

The effect of reaction conditions on the precipitation of sodium hexafluorosilicate produced from waste hexafluorosilicic acid

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The purpose of the study is to investigate the optimum conditions for the precipitation of sodium hexafluorosilicate (Na_2SiF_6) from waste hexafluorosilicic acid, an effluent from the phosphoric acid industry. Sodium chloride and sodium hydroxide were used as reactants to produce Na_2SiF_6 . The effect of various parameters on the precipitation was investigated and includes; the molar ratio of the reactants, contact time, the temperature and the effect of seeding.

The optimum reaction conditions were found to be as follows; excess sodium chloride or sodium hydroxide to hexafluorosilicic acid of 25%, contact time 40 minutes and a reaction temperature of 40°C.

The reaction of hexafluorosilicic acid with an aqueous solution of sodium chloride at optimum conditions gave a maximum yield of 94.26% Na_2SiF_6 while the reaction of hexafluorosilicic acid with the aqueous solution of sodium hydroxide at optimum conditions gave a maximum yield of 97.3% Na_2SiF_6 . The X-Ray diffraction (XRD) analysis reveals that the only crystals present in the precipitate are Na_2SiF_6 . Also, Scanning Electron Microscope (SEM) analysis shows that the different morphology of these crystals depend on the precipitation conditions.

Keywords: Sodium hexafluorosilicate; reaction conditions; hexafluorosilicic acid, fertilizer industry.

INTRODUCTION

Sodium hexafluorosilicate is an odorless, white powder of hexagonal crystals (MW=188.06, density=2.679 g/cm³). It is used as a fluoridation agent for drinking water¹, insecticide, rodenticide and veterinary treatment for lice², production of high purity silicon tetrafluoride³, and the production of enamels for china and porcelain products. Sodium hexafluorosilicate is used widely in industry, for a selective removal of surface acidity in zeolite ZSM-5, in photovoltaic applications⁴, synthesis of mesoporous silica⁵, dealumination of MCM-22 zeolite and ferrihydrite, as active agents in the formulation of mouth washes and dentifrices, synthesis of advanced ceramic materials⁶, and as catalysis products in the frosted glass industry⁷.

Sodium fluorosilicate is produced by the neutralization of hexafluorosilicic acid with sodium hydroxide, sodium carbonate, or sodium chloride under vigorous agitation conditions. The type of conversion depends on the concentration of the waste acid and the availability of neutralization materials. Besides, it is important to find a procedure to prevent gelatinization of the precipitate to assist filtration.

Jordan has huge reserves of phosphate rock. Currently phosphate rock is mined from three main locations; Al-Shediah, Al-Hesa and Al-Abiad. The annual production of phosphate is estimated to be 5.281 million tones during the year 2009, most of which is being exported and only less than 40% is being utilized locally to produce phosphoric acid. One of the main waste by-products of this industry is hexafluorosilicic acid. The amount of phosphate rock used in the production of phosphoric acid in the industrial fertilizers complex in Aqaba is approximately (1.0–1.2) million ton/year. This amount produces approximately (100.000–110.000) ton/year of hexafluorosilicic acid as a waste with a concentration of (18–30%)⁸.

The importance of this study is to investigate the utilization of the waste hexafluorosilicic acid produced in the Industrial Fertilizers Complex in Aqaba – Jordan to produce sodium hexafluorosilicate based on the availability of the local sources, use a new feasible chemically and economically methods for the utilization of the available waste acid to avoid its accumulation in soil and underground water. Furthermore, the world prices and world demand on sodium hexafluorosilicate make the conversion economically attractive.

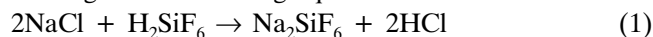
Although the production of hexafluorosilicate is a primitive process, however, the literature data available on this topic is limited⁹. The present work aims to study the various experimental conditions and parameters affecting the precipitation of sodium hexafluorosilicate. These parameters include the nature of the alkaline ion (sodium salt or sodium hydroxide), temperature, sodium salt or sodium hydroxide concentration, and contact time.

MATERIALS AND METHODS

Hexafluorosilicic acid sample of about 5 liters was obtained from the acid storage tank located in the phosphoric acid plant in Aqaba – Jordan. The sample was characterized for specific gravity, H_2SiF_6 and HF, HCl concentrations, P_2O_5 and Fe_2O_3 contents. Sodium chloride and sodium hydroxide used were of reagent grade chemicals and obtained from ALFA AESAR[®].

Stock solutions of sodium chloride and sodium hydroxides (5M) were prepared and stored for further use. A volume of 25 ml of H_2SiF_6 solution was added to 25 ml aliquot with the desired concentration of sodium chloride or sodium hydroxide. Prior to mixing, both solutions were heated to the desired temperature which was maintained until the end of the experiment using a thermostated water bath. The mixture was vigorously agitated at 300 rpm during the course of the experiment. At the end of the

experiment the solid precipitate was separated by vacuum filtration using filter paper and then it was triple washed using distilled water. It was then dried at a temperature of 105°C for 3 hours. The dried precipitate was then weighed for yield calculation. The yield was calculated based on the theoretical amount of sodium hexafluorosilicate according to the following equations:



RESULTS AND DISCUSSION

The chemical analysis of hexafluorosilicic acid produced from the Industrial Fertilizers Complex in Aqaba (Jordan Phosphate Mines Company) is shown in Table 1.

Table 1. Chemical analysis of hexafluorosilicic acid produced from the Industrial Fertilizers Complex in Aqaba

Specific gravity	1.18
Concentration (wt %)	20.1
HF (wt %)	0.76
F (wt %)	16.64
P ₂ O ₅ (mg /L)	300
Cl ⁻ (ppm)	9045
Fe ₂ O ₃ (g/L)	0.11

The effects of various parameters affecting the precipitation of Na₂SiF₆ were studied as follows:

Effect of NaCl and NaOH excess

The effect of excess sodium chloride and sodium hydroxide/ hexafluorosilicic acid on the precipitation of sodium hexafluorosilicate was carried out at a temperature of 20°C and a contact time of 20 minutes (Fig. 1).

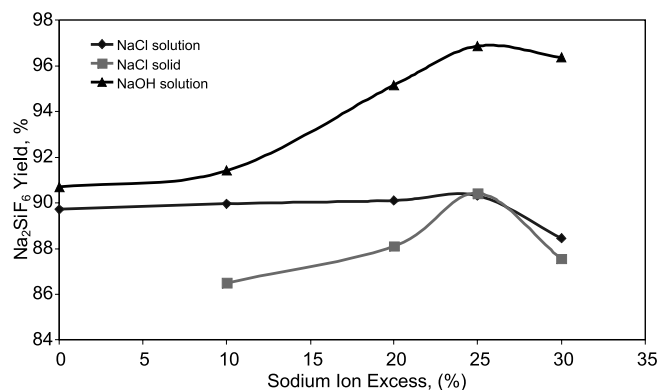


Figure 1. The effect of Na⁺ excess on Na₂SiF₆ yield at the temperature of 20°C over 20 min. reaction times

It was found that at 10% excess of solid NaCl, the Na₂SiF₆ precipitate was of white color with a yield of 86.49%. Filtration speed was slow and pH value of filtrate was acidic 1.42. When the excess was increased to 20% the precipitate was also white in color and the yield increased to 88.1%. The filtration speed was better and the pH value of the filtrate still acidic but dropped to 1.36. In both cases above the solution produced was slightly turbid with dark yellow color which is related to the iron present in the H₂SiF₆ feed. At 25% excess the solution produced was not turbid, which led to a faster filtration process, with clear yellow color and the yield increased to

90.42%. The pH of the filtrate became more acidic and dropped further to 0.96. However, when the excess was increased to 30% the product solution became much more turbid and thick of a yellowish color and the yield dropped to 87.55%. The filtration process was very poor and the pH of the filtrate at this excess became more acidic and dropped further to 0.8.

The drop of Na₂SiF₆ yield at 30% excess of solid sodium chloride is related to the increase in HCl concentration, as evident from the drop of the pH due to the reversible reaction (3), the formation of silica gel, and the product of polymerization of silicic acid¹⁰.



When hexafluorosilicic acid was added to a solution of sodium chloride the yield of Na₂SiF₆ was better at excess of 10 and 20% than that of solid form. The yield became then almost similar for solid and aqueous NaCl at excess of 25 and 30% (see Fig. 1). The maximum Na₂SiF₆ yield was 90.32% which is obtained at 25% excess.

The effect of sodium hydroxide excess (10, 20, 25, and 30%) on the production of Na₂SiF₆ is shown also in Fig. 1. It is clear that the yield is increased with increasing sodium hydroxide excess reaching its maximum value of 96.86% at 25% excess. The yield then decreased when the excess was increased to 30%. This could be related to the formation of soluble NaF^{5, 11}.

In all cases of sodium hydroxide reaction with H₂SiF₆, the color of the permeate was colorless, which is related to the absence of Fe³⁺ ions in the permeate as a result of its precipitation in the form Fe(OH)₃.

Effect of contact time

The effect of contact time on the yield of Na₂SiF₆ was studied at 25% excess of NaCl and NaOH and at a temperature of 20°C. It can be seen from Fig. 2 that the time required to reach the highest yield was 40 minutes. The maximum yield obtained in the case of NaCl was 94.01%, whereas, it reached 97.3% when NaOH was used. After 40 minutes the yield dropped in both cases. The decrease in the yield after prolonged agitation when NaCl was used may be explained by dissolving some of the product in the HCl produced during the reaction. Frayret et al 7 reported the solubility of Na₂SiF₆ increases with the increase of HCl concentration reaching a maximum solubility value of 0.066 M at 1M HCl and a temperature of 20°C, then it drops steadily reaching a 0.05M at 3M HCl. However, the solubility of Na₂SiF₆ in water at 20°C was reported to be 0.036 M^{7, 12}. The other evidence of the back dissolu-

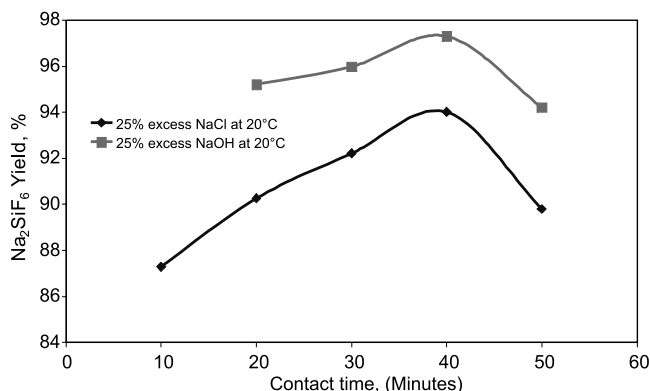


Figure 2. The effect of contact time on Na₂SiF₆ yield at the temperature of 20°C and 25% Na⁺ excess

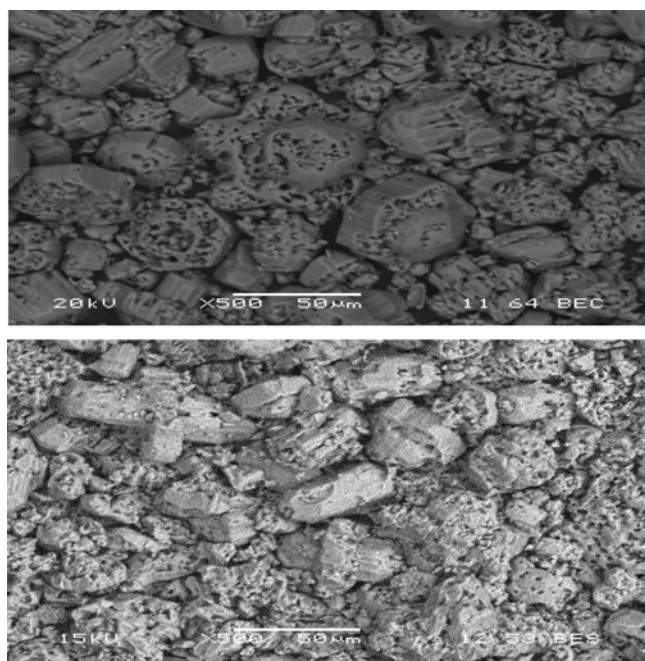
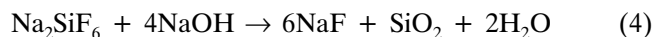


Figure 3. SEM micrographs of Na_2SiF_6 precipitate obtained with 10% excess NaCl (upper) and 30% excess NaCl (lower) ($T=20^\circ\text{C}$, $t=40$ min., 300 rpm)

tion of Na_2SiF_6 in HCl is the morphology of its crystals shown in Fig. 3 which appears to be eroded at higher NaCl excess.

However, the decrease in the yield, when NaOH was used could be related to the slow hydrolysis of the sodium hexafluorosilicate in water according to the following reaction^{5, 11}:



Effect of temperature

The effect of temperature on the yield of Na_2SiF_6 was investigated at an excess of 25% for both NaCl and NaOH and a contact time of 40 minutes. From Figure 4 it can be seen that the increase of temperature, from 20°C to 40°C , causes a slight increase in the yield, after that a slight decrease was observed. In the case of NaCl the

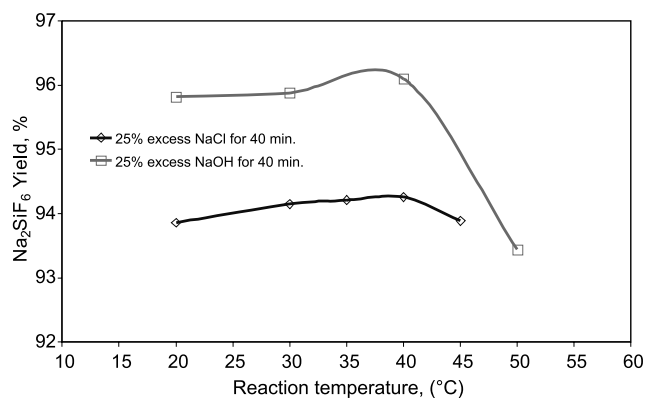


Figure 4. The effect of temperature on the yield of Na_2SiF_6 at 25% excess Na^+ and a reaction time of 40 minutes

Table 2. Comparison between yields of Na_2SiF_6 with and without seeding (0.5 g Na_2SiF_6 seeding)

Reagent	Yield (wt %)	
	with seeding	without seeding
NaCl	94.97	94.26
NaOH	97.62	96.10

highest yield of (Na_2SiF_6) was obtained at a temperature 40°C reaching 94.24%. The reason behind the drop in the yield may be due to the dissolution of the product at high temperature. Additionally, the HCl acid formed during the reaction increase the solubility of product and formation of gel material¹⁰. As for NaOH the highest yield of Na_2SiF_6 was also obtained at a temperature 40°C with a value of 96.1%. With the further increase of temperature the yield was found to drop more significantly than that of NaCl. This is probably related to the increase of solubility of Na_2SiF_6 in water with the increase of temperature¹³. Park et al.¹⁴ reported that solubility of Na_2SiF_6 in hot water is about 0.13 M

Effect of seeding

The effect of seeding on the precipitation and yield of Na_2SiF_6 was studied under the following conditions: 0.5

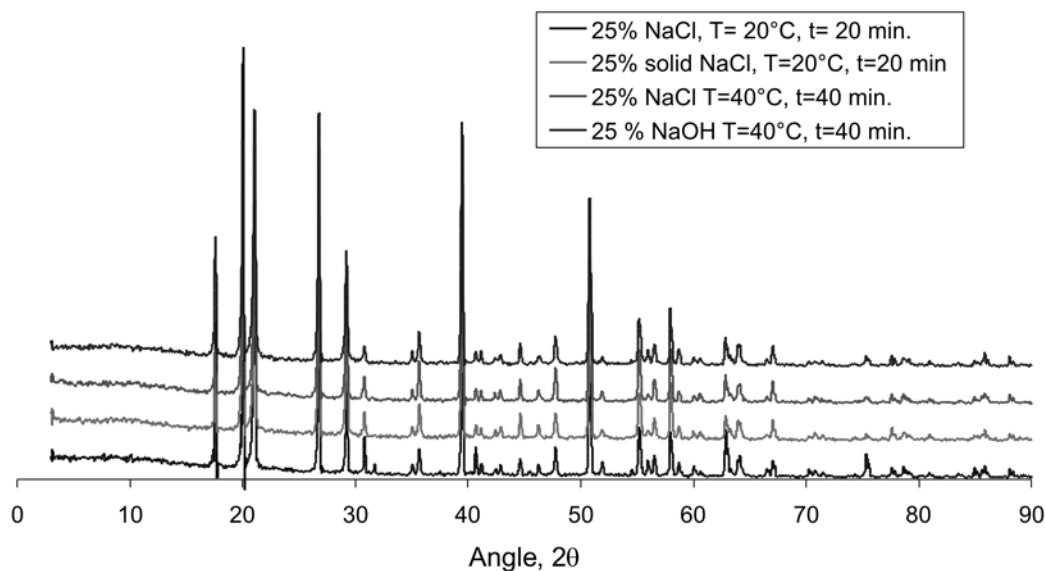


Figure 5. X-Ray diffraction patterns of the produced sodium fluorosilicate under different conditions

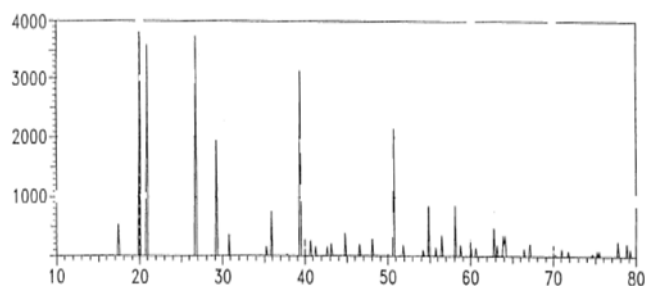


Figure 6. Standard X-ray diffraction pattern of Na_2SiF_6 ¹⁶

gram seeding of Na_2SiF_6 , temperature 40°C , 25% excess and 40 minutes contact time (Table 2). A slight increase of Na_2SiF_6 yield was obtained as a result of seeding for both NaCl and NaOH. The seeding in the crystallization

could change the crystal growth habits and crystal size distribution¹⁵.

CHARACTERIZATION OF SOLID Na_2SiF_6

X-Ray Diffraction (XRD) analysis

The product samples of Na_2SiF_6 which were prepared by the reaction of hexafluorosilicic acid with sodium chloride or sodium hydroxide were analyzed by X-Ray diffraction (XRD). Figure 5 below shows the XRD patterns of the produced Na_2SiF_6 which shows high purity crystalline sodium hexafluorosilicate as compared to the standard XRD patterns of Na_2SiF_6 shown in Fig. 6.

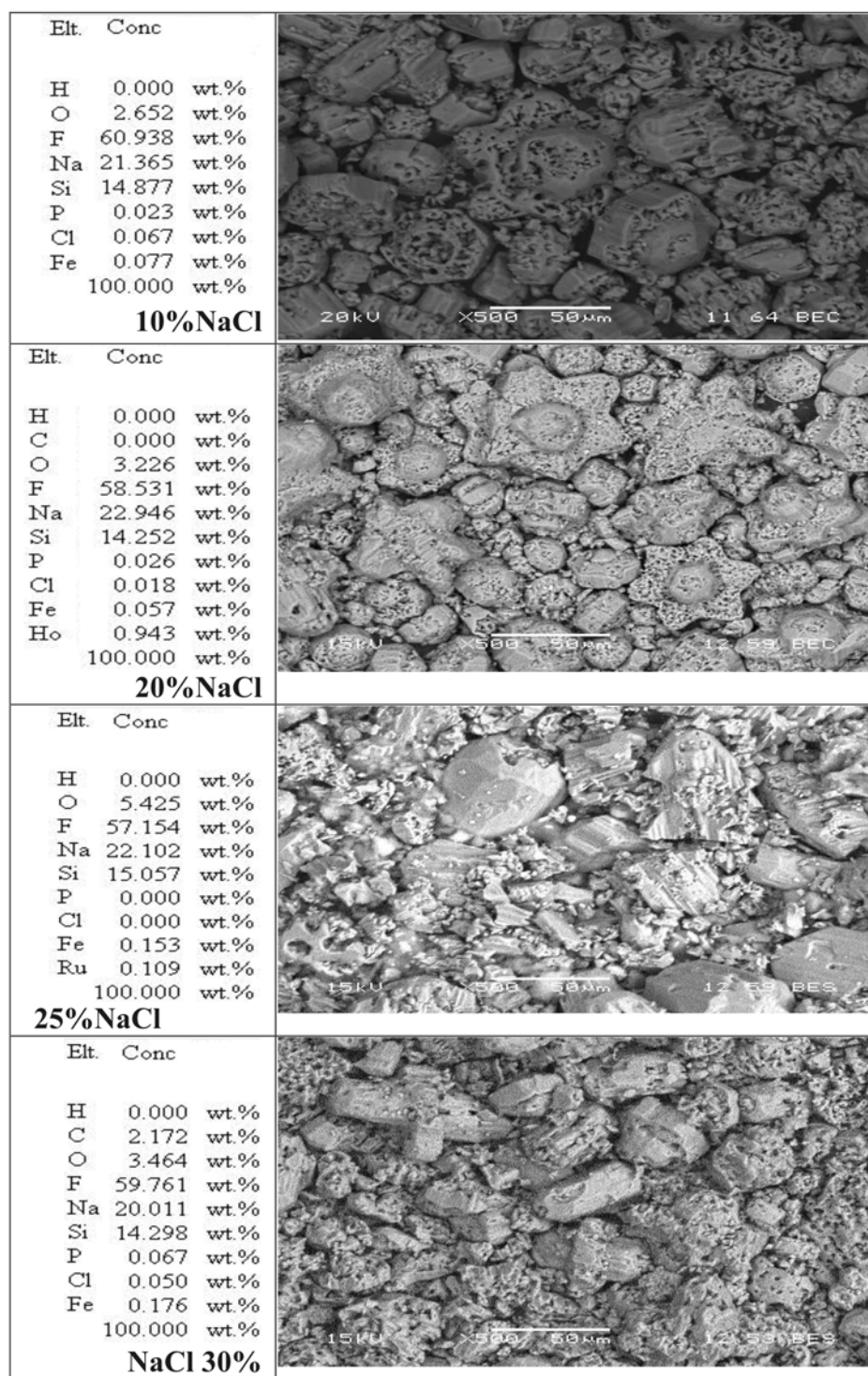


Figure 7. SEM micrographs and corresponding XRD analysis of the produced Na_2SiF_6 precipitate when NaCl was used

Scanning-Electron Microscope (SEM) analysis

Figure 7 below shows SEM images and XRD analysis of sodium hexafluorosilicate crystals produced by reacting H_2SiF_6 with NaCl at a magnification of (X500). It can be seen that most crystals have a similar shape (hexagonal, six armed). All crystals are shown to be porous and the porosity or erosion increases with the increase of NaCl concentration. At concentrations of NaCl higher than 25%, the Na_2SiF_6 crystals start to lose their six armed shape

and become more corroded. As mentioned earlier, this could be due the back dissolution of sodium hexafluorosilicate by HCl formed, the concentration of which increases with the increase of NaCl excess.

Figure 8 below shows SEM images and XRD analysis of sodium hexafluorosilicate crystals produced by reacting H_2SiF_6 with NaOH at a magnification of (X500). It can be seen that there is a variation of particle size under all excess concentration and fine crystals formation are

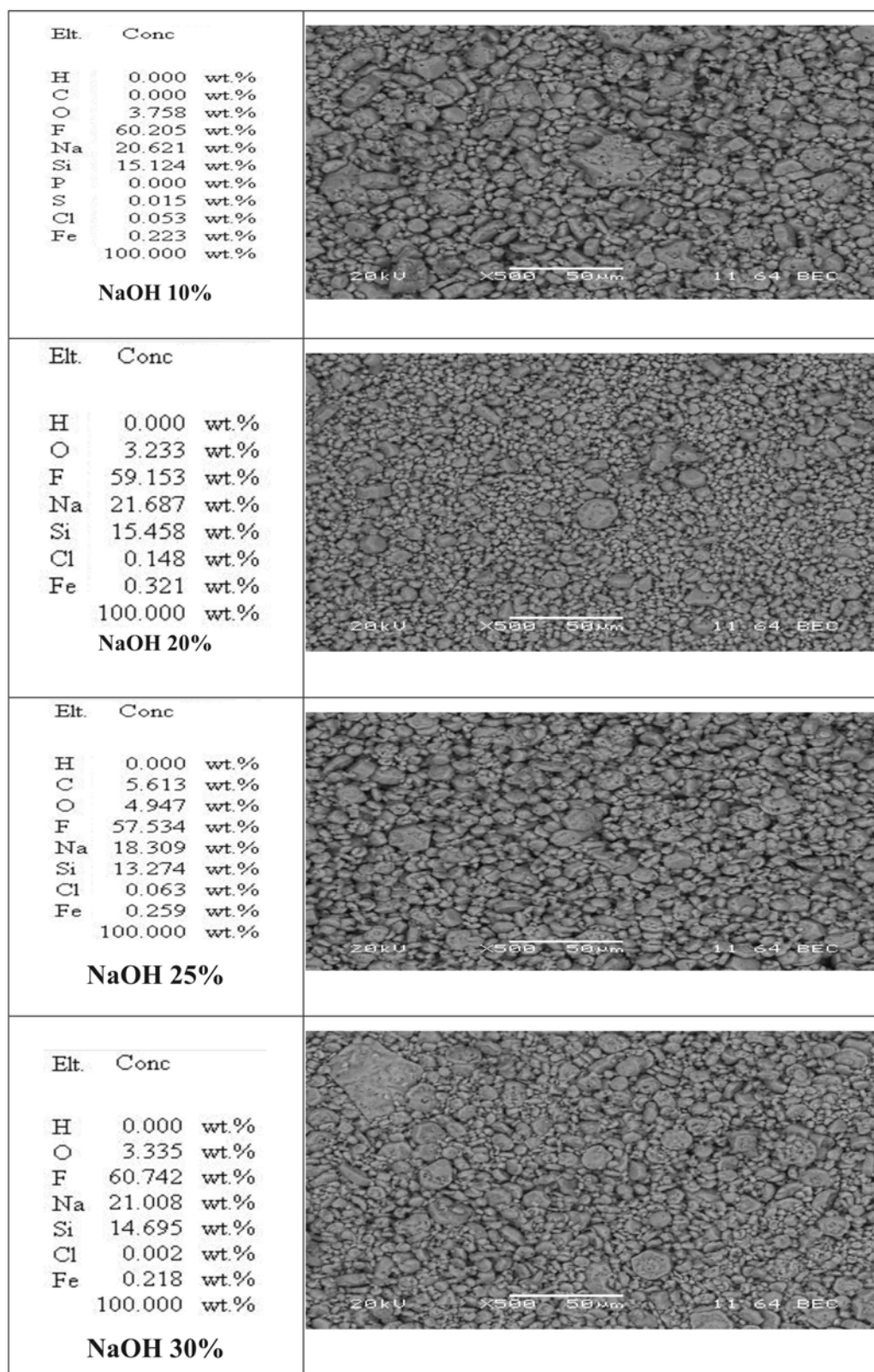


Figure 8. SEM micrographs and corresponding XRD analysis of the produced Na_2SiF_6 precipitate at different excess concentration of NaOH

more predominant. Hexagonal crystals still can be seen but here they seem to be thinner than those obtained with NaCl. Additionally, some crystals shapes are ice-like crystal and others are pyramidal with smooth faces and more compact. The erosion of precipitated crystals is much less compared to that of when NaCl was used. Furthermore, the XRD analysis reveals that the concentration of iron in the precipitate is higher than that when NaCl was used.

X-Ray Fluorescence analysis (XRF)

The product samples of Na₂SiF₆ which were prepared by the reaction of hexafluorosilicic acid with sodium chloride were analyzed using the XRF. The results of the analysis are summarized in Table 3. When the theoretical content of F, Na and Si in Na₂SiF₆ is compared with the experimental values one can notice small variations. In particular there is extra fluoride and silicone present in the precipitate. This could suggest precipitation of silicates and some other fluorides in small quantities.

Table 3. X-Ray Fluorescence analysis for Na₂SiF₆ produced using NaCl

	Theoretical	test 1	test 2	test3	test 4
F%	60.6	60.6	60.4	61.5	61.4
Na%	24.5	23.0	21.9	22.4	22.6
Si%	14.9	15.9	15.9	16.0	16.0
P%		0.04	0.02	0.04	0.04
Al%		0.02	0	0.02	0.03
Ca%		0	0	0.02	0.02
O%		0.33	1.64	0.02	0.022
Cl%		0.10	0.08	0	0
Fe%		0	0.061	0	0

Test 1: Excess 25% solution, 20°C and 20 min

Test 2: Excess 25% solid, 20°C and 20 min

Test 3: Excess 25% solution, 20°C and 40 min

Test 4: Excess 25% solution +seed, 20°C and 20 min

CONCLUSION

The effects of reaction conditions on the precipitation of sodium hexafluorosilicate produced from waste hexafluorosilicic acid of fertilizer industry were investigated in the current work. For Na₂SiF₆ precipitation from H₂SiF₆, two sodium sources were used; NaOH and NaCl. The following conclusions could be drawn:

- The optimum reaction conditions were found as follows: excess sodium chloride or sodium hydroxide to hexafluorosilicic acid of 25%, contact time 40 minutes and a reaction temperature of 40°C.

- The highest Na₂SiF₆ yield was obtained when sodium hydroxide was used at the above mentioned reaction conditions with a yield value of 97.3%.

- XRF and XRD analyses revealed that the use of NaOH for Na₂SiF₆ leads to contamination of the precipitate with iron, while when using sodium chloride the iron remains soluble and is washed out.

- The use of sodium chloride leads to the formation of coarser sodium hexafluorosilicate crystals. Additionally, these crystals were found porous and more eroded especially at

- high NaCl excess concentration;
- Increasing the initial temperature of the reactants to 50°C and above leads to the formation of gel product

which could not be separated in simple filtration. The formation of gel may be due to a slight decomposition of the product or dissolution in the produced hydrochloric acid.

LITERATURE CITED

1. Ozsvath, D.L. (2008). Fluoride and environmental health: a review *Rev. Environ. Sci. Biotechnol.* 8(1), 59–79. DOI: 10.1007/s11157-008-9136-9.
2. Pilat, M. (1935). Histological Researches into the Action of Insecticides on the Intestinal Tube of Insects. *Bull. Entomol. Res.* 26(02), 165–172. DOI: 10.1017/S0007485300038165.
3. Bulanov, A.D., Pryakhin, D.A. & Balabanov, V.V. (2003). Preparation of High-Purity Silicon Tetrafluoride by Thermal Dissociation of Na₂SiF₆. *Russ. J. Appl. Chem.* 76(9), 1393–1395. DOI: 10.1023/B:RJAC.0000012654.22326.e5.
4. Carleton, K.L., Olson, J.M., & Kibbler, A. (1983). Electrochemical Nucleation and Growth of Silicon in Molten Fluorides. *J. Electrochem. Soc.*, 130(4), 782–786 DOI: 10.1149/1.2119803.
5. Wang, L., Tomura, S., Ohashi, S.M.F., Inukai, K. & Maeda M. (2001). Synthesis of mesoporous silica material with sodium hexafluorosilicate as silicon source under ultra-low surfactant concentration. *J. Mater. Sci. Lett.* 20, 277–280. DOI: 10.1023/A:1006761926695.
6. Leal-Cruz, A.L. & Pech-Canul, M.I. (2006). In situ synthesis of Si₃N₄ from Na₂SiF₆ as a silicon solid precursor. *Mater. Chem. Phys.* 98(1), 27–33. DOI: 10.1016/j.matchemphys.2005.08.057.
7. Frayret, J., Castetbon, A., Trouve, G. & Potin-Gautier, M. (2006). Solubility of (NH₄)₂SiF₆, K₂SiF₆ and Na₂SiF₆ in acidic solutions. *Chem. Phys. Lett.* 427, 356–364. DOI:10.1016/j.cplett.2006.06.044.
8. JPMC (2009). 56th Annual Report & Financial Statements for the year 2009. Amman/Jordan: Jordan Phosphate Mines Co. PLC. 1–43.
9. Ghuge, K.D. & R.R. Angadi (1987). *Indian Journal of Technology*, 25, 187.
10. Pozin, M.E. (1989). *Mineral Fertilizers Technology* (in Russian). Leningrad: Khimia.
11. Sikdar, S.K. & Moore, J.H. (1980). Recovery of hydrofluoric acid from fluosilicic acid with high pH hydrolysis. Patent No. 4,213,951 USA.
12. Lide, D.R. (2010). ed. ^ eds. *CRC Handbook of Chemistry and Physics*. 90th Edition ed. CRC.
13. Schroder, F. (1992). in *Gmelin Handbook of inorganic and Organometallic Chemistry: Si, Suppl.* Springer-Verlag: Berlin. 300.
14. Park, H.C., Ryu, B.K., Park, S.S., Shin, H.G., Lee, S.H. & You, Y.W. (1997). Recycling of waste HF solution by Na₂CO₃ treatment for use in cleaning of TV panel glass. *J. Mater. Sci. Lett.* 17(1), 11–13. DOI: 10.1023/A:1006525204074.
15. Ruixiang, Z. (2005). Process optimization in batch crystallization of sodium fluosilicate. *Cryst. Res. Technol.* 40(3), 243–247. DOI: 10.1002/crat.200410332.
16. Bulko, J.B. & Smyser, B.M. (2000). Method for producing silicon tetrafluoride from uranium oxyfluoride. Patent No. WO 00/58212.