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Fluoride removal capacity of cement paste

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Abstract

The objectives of this study are to assess the feasibility of using the cement paste as an alternative agent for fluoride removal and to investigate fluoride removal capacity of the cement paste. Initially, screening experiments were conducted to evaluate Ca-bearing materials (cement, cement paste, lime). The cement paste was competitive to lime, common fluoride removal agent. Various Ca-bearing hydrates such as portlandite, calcium silicate hydrate (CSH), and ettringite in the cement paste were identified to remove fluoride by precipitating CaF_2 and/or adsorbing F^- ions. In the batch slurry experiments using cement paste and lime simultaneously, 50–67% of lime can be substituted by cement paste to satisfy fluoride effluent limitation of 15 mg/L. Fluoride removal reactions in cement paste slurries were strongly affected by pH, and an optimal pH for the cement paste slurries exists between 7.0 and 11.5. From the result of the column experiment to observe the successive fluoride removal capacity of cement paste, the real hydrofluoric acid wastewater concentration of 1150 mg/L immediately reduced to the level of less than 15 mg/L. These results indicate that the cement paste generally has advantageous characteristics as an economical and viable substitute for lime to remove fluoride.

Keywords: Fluoride; Fluoride wastewater; Cement paste; Lime; Cement; Cement hydrates

1. Introduction

Fluorine compounds have been extensively used in semiconductor and display panel making industries. The wastewater from these industries contains high concentrations of fluoride ions and other pollutants such as ammonia, nitrate, and phosphate. As the industries develop, they consume more process water and chemicals, thereby producing more wastewater of highly concentrated pollutants [1–3].

Conventional treatment for fluoride wastewater involves lime precipitation and separate alum coagulation, sometimes followed by adsorption using rare earth metals such as lanthanum, to meet the stricter effluent regulations [2,4–6].

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Problems of the conventional multi-step treatments are their high operation costs and the impossibility of water reuse due to high residual calcium concentration [1,3]. Therefore, recent researches are focused on the development of lower cost agents and highly efficient processes for fluoride removal.

In this study, cement paste, cured mixture of cement and water, was investigated for fluoride removal as abundant and cheaper alternative agent. Cement paste contains substantial amounts of Ca-bearing hydrates such as portlandite, calcium silicate hydrate (CSH), and ettringite for fluoride removal by precipitating CaF_2 and/or adsorbing F^- ions. The objectives of this study are to assess the feasibility of using cement paste as an alternative agent for fluoride removal and to investigate fluoride removal capacity of cement paste.

2. Materials and methods

2.1. Materials

Cement pastes were prepared by crushing 28-day-old cement paste blocks made of an ordinary Portland cement at the water to cement ratio of 0.5. The crushed particles were then passed through ASTM standard sieves. Cement paste particles with sizes less than 0.15 mm were used as cement pastes for batch experiments. Table 1 presents chemical composition of the Portland cement [7] that is expressed in terms of oxides. The source of lime was calcium hydroxide ($Ca(OH)_2$, 95+%, Aldrich Chemical). The source of fluoride solution was prepared daily by dissolving sodium fluoride (NaF, 99+%, Aldrich Chemical) in the deionized water. The acid solution of 2 N H_2SO_4 was used to adjust the pHs of solutions. The reagent grade chemicals from Aldrich were used in preparation of the contaminant, standard references, and reactants.

Table 1
Chemical composition (weight %) of the Portland cement [7]

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Loss on ignition
61.6	21.7	5.7	3.2	2.8	2.2	1.3

2.2. Experimental methods

2.2.1. Batch experiments

To investigate the behavior of fluoride removal by cement, cement paste, and lime, kinetic experiments were performed using a 1-L triangular flask with the silicon seal as a reactor. Appropriate amounts of agents, ranging from 0.1 to 1 dry weight % of the liquid, were transferred into the reactor and then stock solutions of sodium fluoride were spiked to make 100 mg/L fluoride solution. The slurries were continuously mixed with a Teflon-coated magnetic stir bar at room temperature (22 ± 0.5°C). Small volumes (typically 10 mL) of samples were taken at appropriate time intervals, filtered through 0.45-μm membrane syringe filter, and analyzed for fluoride. The change of pH was continuously monitored using a built-in pH electrode.

The effect of pH on fluoride removal in cement paste slurries was investigated using batch pH sweep experiments, similar to the Acid Neutralization Capacity Test [8]. This experiment used 100 mL polyethylene (PE) bottles to react 1% of dry cement pastes, 100 mg/L of initial fluoride concentration, and appropriate aliquots of H_2SO_4 added to yield the final pHs ranging from 12.5 (no acid addition) to 1.7. The reaction bottles were tumbled at a speed of 40 rpm for 48 h. Aqueous samples were extracted by centrifugation and filtration and analyzed for fluoride and pH.

2.2.2. Column experiment

A column experiment was performed to observe the successive fluoride removal capacity of cement paste. The column was

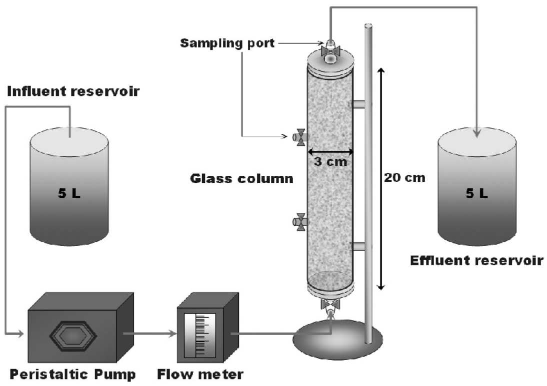

Fig. 1. Schematic diagram of the column apparatus.

filled with 1–2 mm cement paste powder and fed with the real hydrofluoric acid wastewater from a semiconductor plant. The column is made of Pyrex glass and has a volume of 141.4 L (30 ×200 mm; D ×H). The sampling port is made of Pyrex glass with a Teflon-coated tube. The system is designed which supplies wastewater from storage tank to the column in the type of upward flow through the peristaltic pump. Fig. 1 represents schematic diagram of the column apparatus.

2.2.3. Analytical methods

Fluoride concentrations were analyzed by ion chromatograph (Younglin 9100 system) equipped with a Waters detector (Waters 432 conductivity detector) and a Waters anion column (Waters IC-Pak anion column). Calcium concentrations were analyzed by Atomic Adsorption Spectrophotometer (AAS, Vario 6, Analytikjena) and the pHs of solutions were measured by pH meter (685 model, Orion).

3. Results and discussion

3.1. Screening batch experiments

Ca-bearing materials (cement, cement paste, lime) were evaluated in their abilities to remove fluoride. About 1% dose of agent was transferred into the reactor and initial concentration of fluoride in the slurry was 100 mg/L. The acid solution of 2 N H_2SO_4 was prepared to be used for pH control and initial pH value of the slurry was 3.0 ± 0.2. Fig. 2 depicts the kinetics of fluoride removal by the systems tested during the 4-h incubation time. The systems have a high acid neutralization capacity that the pH values of the systems were increased to 12.0–13.0 within 1 h. As shown in Fig. 2, cement paste, cured mixture of cement and water, removed fluoride much better and faster than raw cement. About 92.6% of fluoride in 100 mg F^-/L wastewater was removed by 1% dose of the cement paste powder, whereas the removal efficiencies of raw cement and lime were 47.3 and 96.4%, respectively. The performance of cement paste was competitive to that of lime, the conventional fluoride removal agent. Various Ca-bearing hydrates such as portlandite, CSH, and ettringite in cement paste were identified to remove fluoride by precipitating CaF_2 and/or adsorbing F^- ions.

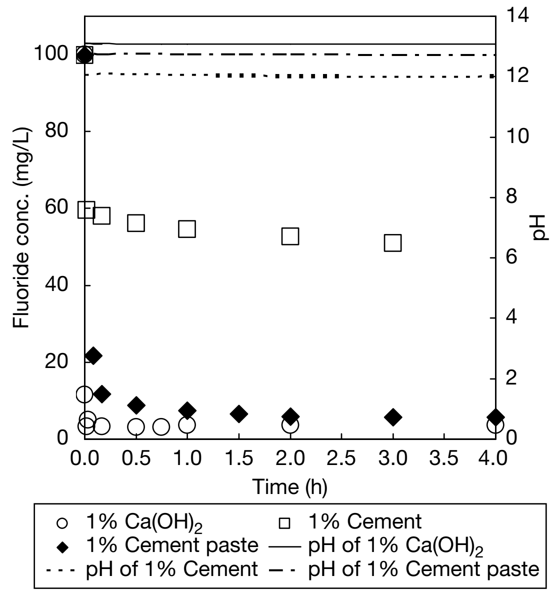

Fig. 2. Kinetics of fluoride removal by lime, cement, and cement paste.

However, the removal efficiency of raw cement was low because Ca-bearing hydrates were not formed sufficiently for fluoride removal during the period. Therefore, cement paste was chosen to be developed into a cheaper alternative agent to remove fluoride.

3.2. Effect of substitution of cement paste for lime on fluoride removal

Fluoride removal reactions in cement paste and lime systems were further characterized using the batch slurry reactors. Fig. 3 shows the effect of substitution of cement paste for lime on fluoride removal. Unlike screening experiments, small amount (0.1 dry weight % of the liquid) of agent was transferred into the reactor. Initial concentrations of fluoride in the slurries were 100 mg/L and initial pH values of the slurries were 3.0 ± 0.2. As shown in Fig. 3, the final pH values of the systems were maintained at 11.2–12.1. This shows that acid neutralization capacity of the cement paste is comparable to that of lime. From the batch slurry experiments using cement paste and lime simultaneously, 50–67% of lime can be substituted by cement paste to satisfy fluoride effluent limitation of 15 mg/L [9]. The cement paste system also decreased a residual calcium concentration, which is considered an advantageous characteristic for water reuse for fluoride removal.

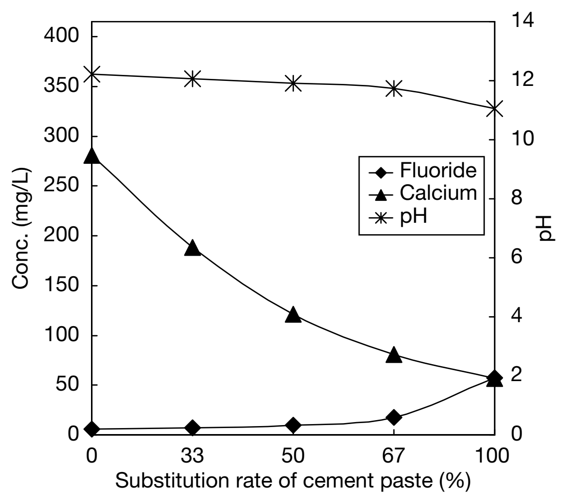

Fig. 3. Effect of substitution of cement paste for lime on fluoride removal.

Batch slurry experiments with the real hydrofluoric acid wastewater were conducted to assess the feasibility of using the cement paste. The wastewater contains 118 mg/L of F^-, 64 mg/L of NO_3^-, and 2110 mg/L of PO_4^{3-}. Table 2 presents the results of batch slurry experiments using the cement paste in this mixed hydrofluoric acid wastewater. The dosage of cement paste and lime mixture were 1000 mg/L. The removal efficiencies were lower than that of the artificial wastewater because available calcium dissolved from the cement paste mixtures was considerably consumed to form Ca-hydroxy-apatite with the large amount of phosphate present in the real mixed hydrofluoric acid wastewater. In addition to this, nitrate was removed by 52%. Nitrate removal is due to anion exchange capability of cement paste minerals such as ettringite. This nitrate adsorption onto cement paste was well described by a linear isotherm of which the coefficient was found to be 43.6 L/kg [10]. Therefore, cement paste has a sound characteristic to remove fluoride and other pollutants

Table 2
The results of batch slurry experiments using the cement paste for treatment of the real hydrofluoric acid wastewater

	F^-		NO_3^-	PO_4^{3-}	pH
Substitution of cement paste for lime (%)	50	70	100	100	–
Raw wastewater (mg/L)	118	118	64	2110	1.2
Treated wastewater (mg/L)	31	38	31	1150	5.7
Removal efficiency	74	62	52	46	–

simultaneously in the wastewater from semiconductor and display panel manufacturing plants.

3.3. Effect of pH on fluoride removal in cement paste slurries

The effect of pH on fluoride removal in cement paste slurries was assessed using batch pH sweep experiments, where slurries of 100 mg/L fluoride and 1% cement paste were reacted for 48 h with different amounts of sulfuric acid. In Fig. 4, fluoride concentrations were plotted on the basis of final pH values (*x*-axis). Fig. 4 shows that fluoride removal reactions in cement paste slurries are dependent on pH. The optimal pH for the cement paste slurries exists between 7.0 and 11.5. A considerable decrease in the reactivity is observed in the cement paste slurries when pH was lowered below 4.7. These results indicate that the cement paste retains a substantial removal capacity for fluoride in the mid or high pH region and cement hydrates have important roles in immobilizing aqueous fluoride. The increase of fluoride concentration in high pH region from pH 11 to 13 is caused by formation of portlandite ($Ca(OH)_2$) and subsequent decrease of available calcium for fluoride precipitation. Fluoride showed lower solubility in pH region of 7–11, which coincide with the existence range of CSH, ettringite, calcium alumina hydrate in cement pastes [11]. This indicates that these Ca-bearing hydrates have important roles in immobilizing fluoride by precipitating with supplied calcium from the minerals and/or by adsorbing onto available anion exchange sites in the minerals.

3.4. Column experiment

A column experiment was performed to observe the successive fluoride removal capacity of cement paste. The column was filled with 1–2 mm cement paste powder and fed with the real hydrofluoric acid wastewater of pH 3.3 and 1150 mg/L of F^- containing the least amount of other pollutants from a semiconductor plant. Fig. 5 is the result of the column experiment. As shown in Fig. 5, the initial fluoride concentration of 1150 mg/L immediately reduced to the level of less than 15 mg/L, in the column effluent. After

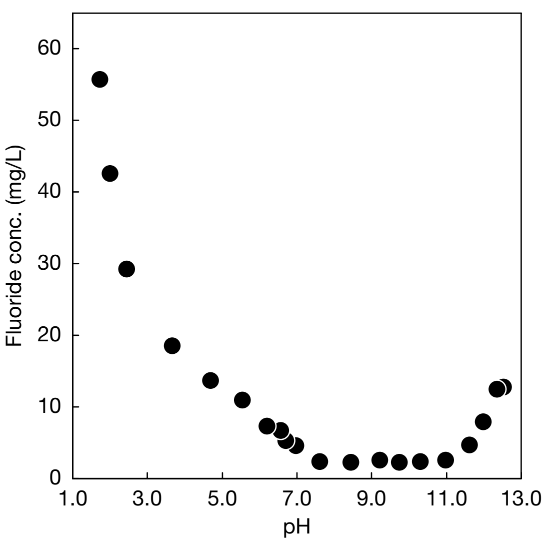

Fig. 4. Effect of pH sweep on fluoride removal in cement paste slurries.

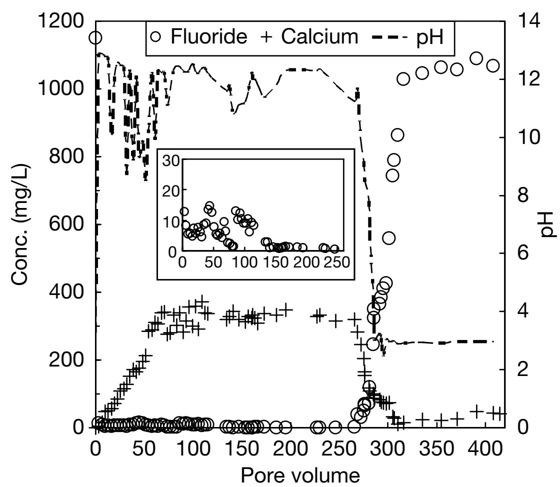

Fig. 5. Breakthrough curve of the cement paste column fed with hydrofluoric acid wastewater of 1150 mg F/L.

120 pore volume, effluent fluoride concentration was remarkably reduced to 1.5 mg/L or less until it broke through at 270 pore volume.

The effluent pH was initially 12.8 and decreased to 10.8 before the breakthrough, indicating that cement paste has strong acid neutralization capacity. The effluent concentration of fluoride was greatly dependent upon the residual calcium concentration as predicted by the solubility product (K_{sp}) of CaF_2. As calcium gradually leached out from cement paste by the acid attack, fluoride concentrations decreased proportionally until 120 pore volume. Then the leached calcium reached the maximum level of 360 mg/L, which was maintained until the breakthrough point. Accordingly the fluoride concentration remained at the lowest value. Afterward the calcium leached out from cement hydrates such as portlandite, CSH, and ettringite was completely used up, thus not forming CaF_2 precipitates anymore to show a sharp increase in the effluent fluoride concentration at the breakthrough point.

Based on the result of column experiment, the capacity of cement paste for fluoride removal was calculated to 0.149 g F^- per g of cement paste, which is 5.7 times higher than that of alum (0.026 g F^- per g). Therefore, cement paste, which can be obtained from waste concrete recycling process, can be developed to more economical and viable substitute for lime to remove fluoride and it may be used to simultaneously remove other pollutants such as nitrate and phosphate in the wastewater from semiconductor and display panel manufacturing plants.

4. Conclusion

From the evaluation of Ca-bearing materials (cement, cement paste, lime), cement paste was found to have a substantial removal capacity for fluoride thus it has the potential to be developed into an abundant and cheaper alternative agent. The low reactivity observed in cement implies that Ca-bearing hydrates such as portlandite, CSH, and ettringite in cement paste are important for precipitating CaF_2 and/or adsorbing F^- ions.

In the batch slurry experiments using cement paste and lime simultaneously, 50–67% of lime can be substituted by cement paste to satisfy fluoride effluent limitation of 15 mg/L. Fluoride removal reactions in cement paste slurries were strongly affected by pH, and an optimal pH for the cement paste slurries exists between 7.0 and 11.5. A considerable decrease in the reactivity is observed in the cement paste slurries when pH was lowered below 4.7. These results indicate that the cement paste retains a substantial removal capacity for fluoride in the mid or high pH region.

From the result of the column experiment to observe the successive fluoride removal capacity of cement paste, the real hydrofluoric acid wastewater concentration of 1150 mg/L immediately reduced to the level of less than 15 mg/L, in the column effluent.

The results obtained from the present study demonstrate that the cement paste generally has advantageous characteristics as an economical and viable substitute for lime to remove fluoride and other pollutants such as nitrate and phosphate simultaneously in the wastewater from semiconductor and display panel manufacturing plants.

Acknowledgements

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