Fluoride and silicon removal from spent glass etching solution by chemical treatment

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The effects of chemical treatment for spent silicon etching solution using a combination of two precipitants, K/NaOH, and calcium salts, have been investigated. The impact of the precipitant dose and the initial and final pH value on fluoride and fluorosilicate removal efficiency has also been evaluated. Fluoride and silicon were removed simultaneously in the form of insoluble $(K/Na)_2SiF_6$ using the precipitant K/NaOH at pH 5, while the residual concentration of soluble fluoride was in the range of 0.013 to 0.016 M. According to the XRD and wet-chemical analysis the purity of the K_2SiF_6 precipitate was 98%. The residual fluoride concentration in the solution was additionally reduced in the form of insoluble CaF_2 using the precipitant $Ca(NO_3)_2$ with [Ca]:[F] = 1:1 at pH 6.7. The basic ingredients in the precipitate were CaF_2 and $Ca(NO_3)_2$, while F and Si concentrations in the supernatant were undetectable. The combination of K/NaOH and $Ca(NO_3)_2$ makes it the best precipitating agent for fluoride and silicon removal from the spent chemical etching solution and production of precipitates suitable for industrial application.

Keywords: precipitation, fluoride, silicon, removal

INTRODUCTION

The chemical etching of silicon using HF–HNO$_3$ mixtures is a widely used process in the processing of silicon wafers for microelectronic or photovoltaic applications [1]. The silicon etching is described by the following equation:

$$3Si + 18HF + 4HNO_3 \rightarrow 3H_2SiF_6 + 4NO + 8H_2O. \qquad (1)$$

During the etching process HF and HNO$_3$ concentrations in the etching solution decrease gradually, whereas the concentration of H$_2$SiF$_6$ increases. In consequence of the formation of silicon wafer and H$_2$SiF$_6$, the etching behaviour changes significantly and the spent etching solution should be either utilized and replaced by a new one or replenished by the addition of concentrated acids. Moreover, the etching process needs much pure water for rinsing and cleaning operation. Consequently, the acid wastewater contains high concentrations of chemicals HF, HNO$_3$ and H$_2$SiF$_6$ that must be removed before water recycling.

Various techniques were investigated to treat the spent etching solution or to clean up the wastewater. Generally, acid waste of fluoride and silicon was removed from the spent solution by the precipitation method [2, 3]. Fluorides from industrial wastewater were effectively removed in the packed bed using calcite and limestone [4, 5], in the fluidized-bed using the crystallization process [6], electrocoagulation [7] and electrochemical treatment [8]. The solvent extraction process recovers the acetic acid from mixed waste acids formed during the semiconductor wafer production process [9]. Nevertheless, the acid waste has been mostly subjected to neutralization without any proper treatment. However, the conventional neutralization treatment has the problems of formation of a precipitate in large quantities, the cost of alkali, sludge disposal and treatment of wastewater to reduce BOD and COD, which in its turn cause an increase in the treatment cost [9].

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Consequently, it is important to find the probability to minimize the acid waste by possible reuse of some components.

The aim of the current research was to compare the influence of precipitants K/NaOH and calcium salts on the behaviour of fluoride and silicon present in the spent chemical etching solution in order to form materials suitable for technical use.

MATERIALS AND METHODS

Materials
The spent etching solution of silicon used in experiments was obtained from the BOD Group Plant in Lithuania. Its composition (M) was 2.5 F, 1.3 Si, 0.17 CH_3COOH, 7.14 HNO_3; pH < 1.

The precipitating agents CaO, $CaCO_3$, $Ca(NO_3)_2$, NaOH, KOH and KNO_3 of certified reagent grade were purchased from Labochema.

The slaked lime (92.28% CaO) was purchased from a building materials shop.

Precipitation experiments
Precipitation experiments were carried out by taking 50 mL of the spent solution and various concentrations of the precipitant in a 500 mL Teflon® beaker, and were mixed for 20 min with a mechanical stirrer at a speed of 60 rpm. The precipitate formed was allowed to settle completely within 3 h. The supernatant was withdrawn from the beaker, the precipitate was separated from the liquid by centrifugation. Except for temperature variation experiments, all other experiments were carried out at room temperature (22 ± 1 °C).

The concentrations of HF$^-$ and H_2SiF_6 in the liquid were measured potentiometricaly [10, 11]; the total fluoride concentration was measured with a fluoride ion-selective electrode (F-ISE) HI4110 (Hanna Instruments USA) and calorimetrically with a zirconium alizarin reagent; the concentration of silicon was determined using a spectrophotometer (Optima 7000 DV, Perkin Elmer).

The X-ray powder diffraction (XRD) data of the precipitate were measured with an X-ray diffractometer SmartLab (Rigaku, Japan) equipped with a 9 kW rotating Cu anode X-ray tube using Bragg–Brentano geometry with a graphite monochromator on the diffracted beam and a step scan mode with the step size of 0.02° (in 2θ scale) and counting time of 1 s per step. The measurements were conducted in the 2θ range of 10–70°. The phase identification was performed using the software package PDXL (Rigaku) and ICDD powder diffraction database PDF-4+ (2013 release).

RESULTS AND DISCUSSION

Simultaneous precipitation of fluoride and silicon using potassium salts
It is known that silicon and hydrofluoric acid can react with divalent and monovalent alkali metals to form corresponding insoluble alkali salts [12]. The chemical reaction that takes place is a two-stage process, which can be written as

$$SiO_2 + 6HF \rightarrow H_2SiF_6(aq) + 2H_2O, \tag{2}$$

$$H_2SiF_6(aq) + 2M \rightarrow M_2SiF_6\downarrow + 2H+, \tag{3}$$
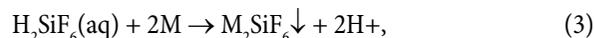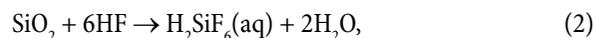
where M represents alkali metals such as K, Ca, etc. In the first stage silicon dioxide reacts with fluoride to form a soluble hexafluorosilicic acid. In the second stage, the hexafluorosilicic acid and any alkali metal form stoichiometrically an insoluble hexafluorosilicate–metal complex: in the case of potassium 2 mol of K, 1 mol of Si and 6 mol of F to form 1 mol of K_2SiF_6, whereas in the case of calcium 1 mol of Ca, 1 mol of Si and 6 mol of F to form 1 mol of $CaSiF_6$. It was reported that in the molar Si:F ratio less than 1:6 (the lowest reported ratio is 1:4.5 [12]), precipitation gives only K_2SiF_6 regardless of the degree of supersaturation.

It is known that the solubility of K_2SiF_6 in 5 M nitric acid is about 0.055 mol/L [3]. Whereas the concentration of HNO_3 in our experiments was about 1.42 fold higher than 5 M (7.14 M), the simultaneous precipitation of fluoride and silicon using potassium salts was tested using KOH as the potassium source to precipitate hexafluorosilicone as K_2SiF_6. Another potential choice could be KNO_3 to avoid contamination of the solution by other anions when the supernatant is supposed to be used as a raw material in agriculture.

The effect of potassium concentration (as KOH) on the fluoride and silicon precipitation efficiency was studied, and the results are depicted in Fig. 1.

From Fig. 1 we can make out that the optimal KOH dose can be determined by measuring the solution pH. The insoluble fluorosilicate can be separated with KOH at pH 4.5–6.5, whereas the residual concentration of soluble fluoride is in the range of 0.013 to 0.016 M/L. Based on the XRD analysis and wet-chemical analysis, the purity of synthesized K_2SiF_6 was calculated to be 98% which is suitable to
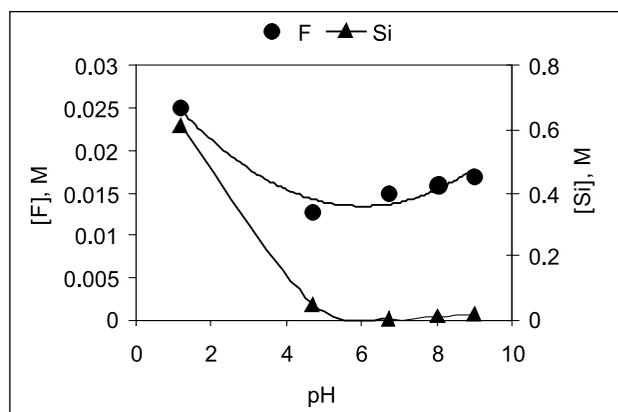

Fig. 1. Residual concentrations of fluoride and silicon in the solution obtained using 0.5 M KOH

be considered as a commercial grade having a good market value (Fig. 2 and Table 1). On the other hand, the supernatant can be replenished by the addition of concentrated HF acids and used again as an etching solution.

Effect of the precipitant on fluoride removal

The behaviour of F^- present in the spent chemical etching solution of silicon against various precipitants like slaked lime, CaO, $CaCO_3$, $Ca(NO_3)_2$, KOH and KNO_3 was assessed and presented in Fig. 3. The best results of fluoride reduction in acidic media were obtained using Ca^{2+} salts, especially $CaCO_3$. But the reaction with $CaCO_3$ is violent, the solution is very sudsy and hot. All other chemicals reduce the fluoride concentration to 0.2 g/L in a very similar way. The duration of the fluoride reduction reaction using $Ca(NO_3)_2$ and KNO_3 was quite long, about 5 h, while the precipitation reaction using slaked lime, KOH and CaO proceeded about 3 h and led to an increase in the solution temperature. Unfortunately, the residual soluble fluoride concentration using all the precipitants was higher than
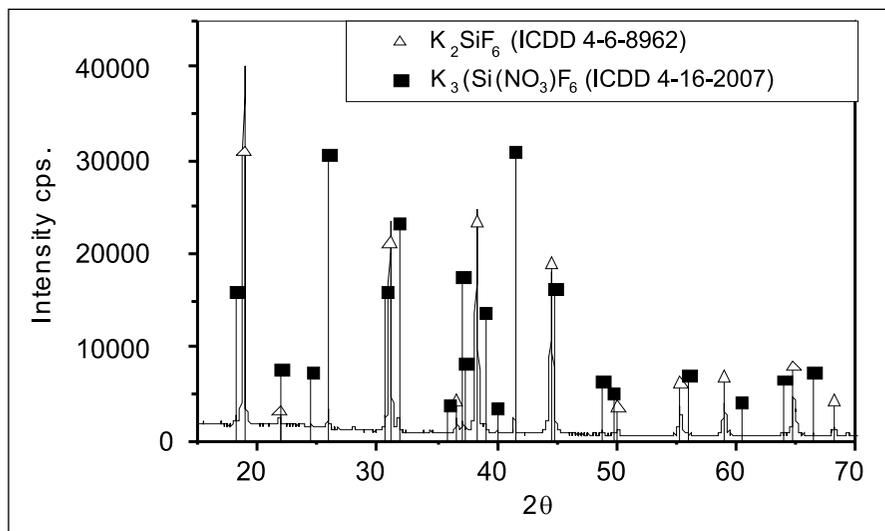

Fig. 2. X-ray diffraction patterns of the sludge obtained at precipitation using KOH, pH 5
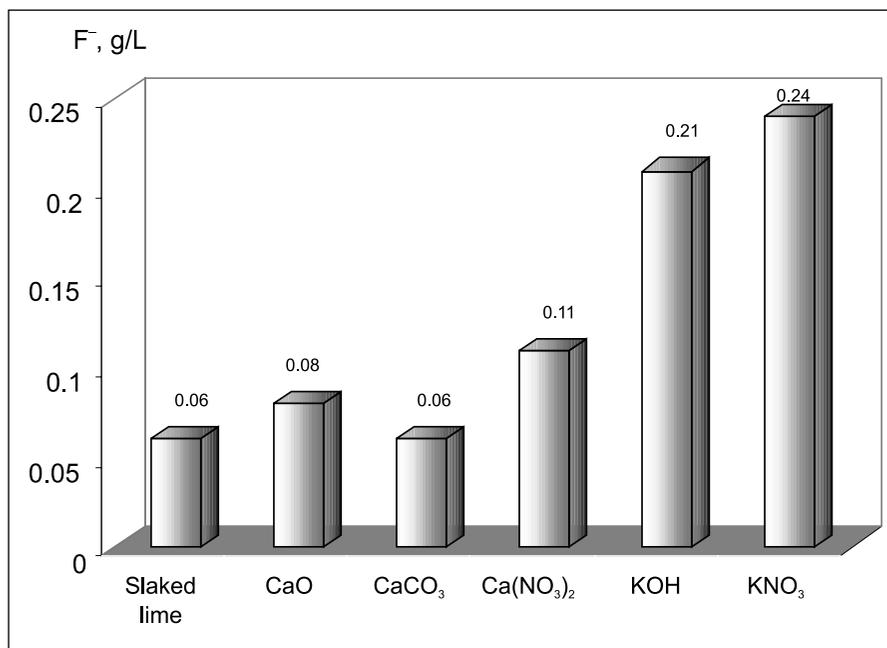

Fig. 3. The residual soluble fluoride concentration after precipitation using various chemicals at molar ratio [Me]:[F] 1:1, pH 1

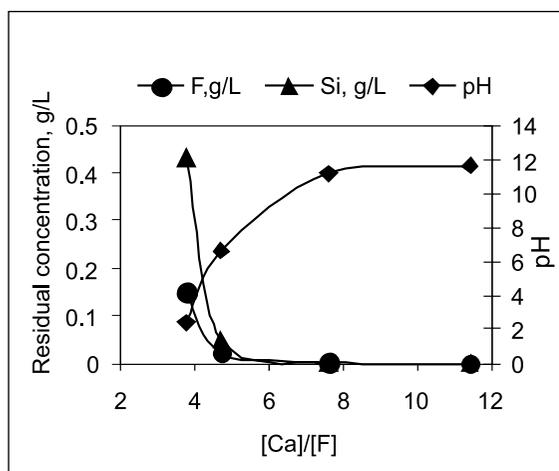Table 1. **The element content of sludge (%) obtained using KOH for precipitation**

Element concentration, %										
O	F	Na	Al	Si	S	Cl	K	Ca	Fe	Zr
0.01	13.5	0.231	0.249	44.3	0.01	0.02	40.6	0.37	0.01	0.01

the maximum allowable level of fluoride in the industrial effluents (15 mg/L).

Various technologies such as coagulation–precipitation, ion exchange, electrocoagulation/electrochemical treatment, membrane processes, nanotechnology, and adsorption are used to reduce fluoride concentration in wastewater to the maximum allowable level [13]. Every process of fluoride removal has its advantages and limitations of operations. The selection of the removal process should be specific as per local needs and prevailing conditions as each technology has some limitations. The most promising method used for the removal of fluoride is adsorption/biosorption due to simplicity and economic efficiency.

On the other hand, the simultaneous precipitation of fluoride and silicon using various chemicals with Ca^{2+}, slaked lime, CaO, $CaCO_3$, $Ca(NO_3)_2$, did not satisfy the economically allowable level of concentrations for deposition. For example, using the widely available slaked lime the effect of precipitation of fluoride was 9–10 times higher than the stoichiometric ratio (0.5:1) of calcium to fluoride, and pH $\geq$ 11.2 is always needed (Fig. 4). Moreover, CaF_2 and $Si(OH)_4$ precipitates are very difficult to separate from water. Calcium salts, especially hydroxide, which is frequently sold as slaked lime, is generally inexpensive, but the quantity of calcium hydroxide that dissolves in water as calcium ions is very low. Therefore, a large amount of the precipitant agent should be added to diminish the concentration of the treatment target fluoride. Excess calcium hydroxide added to the solution is recovered with calcium fluoride and thus increases the total volume of sludge.

The results of the XRD analysis illustrated that the composition of sludge depended on the pH value and [Ca][/F] concentration (Figs. 5, 6). At pH 6.6 (Fig. 6) and [Ca][/F] about 5:1 (Table 2), the silicon in the sludge was 0.39% (Fig. 5, Table 3), whereas at pH 11.4 (Fig. 6) and [Ca][/F] about 8:1 (Table 3), the silicon in the sludge was 5.75%.

It is well documented that the CaF_2 particles are very fine and positively charged [14, 15]. The particle size estimated by the Halder–Wagner method [14] is in the range of 0.086~0.972 µm (average 0.226 µm), and the zeta potential of CaF_2 particles varies from 52.5–22.6 mV in the pH range of 3.19–12.40 [15]. Therefore CaF_2 particles disperse in water and are difficult to settle, coagulation/flocculation
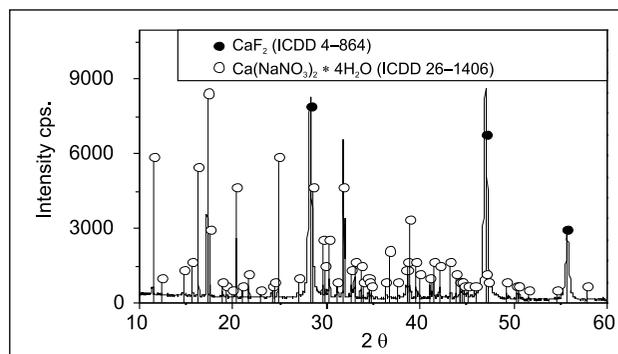
Fig. 5. X-ray diffraction patterns of the sludge obtained at precipitation using slaked lime, pH 6.6; [Ca]:[F] = 4.7

Fig. 6. X-ray diffraction patterns of the sludge obtained at precipitation using slaked lime, pH 11.7; [Ca]:[[F] = 7.6
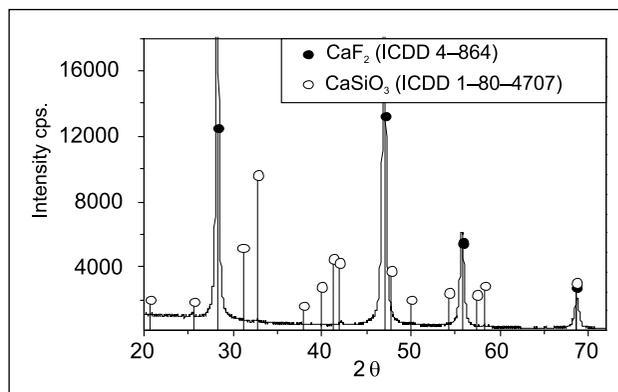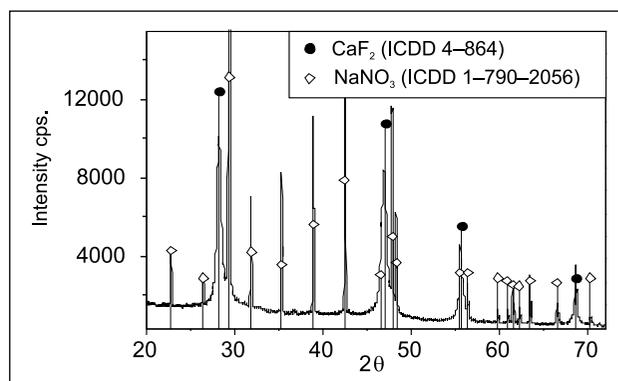

Fig. 4. The pH value and content of fluoride and silicon in the treated etching solution using various concentration of precipitant CaO ([Ca][/F])

Fig. 7. X-ray diffraction patterns of the sludge obtained using NaOH (pH 5) and $Ca(NO_3)_2$ ([Ca]:[F] = 1:1) for precipitation

Table 2. **Residual concentration of fluoride and silicon in the solution obtained using slaked lime**

Test No.	[Ca]:[F]	pH	F⁻, g/L	Si, g/L	Dilution with water
1	3.8	2.4	0.0805	0.433	1:1
2	4.7	6.6	0.022	0	1:1
3	7.6	11.2	0.004	0	1:3
4	11.4	11.7	0	0	1:3

Table 3. **The element content of sludge (%) obtained after precipitation using slaked lime at various pH**

Element content (%) obtained at pH 6.6 and [Ca]:[F] = 4.7							
O	F	Al	Si	Ca	Fe	Sr	Phase formula
47.14	0.29	0.001	0.39	51.82	0.04	0.01	Fluorite CaF_2; Nitrocalcite $Ca(NO_3)_2$
Element content (%) obtained at pH 11.7 and [Ca]:[F] = 7.6							
28.38	8.23	0.01	5.75	57.40	0.01	0.01	Fluorite CaF_2; Calcium Silicate $Ca_2(SiO_4)$

Table 4. **Concentrations of fluoride and silicon in the solution obtained after precipitation**

Index	pH	F⁻, g/L	Si, g/L
Step 1: KOH/NaOH	5	0.243	0.0007
Step 2: supernatant from step 1 + $Ca(NO_3)_2$ at [Ca]:[F] = 1:1	6.7	0	0

is required. Nevertheless, based on the results obtained, the chemical treatment process of the spent glass etching solution should be useful without the coagulation/flocculation procedure, when at the beginning fluorosilicate is separated from fluoride using K/NaOH at pH 5 (Table 4). In the second step the fluoride supernatant from the first step with a small amount of Si was treated using $Ca(NO_3)_2$ with [Ca:[F] = 1:1. The supernatant acquires pH 6.7 and the concentrations of F and Si are undetectable. The diffraction pattern of the precipitate identified the peaks typical of fluorite CaF_2, villiaumite NaF and sodium nitrate $NaNO_3$ (Fig. 7).

Precipitates could be integrated in industrial application, for example: K2SiF6 for wood preservation, HF production, the supernatant with calcium and potassium nitrate – as raw materials in agricultural production purposes.

CONCLUSIONS

The current study has shown that the two-step chemical treatment of spent glass etching solutions using Na/KOH and $Ca(NO_3)_2$ and adjusting pH allowed a separate recovery of fluoride and fluorosilicate ions in the form of their insoluble calcium and potassium based-salts and should be useful without the coagulation/flocculation procedure. The products obtained may be employed as raw materials in several industrial applications. The level of fluoride concentration in residual process wastewater can be reduced by the adsorption and biosorption method using low-cost adsorbents.

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**FLUORIDŲ IR SILIKATŲ CHEMINIS ŠALINIMAS
IŠ PANAUDOTŲ STIKLO CHEMINIO ĖSDINIMO
TIRPALŲ**

S a n t r a u k a

Fluoridams ir silikatams pašalinti iš panaudotų stiklo cheminio
ėsdinimo tirpalų buvo taikomas dviejų pakopų nusodinimo būdas,
nusodikliais naudojant kalio arba natrio hidroksido ir kalcio drus-
kas. Įvertinta nusodiklio kiekio ir apdorojamo tirpalo pH įtaka fluo-
ridų bei fluorsilikatų pašalinimo efektyvumui. Optimali nusodiklio
koncentracija gali būti nustatoma matuojant apdorojamo tirpalo
pH. Pirmoje pakopoje vienu metu pašalinami fluoridai ir silikatai
netirpaus $K(Na)_2SiF_6$ formoje naudojant nusodiklius K / NaOH, kai
pH = 5. Susidariusių K_2SiF_6 nuosėdų grynumas buvo 98 %. Antrame
etape likę tirpale fluoridai nusodinami naudojant nusodikliu kalcio
druskas, kai [Ca]: [F] = 1: 1, o pH – 6,7. Susidariusiose nuosėdose
pagrindiniai ingredientai buvo CaF_2 ir $Ca(NO_3)_2$.