

## Fluoride removal in aluminum coexisting solution by hydrated dolomite

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### Abstract

In this work, we elucidated the role of hydrated dolomite as a neutralizing agent in the removal of fluoride by co-precipitation with  $\text{Al}(\text{OH})_3$ . The hydrated dolomite used in this work contained 60%  $\text{Ca}(\text{OH})_2$  and 40%  $\text{Mg}(\text{OH})_2$ . We investigated the effect of pH (8, 9),  $\text{Al}(\text{OH})_3$  and hydrated dolomite dosages on removal performances and removal mechanism. In the removal experiments with hydrated dolomite as neutralizing agent, a higher fluoride removal was obtained under all investigated conditions. The highest fluoride removal was observed at pH 8. At this pH, the fluoride concentration decreased from the initial  $15 \text{ mg/dm}^3$  to  $8 \text{ mg/dm}^3$  by dosing  $20 \text{ mg/dm}^3$  of aluminum. The removal of fluoride was found to be only slightly dependent on the dolomite concentration in the investigated range. In the removal experiments with NaOH, the XRD spectra of the residual solids exhibited only the broad peaks of  $\text{Al}(\text{OH})_3$ , thus suggesting that the fluoride removal occurred through adsorption onto  $\text{Al}(\text{OH})_3$ . By using hydrated dolomite, the XRD spectra highlighted the presence of the Mg-Al-LDH structure. The obtained results suggest that the higher removal capacity in the presence of hydrated dolomite was due to the promotion of additional removal mechanisms, such as fluoride adsorption onto LDH and/or ion-exchange with the LDH anions.

Keywords: fluoride, hydrated dolomite, co-precipitation, LDH, ion-exchange

### 1. INTRODUCTION

Although fluorine is an essential trace elements in the human body, excessive uptakes of  $\text{F}^-$  can cause health problems like fluorosis [1] [2]. Most of fluoride in groundwater naturally occurs from the breakdown of rocks and soils or from the deposition of atmospheric volcanic particles [3]. However, as a result of anthropogenic activities like semiconductor, fertilizer,

glass and ceramic manufacturing, excessive concentrations of fluorine can be discharged through industrial wastewater. As a consequence, fluoride concentrations can exceed the water standards [4].

According to the suggestion of World Health Organization, the standard fluoride level in drinking water is in the range of  $0.5\text{-}1.5 \text{ mg/dm}^3$  depending on climate, local environment and other sources of  $\text{F}^-$ . Thus, water

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and wastewater containing high  $F^-$  concentration ( $> 1.5 \text{ mg/dm}^3$ ) must be treated before discharging [5].

Several methods such as chemical precipitation, reverse osmosis and electrodialysis have been reported to remove excessive  $F^-$  from several aqueous solutions. However, for a sustainable removal of fluoride, alternative cost-effective and efficient method is highly required.

In this study, we investigated the removal of  $F^-$  from aqueous solution by co-precipitation method with  $Al(OH)_3$  and hydrated dolomite containing 60%  $Mg(OH)_2$  and 40%  $Ca(OH)_2$ . We elucidated the performance of hydrated dolomite as neutralizing agent compared to sodium hydroxide (NaOH).

For this purpose, we performed batch co-precipitation experiments based on a two-step neutralization process. We investigated the effect of pH and dolomite dosage on removal performance and mechanism by ion-chromatography (IC) and x-ray diffraction (XRD).

## 2. EXPERIMENTS

### 2.1 Material

All chemicals and solution used throughout in this study were analytical grades which were purchased from Wako Chemicals, Inc., Japan. The  $F^-$  and  $Al^{3+}$  stock solutions were separately prepared by dissolving desired amounts of NaF and  $Al(NO_3)_3 \cdot 9H_2O$  in distilled water. 1 M  $HNO_3$  and NaOH were utilized to control the pH during the experiments. All experiments were conducted at room temperature ( $20^\circ C$ ).

### 2.2 Experiments

The removal experiments were performed from synthetic  $F^-$  solutions under air atmosphere and magnetic stirring for 60 min. In all experiments, a two-step neutralization process was applied (Figure 1). In the first step, the aluminum hydroxide sludge was formed by raising the pH up to 5.0 (30 min) in the presence of fluoride. In the second step (30-150 min), 1 M NaOH or hydrated dolomite (HD) plus 1 M NaOH were added up to the desired pH upon acidification at pH 2.

The concentration of  $F^-$  was fixed at  $15 \text{ mg/dm}^3$  while the HD dosages were investigated in the range  $50\text{-}300 \text{ mg/dm}^3$ .

After adding HD or NaOH-HD, the removal experiments were prolonged for 60 min. Following this step, the suspension was filtered through  $0.45 \mu\text{m}$  membrane filters. The residual  $F^-$  concentration in the filtrate was analyzed by Ion exchange Chromatography (IC25, DIONEX, Japan) while the solid residues were

freeze-dried at  $-45^\circ C$  for 12 hr and analyzed by XRD (Rigaku RINT UltimaIII) with Cu K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ) operated at 40 kV and 20 mA emission condition.

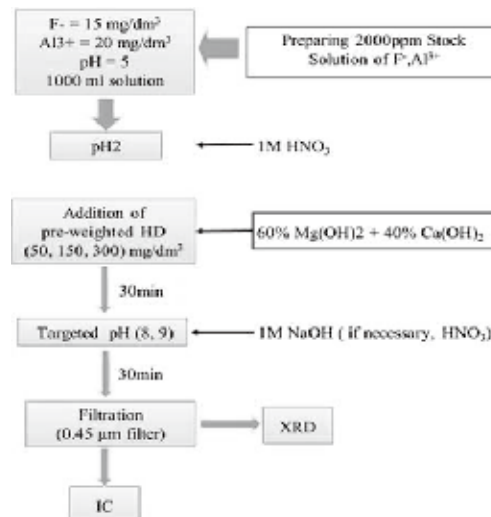


Fig.1 Flow chart of batch co-precipitation experiments

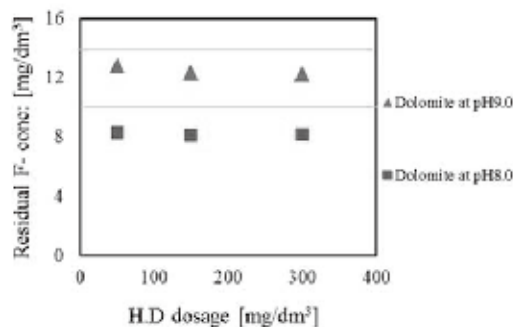


Fig.2 Fluoride removal at different HD dosages with  $20 \text{ mg/dm}^3$  of  $Al^{3+}$  (continuous lines: no HD).

## 3. RESULTS AND DISCUSSIONS

### 3.1. Fluoride removal

Figure 2 shows the residual  $F^-$  concentration with and without HD. Among pH 8 and 9, the higher removal was observed at pH 8 as a consequence of the lower competition fluoride-hydroxyl ions. Interestingly, with HD, the  $F^-$  removal increased about 17% compared with the experiments without HD under the same conditions.

### 3.2. XRD analysis

The crystal structures of solid residues determined by XRD are shown per Figure 3(a) for different samples obtained at different Al/Ca and Al/Mg molar ratios. Under

almost all the investigated Al/Ca ratios, the XRD spectra exhibited amorphous patterns, most likely due to  $\text{Al}(\text{OH})_3$ . Interestingly, when working at the lowest Al/Mg ratio the XRD spectra revealed the presence of Al-Mg layered double hydroxide (LDH) structure  $[(\text{Mg}_{0.833} \text{Al}_{0.167}) (\text{OH})_2 (\text{CO}_3)_{0.083} (\text{H}_2\text{O})_{0.75}]$ . For this evidence, Khan and O'Hare reported that substituting  $\text{M}^{3+}$  cations of a similar ionic radius to  $\text{Mg}^{2+}$  (e.g.  $\text{Al}^{3+}$ ) into  $\text{Mg}(\text{OH})_2$  produces a positively charged framework. Therefore, anions must intercalate between adjacent layers in order to maintain charge neutrality [6]. The molar ratio, Al/Mg in this structure was found to be about 0.2, which is the closest to the used experimental condition (Al/Mg = 0.36). This result highlights that larger amounts of aluminum (or lower amount of magnesium) did not allow the LDH to form, thereby confirming that a certain charge balance is required for the formation of a stable LDH.

In the removal experiments under the same condition (pH 8, Al/Mg = 0.36) the addition of HD determined a significantly higher fluoride removal compared to the experimental conditions where NaOH was used as neutralizing agent. This evidence suggests that hydrated dolomite was capable to promote an additional removal mechanism. Whereas without HD the only removal mechanism was the adsorption onto  $\text{Al}(\text{OH})_3$ , by adding HD and by forming the LDH, the fluoride ion could be also removed by ion-exchange with the anions within the Mg-Al LDH interlayer. A similar result was reported by Lin *et al.* who pointed out that  $\text{Mg}^{2+}$  and  $\text{OH}^-$  can precipitate onto the  $\text{Al}(\text{OH})_3$  surface to form the pre-MgAl LDH hydroxide mixture at pH 8 [7]. In turn, the as-formed LDH can promote further  $\text{F}^-$  removal by ion-exchange [8].

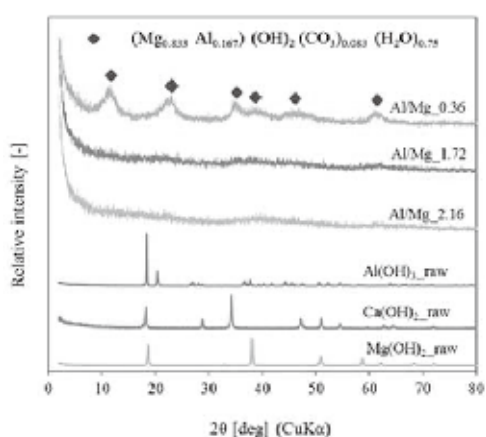


Fig.3(a) XRD patterns of solid residues at different Al/Mg ratios ( $\text{F}^-$  conc:  $15 \text{ mg/dm}^3$ ; HD conc: 50, 150,  $300 \text{ mg/dm}^3$ ,  $\text{Al}^{3+}$  conc:  $20 \text{ mg/dm}^3$ ).

In the experiment at pH 9, the fluoride removal in the presence of HD was also higher than the one obtained by using only NaOH. Under this condition, the LDH was partially detected by XRD along with  $\text{Mg}(\text{OH})_2$  (Figure.3,b). This evidence also supports the consideration about the additional mechanism of ion-exchange between  $\text{F}^-$  and the intercalated  $\text{CO}_3^{2-}$ . A possible explanation for the less crystalline structure of LDH and for the presence of  $\text{Mg}(\text{OH})_2$  peaks could be that the LDH structure decomposes through the time.

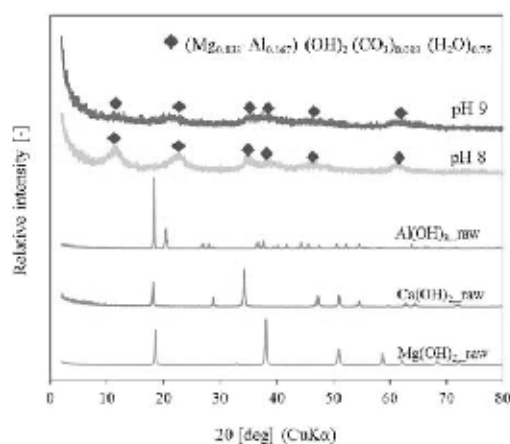


Fig.3(b) XRD patterns of solid residues at pH 8 and pH 9. ( $\text{F}^-$  conc:  $15 \text{ mg/dm}^3$ ; HD conc:  $300 \text{ mg/dm}^3$ ,  $\text{Al}^{3+}$  conc:  $20 \text{ mg/dm}^3$ ).

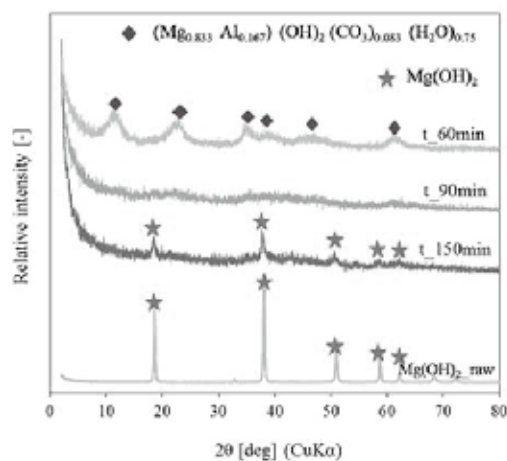


Fig.4 XRD patterns at different reaction times (HD conc:  $300 \text{ mg/dm}^3$ , pH: 8,  $\text{Al}^{3+}$  conc:  $20 \text{ mg/dm}^3$ ).

Indeed, although the LDH formed, under particular operating conditions its structure could be broken. Figure

4 shows the XRD patterns of the solid products obtained at pH 8 with Al/Mg 0.36 at different times. Clearly, the typical LDH peaks disappear after 1 hour while the  $\text{Mg}(\text{OH})_2$  peaks appear. This phenomenon could be a consequence of the altered electrostatic stability due to the exchange of the carbonate in the LDH interlayer with the hydroxyl ions in solution. If this phenomenon occurred at pH 8, it could even be more pronounced at pH 9, due to the higher concentration of hydroxyl ions. This consideration would explain not only the higher removal by HD at pH 9, but it would support also the experimental XRD result.

#### 4. CONCLUSION

The use of hydrated dolomite (HD) as neutralizing agent determined a higher fluoride removal under all investigated conditions. Under the same experimental conditions, the XRD results highlighted the presence of Mg-Al LDH structure. These results suggest that the higher removal by using HD was due to the additional removal mechanism of ion-exchange between fluoride and the anions in the magnesium LDH interlayer. In

addition, the time dependent XRD results suggest that the LDH can decompose through the time, especially at high pH due to the intercalation of hydroxyl ions in the LDH structure with the formation of  $\text{Mg}(\text{OH})_2$ .

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