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FLUORIDE REMOVAL IN A FIXED BED PACKED WITH GRANULAR CALCITE

MIN YANG^{1,*M}, TAKAYUKI HASHIMOTO², NOBUYUKI HOSHI² and HARUKI MYOGA²

¹State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, P.O. Box 2871, Beijing 100085, People's Republic of China and ²Central Research Laboratories, Organo Corporation, 4-9, Kawagishi 1-Chome, Toda City, Saitama Pref. 335-0015, Japan

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Abstract—A fixed bed reactor filled with calcite particles (mean strokes diameter, 0.20 mm) was constructed and the reactor was used to treat synthetic wastewater containing HF, NaF, NH₄F or Na₂SiF₆ under various conditions. Calcium ions (Ca²⁺) were found to exist in the treated effluent and the molar Ca²⁺ concentration ([Ca²⁺]) was related to the molar ratio of H⁺ to F⁻ ($[H^+]_0/[F^-]_0$) in influent as $\log_{10}[Ca^{2+}] = 0.020[H^+]_0/[F^-]_0 - 4.24$. The effluent F⁻ concentration was determined by the concentration of effluent Ca²⁺ as $[F^-][Ca^{2+}]^{0.94} = 3.98 \times 10^{-10}$ under an SV of 1.0 to 5.0 h⁻¹ and 25°C. This equation was similar with that of the solubility product of CaF₂ and could be applied to wastewaters containing HF, NaF, NH₄F or Na₂SiF₆ under an influent F⁻ concentration ranging from 25 to 3000 mg l⁻¹. The effluent F⁻ was also found to be related to effluent pH as $\log_{10}[F^-] = 0.51\text{pH} - 2.91$. The effluent F⁻ was about 6 mg l⁻¹ at an effluent Ca²⁺ of 80 mg l⁻¹ or effluent pH of 6.8 under the above conditions. The effluent F⁻ increased from 6 to 12 mg l⁻¹ and effective calcite conversion rate decreased from ca. 60 to 40% when SV was increased from 1.6 to 16.0 h⁻¹ at a $[H^+]_0/[F^-]_0$ of 0.75. Significant increase of effluent F⁻ as well as decrease of effective calcite conversion rate was observed when reaction temperature was decreased to 8.5°C at an SV of 7 h⁻¹ and $[H^+]_0/[F^-]_0$ of 0.75. The performance of the reactor was affected by the existence of SO₄²⁻ to some extent and significantly inhibited by PO₄³⁻. A molar ratio of PO₄³⁻ to F⁻ higher than 0.05 stopped F⁻ removal at a PO₄³⁻ of 15 mg l⁻¹. © 1999 Elsevier Science Ltd. All rights reserved

Key words—fluoride removal, calcite, replacement, wastewater treatment

INTRODUCTION

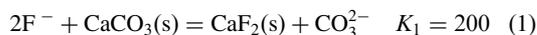
Hydrofluoric acid (HF) and ammonium fluoride (NH₄F) are the essential chemicals for wet processes of LSI (large-scale integration) and LCD (liquid crystal display) production lines. These fluorine compounds (F) have been removed from wastewater by using a calcium fluoride (CaF₂) precipitation reaction followed by a solid-liquid separation process for several decades. The CaF₂ precipitates are usually so fine that they can only be separated from the treated liquid in sedimentation tanks by adding inorganic coagulants like aluminum sulfate (Al₂(SO₄)₃) or polyaluminum chloride (PAC) to help form flocs. In most cases, the effluent F⁻ remains as high as 15 to 30 mg l⁻¹ after CaF₂ precipitation even under a relatively high remaining

Ca²⁺ concentration (Eto and Takadoi, 1978). Therefore, the above coagulants have been used not only for the purpose of removing the fine CaF₂ particles, but also for the purpose of adsorbing the remaining F⁻ in the treated effluent. So, the coagulants are usually used in a very high dose, which results in the increase of sludge and makes the precipitation slurry difficult to dewater.

An alternative process, which utilizes the reaction of F⁻-bearing wastewaters with calcite particles, has been proposed since the 1970's (Augustyn *et al.*, 1978; Simonsson, 1979; Ekdunge and Simonsson, 1984). The reaction is usually expressed as equation (1) and the equilibrium constant *K* was calculated from the solubility products of calcite and fluorite (Simonsson, 1979). This has been considered to be a pseudomorphic replacement involving epitaxial growth of the (110) plane of fluorite in the (1011) plane of calcite, leaving the Ca²⁺ positions nearly unchanged (Glover and Sippel, 1962). The molecular volume of CaF₂ in fluorite is 33% smaller than

*Author to whom all correspondence should be addressed.
[Tel.: +86-10-62923475; fax: +86-10-62923475; e-mail: yang-hu@263.net].

that of CaCO_3 in calcite, so the replacement reaction leaves 33% additional porosity in fluorite, which facilitates the diffusion of F^- ions into and of CO_3^{2-} ions out of the particles (Trautz *et al.*, 1961).



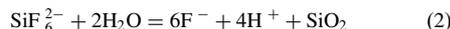
This calcite process was initially applied to the treatment of NH_4F solution from the AUC process for conversion of UF_6 to UO_2 (Simonsson, 1979). Recently, efforts have been made to apply it to the treatment of high strength HF and buffered hydrofluoric acid (BHF, a mixture of HF and NH_4F) wastewater (Sato *et al.*, 1995; Miki *et al.*, 1996; Sato, 1997). However, the applications have been mainly limited to the purpose of sludge reduction and fluoride recovery through CaF_2 formation and the treated effluent needs to be treated further by using a conventional process to satisfy wastewater discharge criteria (below 5 to 15 mg l^{-1} in Japan, varying according to autonomies). While recovery of CaF_2 from the high strength wastewater is of considerable significance from the viewpoint of recycling resource, the problems for treating low to medium strength wastewater remain to be unresolved. Furthermore, since low strength wastewater is more difficult to be treated by the conventional process (Majima and Takatsuki, 1987), the effluent from the calcite process poses new problems for F^- removal. Ekdunge and Simonsson (1984) have found that a semicontinuous fixed bed of limestone particles could reduce the F^- content of NH_4F solution to $10\text{--}20 \text{ mg l}^{-1}$ at 30°C in a series of three columns. Although the result has demonstrated the possibility of the calcite process for wider applications, multistep treatment as well as the need for removing CO_2 and NH_3 from treated water of the first column would become a heavy burden for wastewater treatment. Furthermore, a proper process control strategy is still not available since a quantitative relationship between the effluent F^- concentration and a controllable parameter has not

yet been elucidated, which has also largely prevented the calcite process from wider application.

In this study, a fixed bed reactor filled with calcite particles was constructed and performance of the reactor was evaluated on treating synthetic wastewater containing HF, NaF, NH_4F or Na_2SiF_6 under various conditions. The study was focused on elucidating relations between effluent F^- and some controllable parameters in order to establish a process control strategy. The effects of SV (space velocity), temperature and the existence of SO_4^{2-} and PO_4^{3-} on F^- removal were also investigated.

MATERIAL AND METHODS

A polyacrylic resin column, with an inner diameter of 26 mm and effective height of 600 mm, was used as the fixed bed reactor (Fig. 1). In each batch of experiment, 200 g calcite of a given particle distribution (Table 1) was packed on the saran sheet spread in the lower part of the reactor, giving a fixed-bed volume of 140 cm^3 . Synthetic wastewater, which was prepared by dissolving NaF, NaSiF_6 , HF or NH_4F into pure water and then adjusting the H^+ to F^- molar ratio to given values with NaOH or HCl, was pumped into the bottom of the reactor. Reaction temperature was controlled at 25°C except for specified conditions by immersing reaction part of the reactor into a water bath. Concentrations of F^- and Ca^{2+} were respectively determined on two ionselective electrode meters (IM-40S, TOA Electric Waves Co., Japan). It should be noted that $\text{Na}_2\text{SiF}_6\text{-F}$ could also be measured on the fluoride ion-selective electrode meter operated at a pH of 5.2. It was possible that the fluoride ion-selective electrode responded to the fluoride ions dissociated from Na_2SiF_6 at the measuring pH through equation (2) (Mooney *et al.*, 1982; Ohmi, 1995). Concentrations of SO_4^{2-} and PO_4^{3-} were measured on ion-chromatograph (IC-7000, Yokogawa Instruments Co., Japan).



RESULTS AND DISCUSSION

Characteristics of calcite treatment process

In a conventional F^- removal process, Ca^{2+} ions are added into the wastewater to create CaF_2 precipitate and the remaining F^- concentration is mainly determined by the remaining Ca^{2+} concentration according to the solubility product of fluorite as shown in equation (3). While the calcite treatment process has been considered to be the result of replacement of calcite by fluorite (Glover and Sippel, 1962), the fact that F^- is also removed through formation of CaF_2 indicated that this process is possibly the same as the conventional one in nature. The difference is that Ca^{2+} ions are obtained through substituting carbonate ions (CO_3^{2+}) from calcite by F^- in the case of the calcite process equation (1). Although Ca^{2+} is not added from outside, it is possible that some Ca^{2+} ions are released into the solution during replacement, and the remaining F^- concentration is related to the

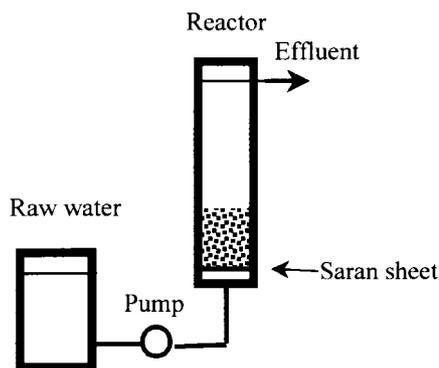


Fig. 1. Schematic diagram of calcite reactor.

Table 1. Physical and chemical properties of the calcite

Physical properties			Chemical composition		
Particle distribution	> 35 mesh	< 1%	CaCO ₃	%	99.0
	35–70 mesh	75–95%	SiO ₂	%	0.1
	< 70 mesh	< 10%	Al ₂ O ₃	%	0.05
Stokes diameter	mm	0.205	Fe ₂ O ₃	%	0.01
Density	g cm ⁻³	2.7	MgO	%	0.15
Apparent density	g cm ⁻³	1.35	P	%	0.001

Ca²⁺ concentration according to equation (3). Since H⁺ is an important factor on Ca²⁺ dissolution, molar ratio of initial H⁺ to F⁻ ($[H^+]_0/[F^-]_0$) was varied from 0 to 125% under the following conditions: space volume (SV), 1.0 to 5.0 h⁻¹; influent F⁻, 25 to 3000 mg l⁻¹. NaF, NH₄F, HF and Na₂SiF₆ were used as F sources, respectively, and the Na₂SiF₆-F was also expressed as F⁻ in this study since it was found that the F concentration of the Na₂SiF₆ solution could be measured on the fluoride ion-selective electrode meter.



$$K_{sp} = [F^-]^2[Ca^{2+}] = 3.5 \times 10^{-11}$$

Figure 2 shows the effects of the initial H⁺/F⁻ ratio on effluent Ca²⁺ and Fig. 3 shows the relationship between effluent Ca²⁺ and F⁻. Figure 2 indicates that dissolution of Ca²⁺ from calcite occurred during the replacement reaction. While a scattering of data at $[H^+]_0/[F^-]_0$ lower than 30% was observed, the logarithm of effluent Ca²⁺ concentration was found to be almost linearly related to $[H^+]_0/[F^-]_0$, and the relation did not change with variation of F source. The relation between $[H^+]_0/[F^-]_0$ and molar concentration of effluent Ca²⁺ ($[Ca^{2+}]$) was established as equation (5) based on Fig. 2. It is interesting that the effluent Ca²⁺ was determined by the molar ratio of H⁺ to F⁻, which indicated the essential difference between

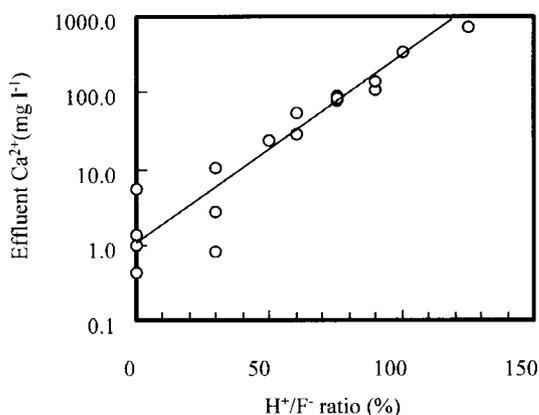


Fig. 2. Effects of H⁺/F⁻ ratio on effluent Ca²⁺. SV, 1–5 h⁻¹; F sources, NaF, NH₄F, HF or Na₂SiF₆; F⁻, 25 to 3000 mg l⁻¹.

the replacement by HF and calcite dissolution by the other acids as shown in equation (4). When calcite particles are put into an HCl or H₂SO₄ solution, the extent of dissolution is mainly determined by the concentration of the acid, i.e. the concentration of H⁺, and the ratio of H⁺ to Cl⁻ or SO₄²⁻ does not have much meaning. Figure 3 shows that similar with the conventional CaF₂ precipitation reaction, the effluent F⁻ concentration depended on the effluent Ca²⁺ concentration in the fixed bed calcite process. It was not necessary to raise reaction temperature or strip NH₃ in order to obtain a high F⁻ removal. An effluent F⁻ of below 10 mg l⁻¹ could be obtained by adjusting the $[H^+]_0/[F^-]_0$ of wastewater to give an effluent Ca²⁺ of more than 50 mg l⁻¹ at 25°C. Difference of F sources did not affect the relation between the effluent F⁻ and Ca²⁺, which could be expressed as equation (6) (at $[Ca^{2+}] > 0.05$ mM), over the whole influent F⁻ range from 25 to 3000 mg l⁻¹. Equation (7) can be obtained by rewriting equation (6). It was clear that equation (7) was very similar to the K_{sp} of CaF₂ in equation (3), which is also plotted in Fig. 3 for comparison. The order of 0.94 for $[Ca^{2+}]$ in equation (7) was perhaps mainly originated from experimental error. The difference of one order between $[F^-]^2[Ca^{2+}]^{0.94}$ (3.98×10^{-10}) and K_{sp} (3.46×10^{-11}) was perhaps because complete equilibrium was not achieved at an SV of 1.0 h⁻¹ or higher.

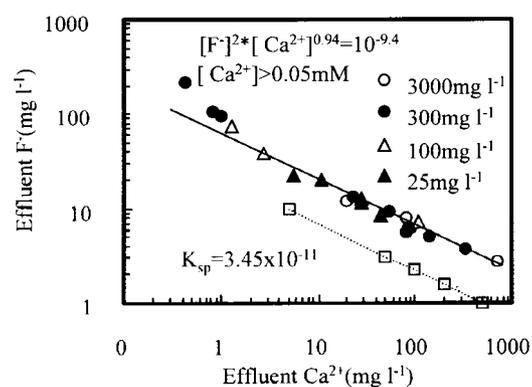
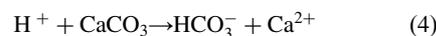


Fig. 3. Effects on effluent Ca²⁺ on F⁻ removal. SV, 1–5 h⁻¹; F sources, NaF, NH₄F, HF or Na₂SiF₆.

$$\log_{10}[\text{Ca}^{2+}] = 0.020[\text{H}^+]_0/[\text{F}^-]_0 - 4.24 \quad (5)$$

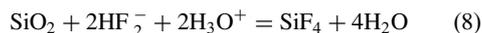
$$\log_{10}[\text{F}^-] = -0.47 \log_{10}[\text{Ca}^{2+}] - 4.70 \quad (6)$$

$$[\text{F}^-]^2[\text{Ca}^{2+}]^{0.94} = [\text{F}^-]^2[\text{Ca}^{2+}] = 3.98 \times 10^{-10} \quad (7)$$

For CaF_2 precipitation, supersaturation of F^- and Ca^{2+} is the major premise. According to equation (3), two F^- react with one Ca^{2+} and the ion product of the reaction can be expressed as $[\text{F}^-]^2[\text{Ca}^{2+}]$. The ion product equation indicates that it is much easier to achieve a supersaturation state at a high initial F^- concentration. So, F^- removal performance of a conventional process not only depends on Ca^{2+} doses, but also is largely affected by the initial F^- concentration, which is why low strength wastewater is difficult to be treated. For wastewater containing F^- lower than 50 mg l^{-1} , it is almost impossible to directly remove F^- through CaF_2 precipitation with a reasonable Ca^{2+} dose (Majima and Takatsuki, 1987).

However, as shown in Fig. 3, F^- removal performance of the calcite process was not affected by variations of influent F^- over the whole F^- range of 25 to 3000 mg l^{-1} , which could be considered to be an important advantage over the conventional method. One of the factors possibly contributing to this result was the continuous dissolution of Ca^{2+} ions from calcite particles. Although the bulk Ca^{2+} concentration was not so high, it was possible that there existed high Ca^{2+} concentration zones around and inside calcite particles during the replacement reaction. The Ca^{2+} concentrations in the locally existing high concentration zones were possibly so high that the influence of the influent F^- concentration could be offset. Fluorite formed on the surface of the calcite particles provided numerous crystal seeds for succeeding F^- to crystallize with Ca^{2+} , which could not be expected from a conventional system since CaF_2 grains formed during treatment will be washed out of the reactor.

In electronic industry, most of HF and BHF are used for etching and washing silicone wafers, and SiF_6^{2-} is formed via equations (8) and (9) (Ohmi, 1995). SiF_6^{2-} has been considered to be difficult to be removed by the conventional method. In this study, however, $\text{Na}_2\text{SiF}_6\text{-F}$ was effectively removed in the fixed bed reactor. This result was also possibly originated from the existence of high Ca^{2+} concentration zones.



When F-bearing wastewater with a certain $[\text{H}^+]_0/[\text{F}^-]_0$ was passed through the fixed bed reactor, most of F^- ions were removed from wastewater to

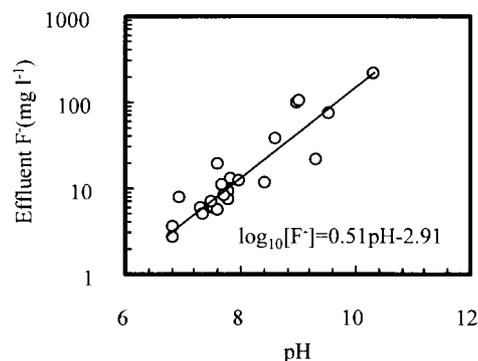
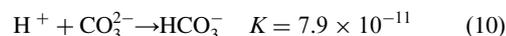


Fig. 4. Relation between effluent pH and F^- . For conditions, see Fig. 3.

form CaF_2 , leaving H^+ ions in the solution. H^+ ions will react with CO_3^{2-} ions replaced by F^- ions as shown in equations (10) and (11) (Cordell, 1968). It is apparent that the effluent pH will be mainly determined by equilibrium of equations (10) and (11). Therefore, it could be estimated that there also existed a certain relation between effluent F^- concentration and pH. The data of effluent F^- concentration and pH obtained in the above experiments are plotted in Fig. 4. It was found that the logarithm of effluent F^- concentration was in direct proportion to effluent pH as shown in equation (12) and an effluent F^- below 10 mg l^{-1} could be obtained at an effluent pH lower than 7.0. This result was consistent with those obtained by Ekdunge and Simonsson (1984), who found that F^- concentrations in effluents from a fixed bed reactor treating wastewater containing high concentration NH_4F were decreased by lowering pH.



$$\log_{10}[\text{F}^-] = 0.51\text{pH} - 2.91 \quad (12)$$

The above results demonstrated that the replacement reaction was actually controlled by $[\text{H}^+]_0/[\text{F}^-]_0$. It is therefore theoretically possible to decrease effluent F^- to any level by selecting a proper $[\text{H}^+]_0/[\text{F}^-]_0$. While it is difficult to measure $[\text{H}^+]_0/[\text{F}^-]_0$ in wastewater directly, the value of $[\text{H}^+]_0/[\text{F}^-]_0$ could be obtained indirectly through measuring effluent Ca^{2+} concentration, F^- concentration or pH. By feeding back the measured results to a controller to adjust acid or alkali feeding rate, it is possible to obtain a proper $[\text{H}^+]_0/[\text{F}^-]_0$. Therefore, a suitable process control strategy could be established on relationship between $[\text{H}^+]_0/[\text{F}^-]_0$ of wastewater and effluent Ca^{2+} concentration, F^- concentration or pH.

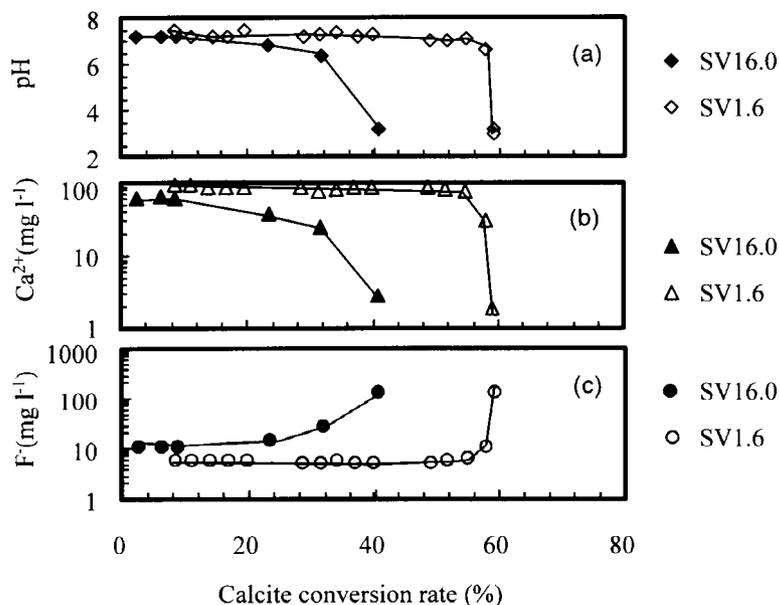


Fig. 5. (a), (b) and (c) Variations of effluent pH, Ca^{2+} and F^- with calcite conversion rate. Inf. F^- , 300 mg l^{-1} ; $[\text{H}^+]/[\text{F}^-]$, 0.75.

Operation conditions

In a solid-liquid reaction system like the one used in this study, diffusion of dissolvable reactants and reaction products inside the particles becomes the rate limiting factor in many cases. So, the reaction time, i.e. HRT or SV, as well as particle size and reaction temperature is usually considered to be an important operation parameter. There have been several studies on the kinetics of calcite treatment processes (Simonsson, 1979; Sato, 1997). Just like other solid-liquid reactions, reducing particle size or raising temperature was found to be useful for improving F^- removal efficiency. In order to evaluate the effects of reaction time, the SV was varied from 1.6 to 16.0 h^{-1} in steps. At each SV, the treatment continued until breakpoint (which is defined as the point when the effluent Ca^{2+} decreased to below 5 mg l^{-1} in this study) was achieved. The $[\text{H}^+]_0/[\text{F}^-]_0$ of wastewater was adjusted to 0.75 to obtain an effluent Ca^{2+} concentration of ca. 80 mg l^{-1} . Fig. 5(a), (b) and (c) show variations of effluent F^- , Ca^{2+} and pH, respectively, with calcite conversion rate, which is defined as the ratio of reacted Ca (the sum of CaF_2 -Ca and effluent Ca) to the initial CaCO_3 -Ca in this study. It was found that effluent pH as well as both of the concentrations of effluent F^- and Ca^{2+} was almost constant for a certain period at the first. Then sudden decreases of effluent Ca^{2+} and pH were observed with a significant increase of effluent F^- . A high SV gave a high F^- concentration and a low calcite conversion rate. The effluent F^- is plotted against Ca^{2+} in logarithmic scale as shown in Fig. 6. It was found that the effluent F^- was also linearly related with effluent Ca^{2+} logarithmically

and the relation was almost not affected by the difference of SV (from 1.6 to 16.0 h^{-1}). The plot in Fig. 3 was also inserted in Fig. 6 for comparison and its slope was found to be smaller than that obtained here. The data from Fig. 3 were obtained before breakpoint was reached, while data from Fig. 5 were obtained through the whole treatment. So, it seemed that the relation between effluent Ca^{2+} concentration and effluent F^- concentration changed a little after the fixed bed reached breakpoint. The reason for this difference is not clear.

Figure 7 shows the relation between SV and calcite conversion ratio. The calcite conversion ratio was almost linearly related with the SV at an SV over 3.0 h^{-1} . During treatment, some lumps as large as 0.5 to 2 cm in diameter were found after the spent calcite particles were pulled out from the reactor. Since both the amount of calcite and the initial F^- concentration were constant, the treat-

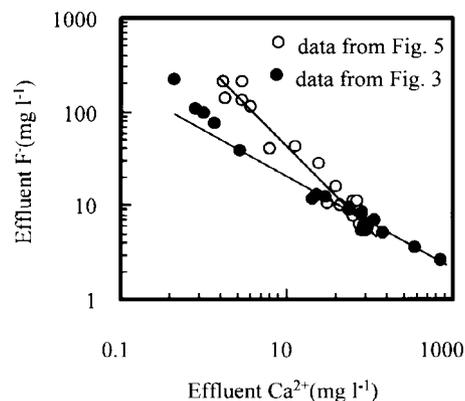


Fig. 6. Relations between effluent Ca^{2+} and F^- .

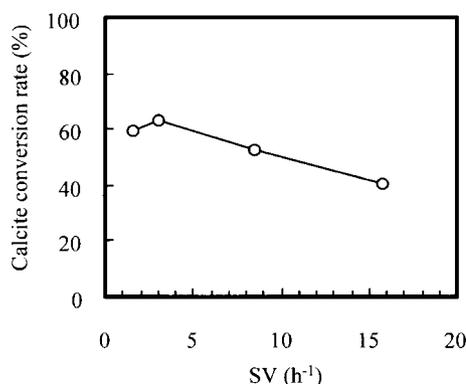


Fig. 7. Effect of SV on calcite conversion rate. For conditions, see Fig. 5.

ment cycle became longer and the upflow linear velocity (LV) decreased with the decrease of SV, which made it easy to form lumps at a lower SV. The irregularity of conversion ratio at SV 2 h⁻¹ was perhaps originated from formation of lumps since the treatment lasted for as long as more than 1 month. It was apparent that a low SV was desirable from the viewpoint of effective utilization of calcite. However, some measures are necessary for preventing formation of lumps in the reactor. On the other hand, more efforts should be made to increase the effective utilization rate of calcite since the highest conversion ratio was about 60% under the above conditions.

Another important factor possibly affecting F⁻ removal efficiency is reaction temperature. Simonsson (1979) considered the calcite replacement reaction at room temperature being too slow to be of practical use. However, the results in our study demonstrated that the process could be put into practical use even at a temperature of 25°C if a proper [H⁺]₀/[F⁻]₀ ratio and SV were selected. In order to investigate performance of the fixed-bed at lower temperatures, F⁻ removal at 16.5 and 8.5°C

were also conducted, respectively (Fig. 8). The reactor was operated at the following conditions: [H⁺]₀/[F⁻]₀ ratio, 0.75; influent F⁻, 300 mg l⁻¹; SV, 7.0 h⁻¹. It is clear that while the difference between 25.0 and 16.5°C was not so significant, the F⁻ removal efficiency decreased drastically when the temperature was decreased to 8.5°C. At 8.5°C, not only an early breakpoint, but also a significantly increased effluent F⁻ was observed.

Effects of co-existing ions

In the calcite treatment process, F⁻ is removed through the formation of CaF₂. So, anions like SO₄²⁻ and PO₄³⁻ are possible to have some effects on F⁻ removal performance since they can react with Ca²⁺ to form precipitates of CaSO₄ and CaHPO₄ (or Ca₃(PO₄)₂, according to reaction pH), respectively. The effects of SO₄²⁻ (added as Na₂SO₄) and PO₄³⁻ (added as Na₂HPO₄) were investigated, respectively, at an [H⁺]₀/[F⁻]₀ ratio of 0.75. The other conditions are shown in respective figures. Fig. 9(a) shows that the effluent F⁻ concentrations increased with the increase of SO₄²⁻ concentration. The existence of 300 mg l⁻¹ SO₄²⁻ gave an increase of F⁻ concentration by 50%. When 2.6 mg l⁻¹ PO₄³⁻ coexisted with SO₄²⁻, effluent F⁻ concentration increased more significantly. It was found that the inhibiting effect of PO₄³⁻ was more profound than that of SO₄²⁻ as shown in Fig. 9(b). Addition of 29 mg l⁻¹ PO₄³⁻ resulted in an increase of effluent F⁻ concentration from 6 mg l⁻¹ to more than 30 mg l⁻¹. So, the existence of an even relatively low concentration of PO₄³⁻ would make it difficult to employ the calcite process to treat F⁻-bearing wastewater.

During treatment, *ca.* 9% of initial SO₄²⁻ was removed from wastewater while PO₄³⁻ was reduced to a level unable to be detected on ion-chromatograph. The solubility products of CaSO₄ and CaHPO₄ (CaHPO₄ should be the dominating specie at an effluent pH of 6.8) are 1.2 × 10⁻⁶ to 2.27 ×

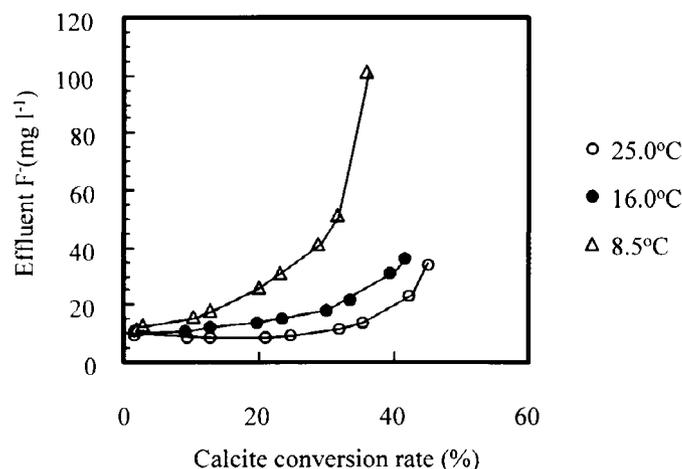


Fig. 8. Effect of temperature on F⁻ removal. SV, 7 h⁻¹; Inf. F⁻, 300 mg l⁻¹; [H⁺]/[F⁻], 0.75.

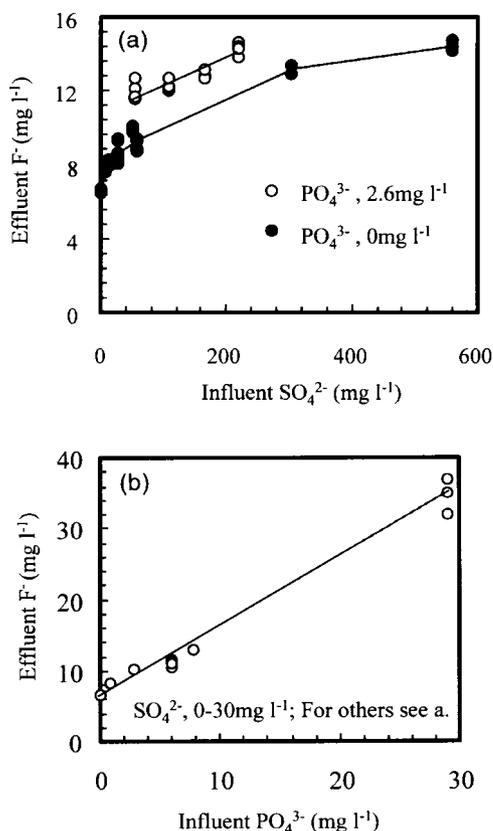


Fig. 9. (a) Effects of SO_4^{2-} and PO_4^{3-} on F^- removal. SV, 6 h^{-1} ; Inf. F^- , 300 mg l^{-1} ; $[\text{H}^+]/[\text{F}^-]$, 0.75 (not including H^+ from NaH_2PO_4). (b) Effects of SO_4^{2-} and PO_4^{3-} on F^- removal.

10^{-5} and 1×10^{-7} to 2.55×10^{-7} (Japan Society on Chemistry, 1975), respectively, considerably higher than that of CaF_2 (3.45×10^{-11}). It is interesting that the ions of SO_4^{2-} and PO_4^{3-} were removed even when the ion products were below the respective solubility product of CaSO_4 and CaHPO_4 . It is clear that inhibition of SO_4^{2-} and PO_4^{3-} on F^- removal was not caused by competition for Ca^{2+} since the effluent Ca^{2+} was relatively constant, being 70 to 80 mg l^{-1} through each run.

In order to investigate inhibition of PO_4^{3-} on F^- removal further, influent F^- concentration was increased stepwise from 5 to 300 mg l^{-1} while PO_4^{3-} was kept constant at 15 mg l^{-1} . NaF was used as the F source, and the effluent Ca^{2+} concentration was adjusted to around 80 mg l^{-1} by adding HCl to synthetic wastewater. The results are shown in Fig. 10. It was found that removal of F^- did not occur until the molar ratio of PO_4^{3-} to F^- was decreased to 0.05 (at initial F^- concentration of 50 mg l^{-1}). Although a slight scattering of data was observed, the C/C_0 of PO_4^{3-} varied in a narrow range between 53 and 60% at a PO_4^{3-} to F^- ratio larger than 0.05 except for one point. The relatively constant PO_4^{3-} removal was perhaps because the effluent Ca^{2+} was almost kept at a constant level. F^- removal began

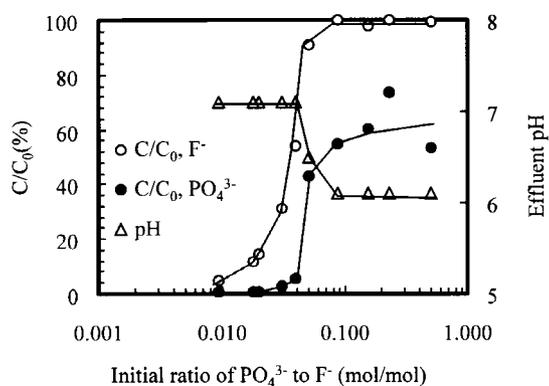


Fig. 10. Effects of PO_4^{3-} to F^- ratio on PO_4^{3-} and F^- removal. SV, 6 h^{-1} ; Inf. PO_4^{3-} , 15 mg l^{-1} .

to be observed when the $\text{PO}_4^{3-}/\text{F}^-$ ratio was reduced to 0.05 and improved significantly with the decrease of ratio. It is interesting that PO_4^{3-} removal also increased significantly at the same time. While the existence of PO_4^{3-} markedly inhibited F^- removal, the existence of certain amount of F^- seemed to be necessary for achieving complete PO_4^{3-} removal. It was possible that some PO_4^{3-} might be included by CaF_2 to form an F^- - PO_4^{3-} - Ca^{2+} complex when F^- was removed. Figure 10 demonstrates that the dominated reaction changed with the variation of $\text{PO}_4^{3-}/\text{F}^-$ ratio: formation of CaHPO_4 dominated at a $\text{PO}_4^{3-}/\text{F}^-$ ratio higher than 0.05, and formation of CaF_2 began to dominate at a $\text{PO}_4^{3-}/\text{F}^-$ ratio lower than 0.05. Variation of effluent pH also supported the above observation. It is interesting that although the solubility product of CaF_2 was much lower than that of CaHPO_4 , the molar concentration of F^- had to be more than 20 times higher than that of PO_4^{3-} in order to initiate F^- removal. It is possible that CaHPO_4 grains formed on the surface of calcite particles had prevented CaF_2 seeds from forming when F^- was insufficient.

CONCLUSION

A fixed bed reactor filled with calcite particles was constructed, and the reactor was used to treat synthetic wastewater containing HF, NaF, NH_4F or Na_2SiF_6 under various conditions. The molar ratio of H^+ to F^- in wastewater was varied to investigate its effects on dissolution of Ca^{2+} and the study was focused on elucidating relations among effluent F^- , Ca^{2+} and pH (H^+) in order to establish a process control strategy. The effects of SV, temperature and coexisting ions on F^- removal were also investigated. The results are summarized as follows:

1. Ca^{2+} was found to exist in the treated effluent and the molar Ca^{2+} concentration ($[\text{Ca}^{2+}]$) was related to the initial ratio of H^+ to F^- ($[\text{H}^+]_0/$

- $[F^-]_0$) as $\log_{10}[Ca^{2+}] = 0.020[H^+]_0/[F^-]_0 - 4.24$.
- The effluent F^- concentration was found to be determined by the concentration of effluent Ca^{2+} as $[F^-]^2[Ca^{2+}]^{0.94} = 3.98 \times 10^{-10}$ under an SV of 1.0 to 5.0 h^{-1} . This relation could be applied to wastewaters containing HF, NaF, NH_4F or Na_2SiF_6 and was not affected by variations of influent F^- concentration from 25 to 3000 mg l^{-1} .
 - The effluent F^- was also found to be related to effluent pH as $\log_{10}[F^-] = 0.51 \text{ pH} - 2.91$, and the effluent F^- was about 6 mg l^{-1} at an effluent pH of 6.8.
 - The effluent F^- increased from 6 to 12 mg l^{-1} and effective calcite conversion rate decreased from ca. 60 to 40% when SV was increased from 1.6 to 16.0 h^{-1} at an $[H^+]_0/[F^-]_0$ of 0.75.
 - Significant increase of effluent F^- as well as decrease of effective calcite conversion rate was observed when reaction temperature was decreased from 25.0 to 8.5°C .
 - The performance of the reactor was affected by the existence of SO_4^{2-} to some extent and significantly inhibited by PO_4^{3-} . A molar ratio of PO_4^{3-} to F^- higher than 0.05 stopped F^- removal at a PO_4^{3-} of 15 mg l^{-1} .
 - Efforts should be made to increase the effective conversion rate of calcite and prevent formation of lumps in the fixed bed.

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