Synthesis of Anion-Exchange Materials from Concrete Sludge and Evaluation of Their Ability to Remove Harmful Anions (Borate, Fluoride, and Chromate)

T. Hongo, Y. Tsunashima, A. Iizuka, and A. Yamasaki

Abstract-Concrete sludge is an industrial waste slurry containing hydrated cement, aggregates, and water. In the study, current anion-exchange materials: ettringite. metaettringite, and Ca-Al layered double hydroxide were synthesized from concrete sludge, and tested to see if they could remove harmful anions (borate, fluoride, and chromate) from solutions. Metaettringite showed high borate and fluoride removal ability, reducing initial concentrations of 100 mg B/L and 300 mg F/L to 6.3 mg B/L and 14.5 mg F/L. The Ca-Al layered double hydroxide showed high fluoride and chromate removal ability, reducing initial concentrations of 300 mg F/L and 180 mg Cr/L to 14.5 mg F/L and 0.4 mg Cr/L.

Index Terms—Anion exchange material, concrete sludge, harmful anions, ettringite, layered double hydroxide, removal.

I. INTRODUCTION

Industrial manufacturing processes generate a considerable amount of wastewater, which contains harmful elements. Wastewater must be treated prior to discharge to the environment. Numerous approaches have been studied for the removal of pollutants from contaminated water [1]-[4]. The removal of harmful ions from contaminated water has been attempted by several researchers, employing a wide variety of techniques [5]-[8]. Ion-exchange resins and chelating agents are often used to remove harmful anions such as phosphate, chromate, borate, and arsenate, but these materials are expensive. Ettringite, metaettringite, and layered double hydroxides (LDHs) have attracted attention as alternative low-cost and high-performance materials for the removal of harmful anions.

Ettringite, $Ca_6Al_2(SO_4)(OH)_{12}\cdot 26H_2O$, is a common hydrated phase of Portland cement. The ettringite structure consists of columns of { $Ca_6[Al(OH)_6]_2\cdot 24H_2O$ }⁶⁺ with the inter-column space (channels) occupied by SO_4^{2-} and H_2O molecules. The SO_4^{2-} is substitutable for other oxyanions such as CrO_4^{2-} , AsO_4^{2-} , and SeO_3^{2-} [9], [10]. Ettringite is thermally unstable and transforms to a less hydrated amorphous phase, $Ca_6Al_2(SO_4)(OH)_{12}\cdot 11-13H_2O$, called metaettringite, at temperatures higher than 120 °C [11], [12]. Metaettringite has a columnar structure similar to that of ettringite, with closer packing in the *a* direction. The SO_4^{2-} in metaettringite is also substitutable for other anions, such as $B(OH)_4^{-}$ [13].

LDHs are anionic clay minerals, and are also known as hydrotalcite-like compounds. The general chemical formula of LDHs is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and tri-valent cations, respectively. The value of *x* is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$, and A^{n-} is an anion [14], [15]. The structure is based on brucite-like hydroxide layers, in which some of the divalent cations have been replaced by trivalent ions, resulting in positively charged sheets [16], [17]. This charge is balanced by intercalated anions in the hydrated interlayer regions, and these anions are exchangeable for other anions such as AsO_4^{2-} , CrO_4^{2-} , and SeO_4^{2-} [18].

Concrete sludge is fresh waste concrete in the form of a slurry of hydrated cement and aggregate in water. About 1–2% of fresh concrete prepared for construction use is discarded as concrete sludge because it is necessary to prepare an excess amount of concrete to avoid shortages at construction sites. Concrete sludge is used as a landfill material after solid/liquid separation followed by neutralization with an acid such as sulfuric acid. This treatment process is costly, and an effective recycling process for concrete sludge is needed.

We recently revealed that sorbents prepared from concrete sludge could remove borate and fluoride from solutions [19], [20]. The removal ability resulted from the ettringite and metaettringite phases contained in the sorbents. In the present study, we synthesized Ca-Al-NO₃ LDH $(Ca_4Al_2(OH)_{12}(NO_3)_2 4H_2O)$, as well as ettringite and metaettringite, from concrete sludge. We then compared the abilities of ettringite, metaettringite, and Ca-Al-NO₃ LDH synthesized from the concrete sludge to remove harmful anions such as borate, fluoride, and chromate.

II. EXPERIMENTAL

A. Synthesis of Ettringite and Metaettringite from Concrete Sludge

A model concrete sludge was prepared by mixing 83.3 g of commercially available Portland cement (supplied by Taiheiyo Cement Corp., Japan) with 250 mL of water for 1 h at 25 °C. Aluminum sulfate (85.0%, Wako Pure Chemical Ind. Ltd.) was added to the concrete sludge to give a molar ratio of Ca/Al = 3.2. The ratio was calculated considering the aluminum content in the raw cement. After addition of aluminum sulfate, the mixed suspension was stirred for 24 h in a constant temperature bath at 25 °C to form ettringite. The

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solid phase was then separated from the liquid phase by filtration, washed thoroughly with distilled water, and dried at 40 $\,^{\circ}$ C for 24 h. Metaettringite was prepared by calcination of the obtained ettringite at 175 $\,^{\circ}$ C for 16 h. The synthesized ettringite and metaettringite were denoted as CS-ettringite and CS-metaettringite, respectively. The crystal structures were identified by powder X-ray diffraction (XRD) using a Rigaku RINT-Ultima IV diffractometer with CuK α radiation.

B. Synthesis of LDH from Concrete Sludge

A model concrete sludge was prepared by mixing 15 g of commercially available Portland cement (supplied by Taiheiyo Cement Corp., Japan) with 200 mL of water for 1 h at 25 °C. 50 mL of 90 wt.% acetic acid (Wako Pure Chemical Ind. Ltd.) was added to the concrete sludge, and stirred for 1 h at 100 $^{\circ}$ C. The obtained suspension was separated into leaching solution and residue by filtration. The concentration of Ca in the leaching solution was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo, iCAP 6000). Aluminum nitrate nonahydrate (Wako Pure Chemical Ind. Ltd.) was added to the leaching solution to give a molar ratio of Ca/Al = 2.3. Then, 2 M NaOH aqueous solution was added to the solution dropwise at 65 $\,$ °C, and the final pH was adjusted to 11.5. The suspension was stirred at 250 rpm for 18 h at the same temperature. The mixture was filtered; the solid phase was washed thoroughly with deionized water and dried at 100 °C for 24 h. The synthesized LDH is denoted as CS-LDH. The crystal structure was identified by powder XRD.

C. Borate, Fluoride and Chromate Ion Removal Experiments

Anion removal experiments were conducted using solutions of boric acid (99.5%; Wako Pure Chemical Industries Ltd., Japan), sodium fluoride (99.0%; Wako Pure Chemical Industries Ltd., Japan), or potassium chromate (99.0%; Kanto Chemical Co., Inc) as model wastewaters. The initial concentrations of borate, fluoride, and chromate were set at 100 mg B/L, 300 mg F/L, and 180 mg Cr/L, respectively. The removal agent to be tested was added to model wastewater in a polypropylene beaker and stirred at 350 rpm with a magnetic stirrer. The weight ratio of the sample to model wastewater solution was 30 g/L for borate, 2.0 g/L for fluoride, and 10 g/L for chromate removal experiments. The initial concentrations and the weight ratio were determened by preliminary experimental results. Sampling of the solution phase was conducted intermittently through a 0.2-µm nitrocellulose filter. The concentrations in the filtrates were measured by ICP-AES for fluoride and chromate, and ion-chromatography (IC; HIC-6A; Shimadzu) for fluoride. The pH of the solutions was also measured intermettedly. Each experiment was conducted for three times to examine the reproducibility of the results. The experimental results were evaluated by the average of the three measurements. After the experiment, the sample was recovered by filtration, dried, and analyzed with XRD.

III. RESULTS AND DISCUSSION

Fig.	1	shows	XRD	patterns	of	CS-ettringite
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CS-metaettringite, and CS-LDH. Characteristic peaks attributed to the ettringite phase were observed in CS-ettringite, indicating the ettringite compound was successfully synthesized from concrete sludge. Peaks assigned to gypsum (CaSO₄ \cdot 2H₂O) and calcite (CaCO₃) were observed as well as those corresponding to ettringite. The XRD pattern of the CS-metaettringite showed small diffraction peaks assigned to bassanite (CaSO₄·0.5H₂O) and calcite. Although the CS-metaettringite was prepared by calcination of the CS-ettringite at 175 °C, the peaks from ettringite disappeared completely and an amorphous halo was observed. This indicates that metaettringite, which is an amorphous material, was formed [21]. The gypsum (CaSO₄ 2H₂O) in CS-ettringite was dehydrated and transformed to bassanite by calcination. Characteristic difference in the surface morphology was not observed between CS-ettringite and CS-metaettringite by scanning electron microscope (SEM) observations. The XRD pattern of the CS-LDH showed characteristic peaks attributed to the Ca-Al-NO₃ LDH phase, indicating the LDH compound was successfully synthesized from concrete sludge. Peaks assigned to katoite (Ca₃Al₂(SiO₄)(OH)₈) were observed as well as those corresponding to LDH.



Fig. 1. XRD patterns of the CS-ettringite, CS-metaettringite, and CS-LDH.



Fig. 2. Borate concentration as a function of time during removal using CS-ettringite, CS-metaettringite, and CS-LDH.

Fig. 2 shows the changes with time in borate concentrations in the aqueous phase during the borate removal experiments. The CS-ettringite showed no noticeable borate removal ability. The concentration of borate after 240 min was 98.4 mg/L. With CS-metaettringite as the adsorbent, the concentration decreased immediately, and reached adsorption equilibrium within the first 60 min; the concentration of borate after 240 min was 6.3 mg/L. The CS-LDH showed some removal ability, and reduced the concentration of borate to 84.1 mg/L after 240 min. The amounts of borate removed over the 240-min period by the CS-ettringite, CS-metaettringite and CS-LDH were 0.13, 2.97, and 0.71 mg-borate/g, respectively.



Fig. 3. Changes of pH during borate removal experiments using the CS-ettringite, CS-metaettringite, and CS-LDH.

Fig. 3 shows changes of pH during the experiments. A rapid increase of pH was observed immediately after sample addition, especially for the CS-metaettringite and CS-LDH. The pH changes of the CS-ettringite were more gradual. The pH values at 240 min for CS-ettringite, CS-metaettringite, and CS-LDH were 10.2, 9.9, and 12.0, respectively. This pH increase is due to the partial dissolution the samples, resulting in the release of OH⁻. According to the dissociation equilibrium of borate in the aqueous phase, the dominant form of borate under the pH conditions of this study was $B(OH)_4^-$.



Fig. 4. XRD patterns of the CS-ettringite, CS-metaettringite, and CS-LDH after borate removal.

Fig. 4 shows the XRD patterns of the samples after borate removal experiments. The CS-ettringite showed little change compared with the XRD pattern before borate removal. The CS-metaettringite transformed into crystalline ettringite through hydration; this phenomenon is observed when metaettringite is immersed in water [21], and facilitates the ion exchange of sulfate ions for borate ions in metaettringite [22]. For the CS-LDH, katoite $(Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x})$ and LDH phases were observed. The intensities of the diffraction lines from katoite were increased after the borate removal experiment. The (003) diffraction line of the LDH was split into two peaks at around 10.0 ° and 11.5 °. The peak position of the (003) diffraction line changes with the size of the interlayer anion. The peak at around 11.5° is assigned to Ca-Al-CO₃ LDH. The Ca-Al-CO₃ LDH was generated by the anion-exchange of CO_3^{2-} in the borate solution for interlayer NO_3^{-1} in the CS-LDH during the experiment, because CO_3^{2-1} is adsorbed onto LDHs in preference to NO_3^{-} [18]. The katoite and the Ca-Al-CO₃ LDH are considered to barely contribute to the borate removal. The CS-LDH removed the borate by ion exchange for the interlayer NO3. The broadness of the (003) diffraction line at around 10.0 ° can be explained by the coexistence of $B(OH)_4^-$ (borate) and NO_3^- (nitrate) in the interlayer, because their ionic sizes are slightly different: NO₃ $(0.400 \text{ nm}) < B(OH)_4^- (0.458 \text{ nm}) [23].$



Fig. 5. Fluoride concentration as a function of time during removal using CS-ettringite, CS-metaettringite, and CS-LDH.

Fig. 5 shows the changes with time of fluoride concentrations in the aqueous phase during fluoride removal experiments. A decrease in the concentration of fluoride ions was observed for all the samples studied. Using the CS-ettringite as an adsorbent, the concentration reached adsorption equilibrium within the first 30 min, and the concentration after 60 min was 73.9 mg/L. With the CS-metaettringite or CS-LDH adsorbents, the concentration rapidly decreased within 5 min, and gradually decreased after that. The concentrations after 60 min for CS-metaettringite and CS-LDH were 14.5 and 14.1 mg/L, respectively. The amounts of fluoride removed over a period of 60 min by the CS-ettringite, CS-metaettringite, and CS-LDH were 114, 146, and 138 mg fluoride/g, respectively.



Fig. 6. Changes of pH during fluoride removal experiments using CS-ettringite, CS-metaettringite, and CS-LDH.

Fig. 6 shows the changes of pH during these experiments. A rapid increase of pH was also observed immediately after sample addition. The pH values at 60 min for CS-ettringite, CS-metaettringite, and CS-LDH were 11.5, 11.4, and 12.0, respectively.



Fig. 7. XRD patterns of the CS-ettringite, CS-metaettringite, and CS-LDH after fluoride removal.

Fig. 7 shows the XRD patterns of the samples after fluoride removal experiments. The diffraction lines assigned to ettringite and Ca-Al-NO₃ LDH disappeared from CS-ettringite and CS-LDH, respectively. Instead, diffraction lines for calcium fluoride (CaF₂) were observed after fluoride ion removal in all three samples. This result indicates that the fluoride ions were removed by precipitation in the form of calcium fluoride.



Fig. 8. Chromate concentration as a function of time during removal using CS-ettringite, CS-metaettringite, and CS-LDH.

Fig. 8 shows the changes with time of chromate concentrations in the aqueous phase during the chromate removal experiments. The CS-ettringite and CS-metaettringite showed no noticeable chromate removal ability. The concentrations of chromate after 240 min were 188.0 and 173.6 mg/L, respectively. Using the CS-LDH as an adsorbent, the concentration decreased rapidly within the initial 5 min, and reached adsorption equilibrium after 60 min. The concentration of chromate after 240 min was 0.4 mg/L. The amounts of chromate removed over a period of 240 min by the CS-ettringite, CS-metaettringite, and CS-LDH were 0.12, 1.56, and 17.6 mg chromate/g, respectively.

Fig. 9 shows the changes of pH during these experiments. A rapid increase of pH was also observed immediately after sample addition. The pH values at 240 min for CS-ettringite,

CS-metaettringite, and CS-LDH were 11.0, 10.5, and 12.0, respectively. According to the dissociation equilibrium of chromate in the aqueous phase, the dominant form of chromate under the pH conditions of this study was CrO_4^{2-} .



Fig. 9. Changes of pH during chromate removal experiments using CS-ettringite, CS-metaettringite, and CS-LDH.



Fig. 10. XRD patterns of the CS-ettringite, CS-metaettringite, and CS-LDH after chromate removal.

Fig. 10 shows the XRD patterns of the samples after chromate removal experiments. The CS-ettringite showed little change compared with the XRD patterns before the chromate removal experiment. The CS-metaettringite transformed to ettringite through hydration. For the CS-LDH, the (003) diffraction line at around 10 °became broader. This can be attributed to the coexistence of CrO_4^{2-} (chromate) and NO_3^- (nitrate) in the interlayer, because their ionic sizes are also slightly different: NO_3^- (0.400 nm) < CrO_4^{2-} (0.458 nm) [23]. This result indicated that the ion exchange of nitrate ions for chromate ions occurred.

IV. CONCLUSIONS

Ettringite, metaettringite, and Ca-Al-NO₃ LDHs were successfully synthesized from concrete sludge. The CS-ettringite showed some ability to remove fluoride, although it was not as effective as the CS-metaettringite and CS-LDH. The CS-metaettringite showed high removal ability for borate and fluoride. It reduced the borate concentration from 100 to 6.3 mg B/L and the fluoride concentration from 300 to 14.5 mg F/L. The CS-LDH showed high removal ability for fluoride and especially for chromate, reducing the fluoride concentration from 300 to 14.5 mg F/L and the chromate concentration from 180 to 0.4 mg Cr/L.

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