised for this process. The other parameters were identical to those used in the above caustification process. Figure 3 illustrates the experimental set-up for the caustification of sodium fluoride precipitated by ethanol.

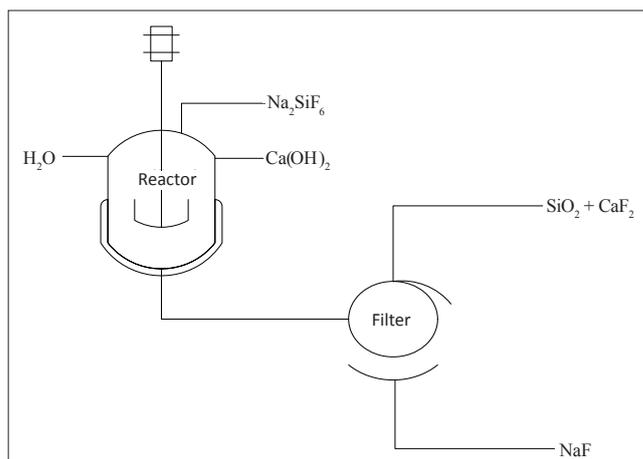


FIGURE 1: A schematic showing the process of producing sodium fluoride solutions.

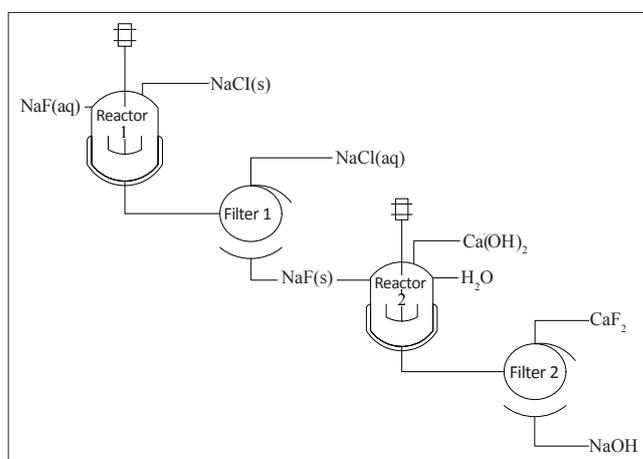


FIGURE 2: A schematic of the caustification of sodium fluoride precipitated by sodium chloride.

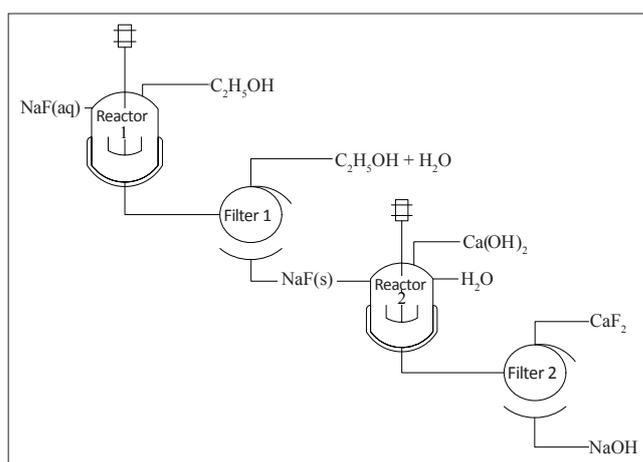


FIGURE 3: A schematic of the caustification of sodium fluoride precipitated by ethanol.

Analytical methods

Normalities of the sodium hydroxide produced were estimated by volumetric analysis using a hydrochloric acid solution with normality of 0.1 N \pm 0.01 N.

The mixture of calcium fluoride and silica was characterised by X-ray fluorescence using an ARL 9800 XP analyser (Thermo ARL, Ecublens, Switzerland).



Results and discussion

Caustification of sodium fluoride precipitated by sodium chloride

Product characterisation

Sodium fluoride solutions were obtained at 25 °C, 50 °C and 80 °C according to the experimental method illustrated in Figure 1. The pH and density measurements of these sodium fluoride solutions are reported in Table 1.

Optimisation of operating parameters

Improvements in precipitation (measured by weight) were achieved by increasing the quantity of sodium chloride and the temperature (Table 2).

Table 2 shows that more sodium fluoride was precipitated by adding 70 g ± 0.001 g of sodium chloride. Knowing that the solubility limit of sodium chloride in an aqueous medium is about 360 g/L at 20 °C, we used a volume of sodium fluoride of 200 mL ± 0.2 mL and introduced 70 g ± 0.001 g of sodium chloride. At this quantity of sodium chloride, the solution tended to its limit of sodium chloride solubility and all the sodium fluoride was precipitated.

Caustification tendencies were similar for temperatures of 25 °C, 50 °C and 80 °C. However, operation at 50 °C or 80 °C produced a more concentrated caustic soda. The choice between these two temperatures would thus depend mainly on energy costs and the filtration facility.

The solubility of sodium chloride is improved when the temperature is increased.⁹ Hence, the temperature and the amount of the solubility suppressant act antagonistically in the precipitation of the completely dissolved sodium fluoride. Fortunately, at all temperatures investigated, the caustic soda concentrations obtained increased with increasing temperature and the amount of solubility suppressant.

Product analysis

Caustic soda: Volumetric dosages of caustic soda enable the identification of caustic soda in a 6.1% solution with a yield

TABLE 1: Characterisation of sodium fluoride solutions.

Solution temperature (°C)	Density (g/cm ³)	pH (± 0.01)
25	1.01	7.34
50	1.04	7.38
80	1.50	7.40

TABLE 2: Influence of sodium chloride on caustification at 80 °C.

Mass of NaCl (g)	Volume of NaOH (mL)	Density of NaOH (g/cm ³)	Normality of caustic soda (N)	NaOH (%)	Yield of NaOH (%)
14	90	1.031	0.80	3.10	40.3
28	90	1.048	1.09	4.16	50.1
42	88	1.056	1.48	5.61	64.8
56	88	1.057	1.58	5.98	69.2
70	86	1.058	1.62	6.13	69.3

TABLE 3: Composition of the mixture of silica and calcium fluoride.

Molar ratio	Oxide (%)									Element (%)	
	CaO	SiO ₂	MgO	SO ₃	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	Na ₂ O	Cr ₂ O ₃	F	
Ca ²⁺ /SiF ₆ ²⁻	18.9	9.9	0.36	0.3	550 ppm	–	–	8.65	6 ppm	61.7	

of 70%. Caustification of sodium fluosilicate can generate silica in the caustic soda produced. The amount of silica generated depends effectively on the stoichiometry of the reaction and the nature of the limestone or lime that is used.¹¹ The caustification of sodium fluoride precipitated by sodium chloride produces caustic soda without silica in solution.

Mixture of calcium fluoride and silica: The mixture of calcium fluoride and silica, generated by the caustification of sodium fluoride at 80 °C for 2 h and at 50 °C for 3 h, was characterised by X-ray fluorescence, the results of which are reported in Table 3.

This mixture of calcium fluoride and silica can replace the calcium fluoride that is used in the production of white cement. This replacement would be beneficial because the use of calcium fluoride can lead to corrosion problems.

Modelling caustification

With a practical use in mind, we have developed a semi-empirical model which relays the normality of the final solution to the mass fraction of sodium chloride and the temperature [Eqn 1]. The following were assumed: the decrease in the solubility of sodium fluoride depends on the quantity of solubility suppressant used and precipitation varies with temperature following the Arrhenius law.

$$N_{is} = \alpha_1 \left(\frac{m_s}{\rho_{sol} V_{sol}} \right) \beta_1 \left(e^{-\frac{E_A}{RT}} \right) \quad [\text{Eqn 1}]$$

where:

$\alpha_1 = 6.381$ mol/L (a constant in the Arrhenius equation determined by calculation)

$\beta_1 = 0.436$ (a dimensionless coefficient determined by calculation)

$E_A = 7452.405$ J/mol (the activation energy of precipitation determined by calculation)

m_s is the mass of sodium chloride (kg)

ρ_{sol} is the volumic mass of sodium fluoride (kg/L)

V_{sol} is the volume of sodium fluoride (L)

R is the constant of ideal gases (J/mol.K)

T is the temperature (K).

The criteria used to judge the model quality are the correlation coefficient (r^2) and the statistical parameter (χ^2) given by the following equation:



$$\chi^2 = \sum_{i=1}^{i=N} \frac{(C_{lsexp,i} - C_{lscalc,i})^2}{N} \quad [\text{Eqn 2}]$$

$N_{lsexp,i}$ is the experimental concentration and $N_{lscalc,i}$ is the calculated concentration of caustic soda. Figure 4 shows the correlation between the two concentrations.

The considerable difference between the experimental and the calculated concentration is influenced by tests conducted at 25 °C. This temperature is less favourable for caustification. In a previous study,¹¹ we supposed that this process which includes precipitation was better than the caustification of an aqueous solution of sodium fluoride. However, the solubility in water of the constituents (sodium fluoride and sodium chloride) is limited.

Caustification of sodium fluoride precipitated by ethanol

Reactants characterisation

The compounds used for this caustification process were an aqueous solution of sodium fluoride (near its limit of solubility) and ethanol. Solutions of sodium fluoride are used in similar conditions of achievement, as illustrated in Figure 1.

Optimisation of operating parameters

The results of this optimisation are shown in Table 4. The results indicate that it is not necessary to use volumes of ethanol greater than 400 mL, as this volume was sufficient to obtain good results. The yield of sodium hydroxide is proportional to the volume of sodium hydroxide and depends on the operating conditions of the filtration device (Table 4).

The results shown in Table 4 are for optimisation of caustification using the solution of sodium fluoride obtained at 80 °C for 2 h. Tendency of caustification was also confirmed at 25 °C and 50 °C. There was no significant difference between the caustification of the solutions of sodium fluoride obtained at the different temperatures. The optimisation highlights the precipitation of all the sodium fluoride present in each of the aqueous solutions. The normalities of sodium hydroxide show that precipitation by ethanol is better for the caustification of sodium fluoride than precipitation by sodium chloride.

Product analysis

Caustic soda: As mentioned previously, volumetric analysis showed an aqueous solution of caustic soda (6.6% NaOH) with a yield of approximately 80%.

TABLE 4: Influence of ethanol on caustification at 80 °C.

Volume of ethanol (mL)	Volume of NaOH (mL)	Density of NaOH (g/cm ³)	Normality of caustic soda (N)	NaOH (%)	Yield of NaOH (%)
100	90	1.039	1.29	4.97	57.8
200	90	1.048	1.53	5.84	68.5
300	90	1.053	1.63	6.19	72.9
400	91	1.055	1.73	6.56	78.3
500	91	1.058	1.75	6.62	79.2

Mixture of calcium fluoride and silica: The mixture of calcium fluoride and silica was basically the same product when experiments were performed under the same conditions (Table 4). Therefore, any analytical method can be used to determine the composition.

Modelling caustification

The parameters considered were the volume ratio of ethanol and the temperature. The following model describes the caustification process:

$$N_{ls} = \alpha_2 \left(\frac{V_e}{V_e + V_{sol}} \right)^{\beta_2} \left(e^{-\frac{E_A}{RT}} \right), \quad [\text{Eqn 3}]$$

where:

$\alpha_2 = 2.774$ mol/L (a constant in the Arrhenius equation determined by calculation)

$\beta_2 = 0.406$ (a dimensionless coefficient determined by calculation)

$E_A = 933.536$ J/mol (the activation energy of precipitation determined by calculation)

V_e is the volume of ethanol (L)

V_{sol} is the volume of solution of sodium fluoride (L)

R is the constant of ideal gases (J/mol.K)

T is the temperature (K).

The observed normality of the caustic soda and the calculated normality of the caustic soda were approximately equal, as illustrated in Figure 5.

The calculations made previously confirm that sodium fluoride precipitation by ethanol is more successful than precipitation by sodium chloride. The fundamental difference of these two methods of precipitation derives from experiments carried out at 25 °C. This precipitation by ethanol

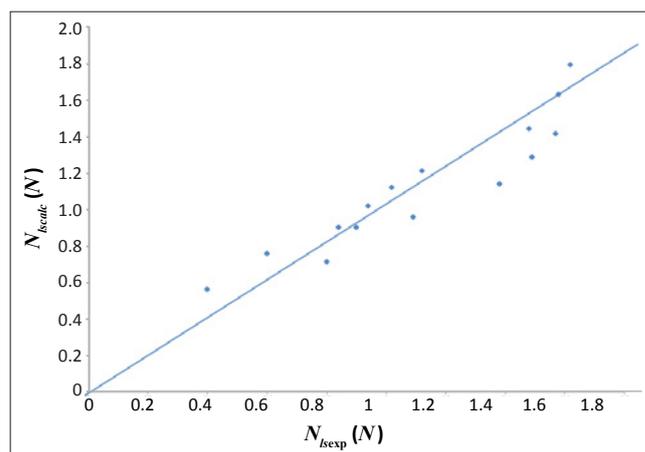


FIGURE 4: Correlation between the experimental concentration N_{lsexp} and the calculated concentration N_{lscalc} of caustic soda measured by normality (N) after precipitation with sodium chloride.

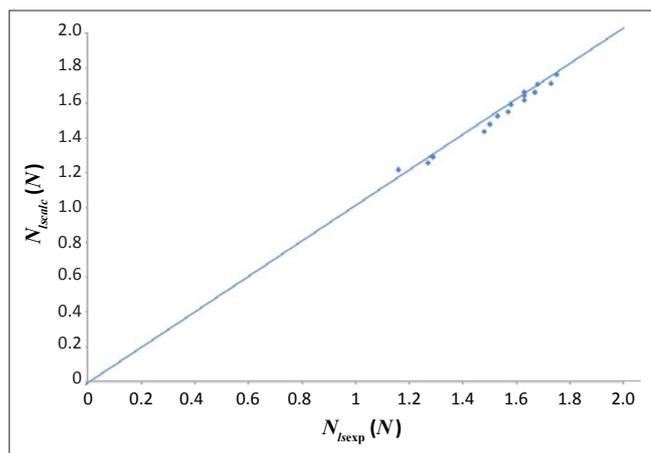


FIGURE 5: Correlation between the experimental concentration N_{hexp} and the calculated concentration N_{hcalc} of caustic soda measured by normality (N) after precipitation with ethanol.

produced the best results but its main disadvantage was the use of its precipitant and the large quantities required. The use of sodium chloride for precipitation is more economical than the use of ethanol. Precipitation by ethanol requires another operation for ethanol regeneration which decreases its profitability.

Conclusion

Caustification processes carried out at 25 °C, 50 °C and 80 °C allowed for the consumption of all fluosilicic acid, which produced caustic soda in a 6% – 7% solution with yields of approximately 70% – 80% and a useful mixture of calcium fluoride and silica for the cement industry. Elsewhere, activation energies of precipitation determined by semi-empirical correlations show that precipitation by ethanol ($E_A = 933.536$ J/mol) is more successful than precipitation by sodium chloride ($E_A = 7452.405$ J/mol).

Acknowledgements

This work is realised in the framework of recovering and working-up fluosilicic acid which is an industrial waste in phosphoric acid manufacturing for the production of caustic

soda and a mixture of calcium fluoride and silica usable in the production of cement. We thank I.C.S. (Chemical Industries of Senegal) and SOCOCIM industries (Senegal) for their technical help.

Competing interests

We declare that we have no financial or personal relationships which may have inappropriately influenced us in writing this paper.

Authors' contributions

A.O.T. was responsible for the experimental and project design; F.M.S. and D.K. contributed to the project design; and C.M.G.D. and O.S. were the project leaders.

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