

Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation

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Abstract

The effect of the molar ratio of hydroxide and fluoride ions to Al(III) ions (γ_{OH} and γ_{F}) on coagulation and electrocoagulation (EC) was studied to solve the problem of the over addition of acid or base. The efficiency of defluoridation was approximately 100% when the sum of γ_{OH} and γ_{F} ($\gamma_{\text{OH}+\text{F}}$) was close to 3. This finding reveals that the fluoride ions and the hydroxide ions can co-precipitate with Al(III) ions and the formula of the precipitate is $\text{Al}_n\text{F}_m(\text{OH})_{3n-m}$. However, when γ_{OH} was less than 2.4, the defluoridation efficiency, given that $\gamma_{\text{OH}+\text{F}} = 3$, dropped as γ_{OH} fell, because the amount of aluminum polymer formed dropped. The efficiency of defluoridation of EC exceeded that of coagulation for equal γ_{OH} and $\gamma_{\text{OH}+\text{F}}$, when $\gamma_{\text{OH}+\text{F}} > 3$, proving the existence of an electrocondensation effect.
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1. Introduction

The removal of fluoride has been very important to environmental engineers because large amounts of hydrogen fluoride are used in the semiconductor industry [1–3]. Coagulation with aluminum salts has been employed for a long time to remove fluoride ions [4–7]. Coprecipitation or adsorption may occur when Al(III) ions are added to fluoride-containing water. The efficiency of removal of fluoride by a fixed amount of aluminum salt depends on pH, alkalinity, the coexisting anions, and other characteristics of the solution [6]. The pH that is most appropriate for defluoridation by coagulation is 5.5–6.5 [3,8]. Predetermining the amount of acid or base added to the solution in the defluoridation process to determine the ideal pH is difficult because the pH in this range is very sensitive to the concentration of the acid or base. Furthermore, as the fluoride ions coordinate with

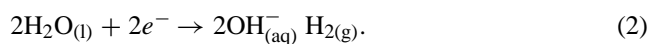
Al(III) or are absorbed by aluminum hydroxide, the pH of the solution changes because hydroxide ions are liberated from the aluminum hydroxide. Therefore, the pH measured may not be the pH when the reaction is complete. Thus, acid or base is frequently overadded in practice.

The initial concentration of hydroxide ions and the amount of Al(III) affect the pH of the solution. If the relationship for the efficiency of defluoridation is determined in terms of the initial molar ratio of OH^- to Al(III) (γ_{OH} , $\gamma_{\text{OH}} = [\text{OH}^-]/[\text{Al}^{3+}]$), then the problem of over-adding acid and base can be solved. Moreover, since defluoridation by aluminum hydroxide causes the liberation of hydroxide ions, the relationship between the efficiency of defluoridation and the initial molar ratio of F^- to Al(III) (γ_{F} , $\gamma_{\text{F}} = [\text{F}^-]/[\text{Al}^{3+}]$) of the solution should also be considered.

Electrocoagulation using aluminum electrodes is a new method for defluoridation. When an electric current passes through the aluminum electrodes, an anodic reaction releases Al(III) ions which then react with the hydroxide ions produced on the cathode and with the fluoride ions:

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Liu et al. [9] stated that the defluoridation efficiency of the EC system may exceed that of the traditional coagulation process because of the electrocondensation. Fluoride ions are attracted to the anode, so the fluoride concentration near the anode exceeds that in the bulk solution. Consequently, the defluoridation efficiency of EC should be higher than that of coagulation. However, Liu et al. did not conduct any experiment to compare EC with traditional coagulation. Therefore, this inference has not been proven.

A lower initial pH has been reported to improve the efficiency of defluoridation in the EC process [10], but the improvement is not significant because the final pH of the system changes very little, since the Al(III) ion is a buffer species. Shen et al. [3] demonstrated that the optimal final pH in EC is about 6. The problem of overloading may also occur in EC if the effects of the initial γ_{OH} and γ_{F} on defluoridation are not quantified. Controlling the defluoridation efficiency by controlling the initial γ_{OH} is more convenient than doing so by controlling the initial pH because the amount of acid or base added can be predetermined.

This study investigates the effects of γ_{OH} and γ_{F} on defluoridation in coagulation and EC systems and compares the defluoridation efficiencies of the two systems to prove the existence of the electrocondensation effect.

2. Materials and methods

2.1. Coagulation

Stock solutions of Al^{3+} , OH^{-} , and F^{-} ions were prepared using NaF, NaOH, and $\text{Al}(\text{NO}_3)_3$ salts, respectively, dissolved in distilled water. Predetermined amounts of stock solutions of Al^{3+} and F^{-} ions were added to a 50-ml volumetric flask and stock solution of OH^{-} was added to another 50 ml volumetric flask. Then both of the solutions were diluted to 50 ml and combined in a plastic bottle. The bottle was shaken constantly on a shaker (Yihder, BT-350R) at 150 rpm and 25 °C. Samples were extracted after 24 h and filtered through a Millipore filter (MES, 25 mm diam., 0.2 μm pore size). The pH and fluoride concentration in the filtered water were determined by a pH electrode and a specific fluoride electrode, respectively. The precipitate was analyzed by solid state nuclear magnetic resonance (Bruker, DSX-300 NMR) at a frequency of 8 kHz.

2.2. Electrocoagulation

Experiments were performed in a bipolar batch reactor with seven aluminum electrodes connected in parallel, as was used by Hu et al. [11]. Only the outer electrodes were connected to the power source, and anodic and cathodic reactions occurred on each surface of the inner electrode when

the current passed through the electrodes. The volume (V) of the solution of each batch was 1 l. The active area of each electrode, except the outer electrodes, was $8 \times 9 \text{ cm}$ and the dimensions of the outer electrodes were reduced to prevent dispersion of the electric field. Thus, the area/volume ratio of each batch was 40.9 m^{-1} —higher than the required value reported by Mameri et al. [10]. The distance between each pair of electrodes was 1 cm. A constant current was maintained using a potentiostat in intensiostat mode. The current density was $8.16 \times 10^{-3} \text{ A/cm}^2$ for the outer electrodes and $5.56 \times 10^{-3} \text{ A/cm}^2$ for the inner electrodes. Magnetic stirring at 400 rpm maintained a homogeneous solution in the batch reactor. The temperature of each system was maintained at $25 \pm 1 \text{ }^\circ\text{C}$.

Samples were extracted every minute and then immediately filtered through a 0.2- μm mixed cellulose ester membrane. The residual fluoride concentration ($[\text{F}^{-}]_{\text{res}}$), including the final fluoride concentration ($[\text{F}^{-}]_{\text{f}}$) in each sample, was determined using an ion chromatograph (Dionex, DX-100). The initial fluoride concentration ($[\text{F}^{-}]_0$) in each system was 25 mg/l. The following equation defines the efficiency of defluoridation in each batch:

$$\varepsilon_{\text{F}} = 1 - [\text{F}^{-}]_{\text{f}}/[\text{F}^{-}]_0. \quad (3)$$

After each reaction, the total concentration of Al(III) obtained from a digested sample was measured using an atomic absorption spectrophotometer (standard method, Section 3030E). The Al(III) dosage ($[\text{Al}^{3+}]_{\text{T}}$) was thus determined. According to Faraday's law, the theoretical Al(III) dosage ($[\text{Al}^{3+}]_{\text{theo}}$) can be calculated as

$$[\text{Al}^{3+}]_{\text{theo}} = nIT/VZF, \quad Z = 3 \text{ for Al(III)}, \quad (4)$$

where n is the number of cells, I is the electric current, T is the retention time of reaction, V is the volume of solution, Z is the valence of aluminum, and F is the Faraday constant ($F = 96487$).

The ratio of the Al(III) dosage obtained from the digested sample after electrocoagulation to the theoretical Al(III) dosage, is defined as the electric efficiency (ε_{c}),

$$\varepsilon_{\text{c}} = [\text{Al}^{3+}]_{\text{T}}/[\text{Al}^{3+}]_{\text{theo}}. \quad (5)$$

The Al(III) dosage at a certain time ($[\text{Al}^{3+}]_{\text{t}}$) during the EC reaction can be estimated as follows:

$$[\text{Al}^{3+}]_{\text{t}} = \varepsilon_{\text{c}}nIt/VZF, \quad Z = 3 \text{ for Al(III)}. \quad (6)$$

The γ_{OH} is 3 if no base or acid is present in the initial solution during EC because the amounts of Al(III) and hydroxide ions produced are stoichiometrically equivalent (Eqs. (1) and (2)) when the electric current passes through the electrodes. The initial acidity ($[\text{H}^{+}]_0$) or alkalinity ($[\text{OH}^{-}]_0$) can be varied to adjust the final γ_{OH} in the EC system, as follows:

$$\gamma_{\text{OH}} = 3 + [\text{OH}^{-}]_0/[\text{Al}^{3+}]_{\text{t}} - [\text{H}^{+}]_0/[\text{Al}^{3+}]_{\text{t}}. \quad (7)$$

The aluminum dosages in the coagulation experiments in this study ranged from 1 to 5 mM. The ε_{c} of Eq. (6) in

this study ranged from 1.2 to 1.3 owing to the change of the corrosion conditions in the electrodes. According to Eq. (6), when $[Al]$ is 5 mM and ε_c is 1.2, T is 8.34 min. To compare the results of EC with the results of the coagulation experiment, a reaction time of 9 min was chosen.

All analyses were conducted in duplicate for reproducibility of data, and all of the data in the figures and tables were the average ones.

3. Results and discussion

3.1. Coagulation

Fig. 1 plots the residual fluoride concentration against γ_{OH} for various initial aluminum dosages. The optimum γ_{OH} fell as γ_F increased. The sum of the optimum γ_{OH} and γ_F (γ_{OH+F}) seemed to be constant. Therefore, the variation of residual fluoride concentration with γ_{OH+F} was investigated with various initial Al(III) dosages, as shown in Fig. 2. The optimum γ_{OH+F} was close to 3 if the initial alu-

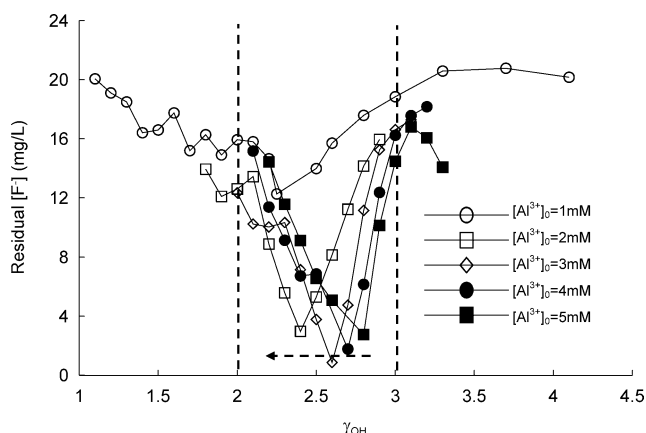


Fig. 1. Variation of residual fluoride concentration with γ_{OH} with different aluminum dosages. The optimum γ_{OH} declined with the decrease of $[Al^{3+}]_0$. Because the initial fluoride concentrations in all systems were constant ($[F^-]_0 = 25$ mg/l), the γ_F increases with the decrease of $[Al^{3+}]_0$.

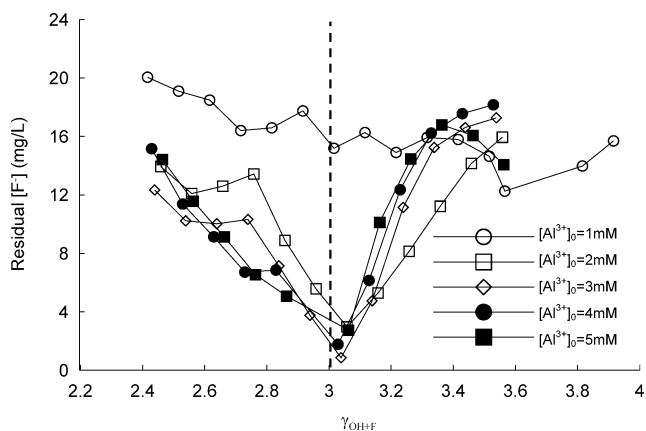
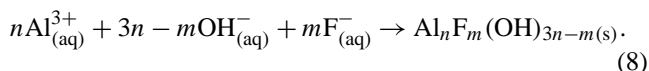
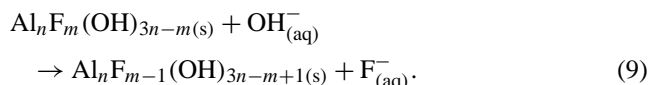


Fig. 2. Variation of residual fluoride concentration with the γ_{OH+F} with different aluminum dosages ($[F^-]_0 = 25$ mg/l).

minum dosage was greater than 1 mM. Fig. 2 also shows that the residual fluoride concentration rose rapidly with γ_{OH+F} when γ_{OH+F} exceeded 3. The molar ratio of hydroxide to Al(III) ions in the $Al(OH)_3$ precipitate is 3. Accordingly, the fluoride ions and the hydroxide ions can clearly coprecipitate with Al(III) ions to form $Al_nF_m(OH)_{3n-m}$:



However, the fluoride ions in the precipitate are very easily substituted for hydroxide ions when γ_{OH+F} exceeds 3:



The hydroxide ions have a greater affinity than fluoride ions for Al(III). Hence, fluoride ions are only substituted for hydroxide ions in coordination with Al(III) ions if the amount of hydroxide does not suffice to neutralize the positive charge of Al(III).

Fig. 3 plots pH against γ_{OH} , with and without the presence of fluoride in the coagulation process. The pH values measured in the two systems differ only in the range $\gamma_{OH} = 2.5$ –3. Except in that range, the pH values of the two systems were almost the same. The pH increased rapidly at $\gamma_{OH} = 2.5$ in the system with the fluoride, but at $\gamma_{OH} = 2.8$ in the system without the fluoride, verifying the inference that the fluoride is a substitutive ion for hydroxide. Furthermore, optimum pH for defluoridation was at the inflection point of curve with fluoride, which explains why the optimum pH in the system is so difficult to reach.

The concentration of OH^- can be regarded as the alkalinity of the water in these experiments. However, the alkalinity of natural water is primarily caused by the dissolution of the salts of weak acids, such as carbonate or bicarbonate. Accordingly, carbonate was used to examine the effect of the molar ratio of Al(III) and alkalinity on the removal of fluoride from natural water. Double the molar ratio of Al(III) to carbonate is defined as γ_{Alk} ($\gamma_{Alk} = 2[CO_3^{2-}]/[Al^{3+}]$) and the sum of γ_{Alk} and γ_F is defined as γ_{Alk+F} . As shown

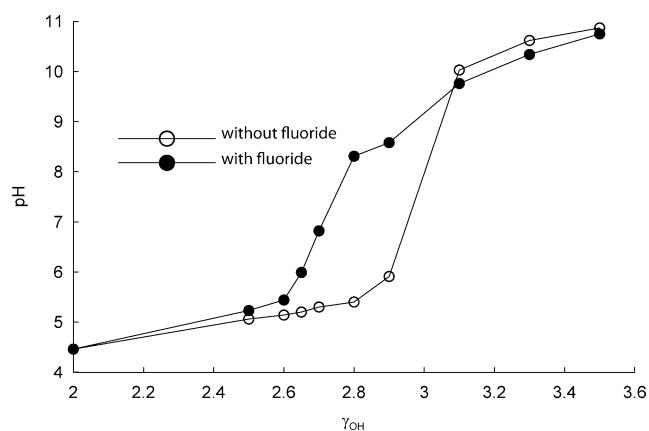


Fig. 3. Variation of pH with the γ_{OH} with and without fluoride ions ($[Al^{3+}] = 3$ mM, $[F^-]_0 = 25$ mg/l).

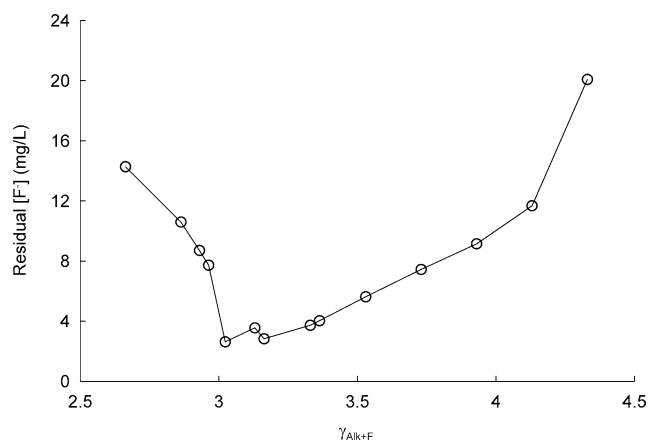


Fig. 4. Variation of residual fluoride concentration with γ_{Alk+F} in coagulation process as the Na_2CO_3 was used as alkalinity ($[\text{Al}^{3+}] = 3 \text{ mM}$, $[\text{F}^-]_0 = 25 \text{ mg/l}$).

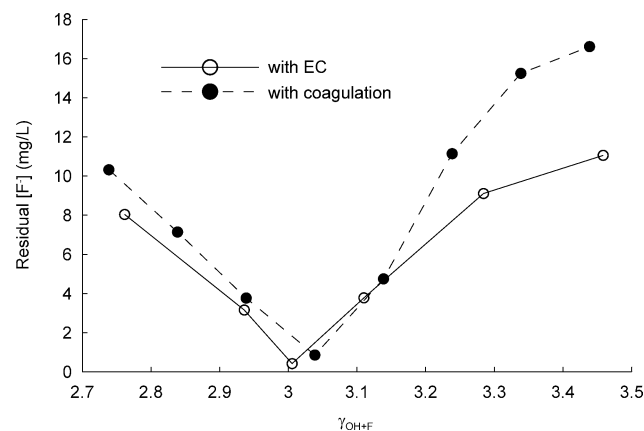


Fig. 5. Variation of residual fluoride concentration with the γ_{OH+F} in EC process and coagulation systems. ($[\text{Al}^{3+}] = 3 \text{ mM}$, $[\text{F}^-]_0 = 25 \text{ mg/l}$).

in Fig. 4, the optimum γ_{Alk+F} was also close to 3, but the residual concentration of fluoride rose more slowly as γ_{Alk+F} increased than it did in the system in which hydroxide was used, because of the formation of bicarbonate (HCO_3^-) rather than hydroxide when γ_{Alk+F} exceeds 3. The affinity of bicarbonate for Al(III) is less than that of fluoride. Therefore, the residual fluoride concentration rose very slowly with γ_{Alk+F} .

3.2. Electrocoagulation (EC)

Fig. 5 compares the variations of residual fluoride concentration, in EC with that in coagulation. The results of the coagulation experiment demonstrate that the defluoridation efficiency is almost zero if the γ_{OH} exceeds 3. Therefore, only variation in the range $\gamma_{OH} < 3$ was considered. The optimum γ_{OH+F} of the EC system was also close to 3. Moreover, the residual fluoride concentrations in the EC system were less than those in the coagulation system if $\gamma_{OH+F} > 3$, proving the existence of electrocondensation effect.

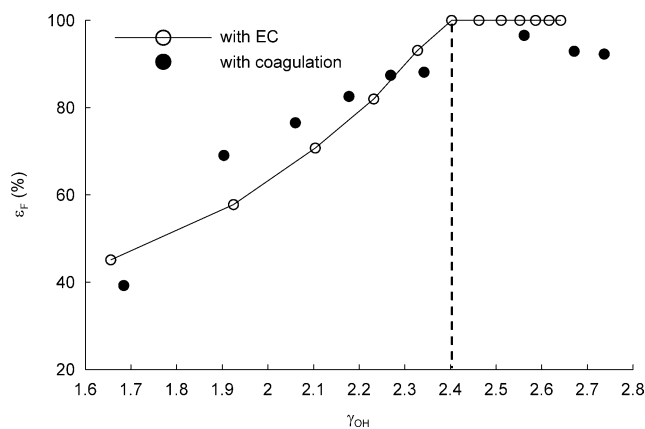


Fig. 6. Variation of defluoridation efficiency with the γ_{OH} in EC and coagulation processes as $\gamma_{OH+F} = 3$ ($[\text{F}^-]_0 = 25 \text{ mg/l}$).

From Eq. (7), the γ_{OH+F} in EC system can be calculated as follows:

$$\gamma_{OH+F} = 3 + \frac{[\text{OH}^-]_0}{[\text{Al}^{3+}]_t} - \frac{[\text{H}^+]_0}{[\text{Al}^{3+}]_t} + \frac{[\text{F}^-]_0}{[\text{Al}^{3+}]_t}. \quad (10)$$

If the initial alkalinity is zero and the initial acidity equals the initial fluoride concentration ($[\text{H}^+]_0 = [\text{F}^-]_0$), then γ_{OH+F} is independent of the Al(III) dosage and always equals 3 during the EC reaction. As mentioned earlier, the Al(III) dosage is proportional to the reaction time in the EC, as indicated in Eq. (8). Therefore, the relationship between the residual fluoride concentration and the Al(III) dosage at $\gamma_{OH+F} = 3$ can be established by measuring the fluoride concentration at different retention times in the EC system. Fig. 2 reveals that when the initial aluminum dosage was 1 mM, the optimum γ_{OH+F} exceeded 3 and the optimum efficiency of defluoridation in that system was much less than in other systems. Accordingly, a minimum Al(III) dosage is required to maintain a high ε_F in coagulation when $\gamma_{OH+F} = 3$. Since the ε_F in EC and coagulation are very close when $\gamma_{OH+F} = 3$, EC can be employed to find the minimum γ_{OH} in coagulation. The use of EC by environmental engineers to determine the minimum γ_{OH} is more convenient and faster than the use of coagulation. The γ_{OH} varies with reaction time in EC, so only one EC process is required to determine the optimum γ_{OH} . However, if the optimum γ_{OH} is determined by coagulation, then many experiments must be conducted.

Fig. 6 plots residual fluoride concentration against γ_{OH} of coagulation and EC when $\gamma_{OH+F} = 3$. When $\gamma_{OH} \geq 2.4$, then ε_F was nearly 100% and ε_F fell as γ_{OH} declined in both systems. This phenomenon implies that the molar ratio of hydroxide ions to Al(III) ions in the hydrofluoroaluminum precipitate should exceed a limit to keep the precipitate stable. Accordingly, the first step of the co-precipitation of the Al(III) ions with hydroxide and fluoride ions should be the formation of the hydroaluminum polymer. The hydroaluminum polymer forms if the γ_{OH} is less than 2.46 and the ratio of the hydroaluminum polymer to total aluminum dosage

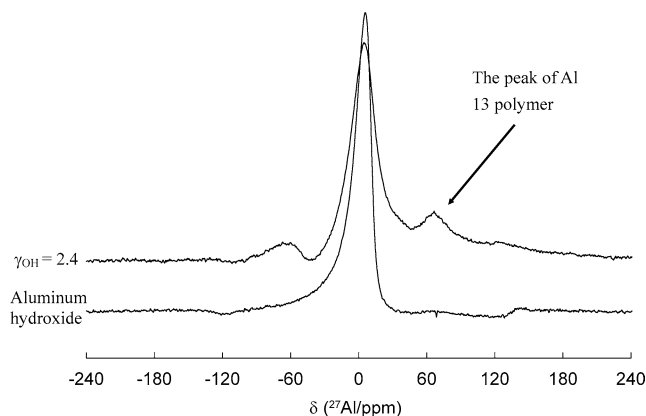


Fig. 7. The solid state NMR spectra of aluminum fluoroaluminum hydroxide at OH/Al ratio of 2.4 ($\gamma_{\text{OH}+\text{F}} = 3$) and aluminum hydroxide.

is a linear function as follows [12]:

$$[\text{AlP}]/[\text{Al}^{3+}]_{\text{T}} = \gamma_{\text{OH}}/2.46, \quad \text{for } \gamma_{\text{OH}} < 2.46. \quad (11)$$

Adding anions with a high affinity for Al(III), such as sulfate, phosphate, and silicate, would cause the polymer to aggregate rapidly because of the reduction in electrostatic repulsion between the polymers [13–18]. Buffle et al. [5] reported that adding fluoride ions also leads to the rapid precipitation of the polymer. Thus, the fluoride ions removed should be proportional to the amounts of hydroaluminum polymer formation. Therefore, as shown in Fig. 6, ε_{F} is proportional to γ_{OH} if $\gamma_{\text{OH}} < 2.4$ and close to 100% if $\gamma_{\text{OH}} > 2.4$.

Above inference also explains why the efficiencies of fluoride removal in EC and coagulation process are almost the same when $\gamma_{\text{OH}+\text{F}} < 3$. Since the efficiency of fluoride removal is mainly controlled by the amounts of the hydroaluminum polymer when $\gamma_{\text{OH}+\text{F}} < 3$, the increase of fluoride concentration due to the electrocondensation effect cannot raise the efficiency of fluoride removal. Therefore, although the electrocondensation effect also occurred when $\gamma_{\text{OH}+\text{F}} < 3$, the efficiency of fluoride removal did not rise.

The nuclear magnetic resonance (NMR) can be used to determine the “Cage-like” Al 13 polymer. The ^{27}Al NMR spectrums of the aluminum fluoroaluminum hydroxide precipitate at OH/Al ratio of 2.4 and aluminum hydroxide were demonstrated in Fig. 7. There was an obvious peak at 62.5 ppm, which is the peak of the Al 13 polymer, in the spectrum of the precipitate at OH/Al ratio of 2.4 but no peak at 62.5 in the spectrum of the aluminum hydroxide. This fact provided that the “Cage-like” Al 13 polymer exists in the precipitate of aluminum fluoroaluminum hydroxide at OH/Al ratio of 2.4. However, various Al polymeric species form in partially neutralized Al^{3+} solution depending on the concentration of Al^{3+} and base, stirring strength, temperature, rate of base injection, and aging time [19]. It needs 1–5 days for the unstable polymeric Al species, which is undetectable by NMR, to self-assemble into the “Cage-like” Al 13 polymer [20]. The

aging time in this study was less than 5 min. Therefore, other aluminum hydroxide polymer species could be present in the precipitate prepared at an OH/Al ratio of 2.4.

4. Conclusions

The γ_{OH} and γ_{F} govern defluoridation by aluminum salts. The optimum $\gamma_{\text{OH}+\text{F}}$ for defluoridation in coagulation and electrocoagulation are both close to 3, if γ_{OH} exceeds 2.4. The efficiency of defluoridation drops rapidly as γ_{OH} increases when $\gamma_{\text{OH}+\text{F}}$ is over 3. If γ_{OH} is less than 2.4, the defluoridation efficiency drops as γ_{OH} falls, when $\gamma_{\text{OH}+\text{F}}$ is 3, because the amount of aluminum polymer formed decreases. The efficiency of defluoridation by electrocoagulation exceeds that by coagulation for the same $\gamma_{\text{OH}+\text{F}}$ and γ_{OH} when $\gamma_{\text{OH}+\text{F}}$ is over 3, because of the electrocondensation effect.

The use of γ_{OH} or γ_{Alk} and γ_{F} is more convenient than the use of pH to maximize the ε_{F} in coagulation or EC system. The problem of overadding acid or base can be solved by precisely measuring the alkalinity, acidity, and fluoride concentration in treated water.

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References

- [1] C.J. Huang, J.C. Liu, *Water Res.* 33 (1999) 3403.
- [2] T.C. Chuang, C.J. Huang, J.C. Liu, *J. Environ. Eng.* 128 (2002) 974.
- [3] F. Shen, X. Chen, P. Gao, G. Chen, *Chem. Eng. Sci.* 58 (2003) 987.
- [4] W.W. Choi, K.Y. Chen, *J. Am. Water Works Assoc.* 71 (1979) 562.
- [5] J. Buffle, N. Parthasarathy, W. Haerdi, *Water Res.* 19 (1985) 7.
- [6] O.J. Hao, C.P. Huang, *J. Environ. Eng.* 112 (1986) 1054–1069.
- [7] N. Parthasarathy, J. Buffle, W. Haerdi, *Water Res.* 20 (1986) 443.
- [8] M.G. Sujana, R.S. Thakur, S.B. Rao, *J. Colloid Interface Sci.* 206 (1998) 94.
- [9] M. Liu, R.Y. Sun, J.H. Zhang, Y. Bina, L. Wei, P. Liu, C.F. Kei, *Fluoride* 20 (1983) 54.
- [10] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Baricou, *Water Res.* 32 (1998) 604.
- [11] C.Y. Hu, S.L. Lo, W.H. Kuan, *Water Res.* 37 (2003) 4513.
- [12] D.R. Parker, P.M. Bertsch, *Environ. Sci. Technol.* 26 (1992) 914.
- [13] C.J. Serna, J.L. White, S.L. Hem, *Soil Sci. Soc. Am. J.* 41 (1977) 1009.
- [14] H. DeHek, R.J. Stol, P.L. DeBruyn, *J. Colloid Interface Sci.* 64 (1978) 72.
- [15] P.H. Hsu, *Soil Sci.* 127 (1979) 219.
- [16] J.Y. Bottero, J.M. Cases, F. Fiessinger, J.E. Poirier, *J. Phys. Chem.* 84 (1980) 2933.
- [17] J.Y. Bottero, D. Tchoubar, J.M. Cases, F. Fiessinger, *J. Phys. Chem.* 86 (1982) 3667.
- [18] J.Y. Bottero, M. Axelos, D. Tchoubar, J.M. Cases, J.J. Fripiat, F. Fiessinger, *J. Colloid Interface Sci.* 117 (1987) 47.
- [19] S. Bi, C. Wang, Q. Cao, C. Zhang, *Coord. Chem. Rev.* 248 (2004) 441.
- [20] J.W. Akitt, J.M. Elders, *J. Chem. Soc. Dalton. Trans.* (1988) 1347.