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A Comparative Borate Adsorption Study of Ettringite and Metaettringite

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Ettringite and metaettringite samples were used to compare adsorption capacity for borate. The metaettringite, prepared from the ettringite calcined at 175 °C, showed approximately five times higher adsorption capacity for borate.

Boron is naturally found in groundwater and usually appears in the form of borates.[1–3] Its presence in surface water occurs frequently as a consequence of the discharge of treated sewage effluents, industrial wastewater, and chemical products used in agriculture.[4] Boron is an essential micronutrient for plants, but it is toxic at higher levels. In Japan, the maximum permissible concentration of boron in industrial wastewater is 10 mg L^{-1}. For humans and animals, boron is an essential element, but regular intake adversely affects their health.[5] The boron concentration recommended by the World Health Organization (WHO) for drinking water is 0.5 mg L^{-1},[6] but some places in the world present a much higher level of this element in water. Therefore, boron removal from water is of great importance in several situations.

The removal of boron from contaminated water bodies has been attempted by several researchers employing a variety of techniques.[7–9] These investigations have shown that treatments using ion-exchange resins are most suitable for the treatment of agricultural and drinking water,[10] but they are expensive. Ettringite has attracted attention as an alternative low-cost adsorption material for borate.

Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, is a commonly hydrated phase of Portland cement. Ettringite is thermally unstable and transformed to dehydrated amorphous phase, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 11\text{–}13H_2O$, called metaettringite at temperature higher than 120 °C.[11,12] Metaettringite has a columnar structure similar to ettringite with closer packing in the *a* direction. The adsorption for various anions of ettringite has been studied by many researchers.[13–15] However, the adsorption ability of metaettringite has not been elucidated. In this work, borate adsorption of ettringite and metaettringite was studied.

Ettringite was synthesized as follows. 0.06 mol of $Ca(OH)_2$ and 0.01 mol of $Al_2(SO_4)_3$, which is the stoichiometric Ca/Al ratio for ettringite, were mixed in 500 mL of distilled water. The mixed solution was stirred for 4 h at 25 °C. The solid phase was separated from the liquid phase by filtration and washed thoroughly with distilled water. Finally, the solids were dried at 40 °C for 24 h. Metaettringite was prepared by calcination at 175 °C for 16 h of the obtained ettringite sample.

The XRD pattern of the obtained ettringite sample (Figure 1a) confirms the high crystallinity and single phase of ettringite (ICDD file No. 72-0646). Figure 1b shows the XRD pattern of the calcined sample of the ettringite at 175 °C. The reflections of ettringite disappeared completely, and amorphous halo was observed. This indicates that metaettringite was formed, because metaettringite is amorphous material.[11] A very small reflection at 29.4° is assigned to calcite (ICDD file No. 71-3699).

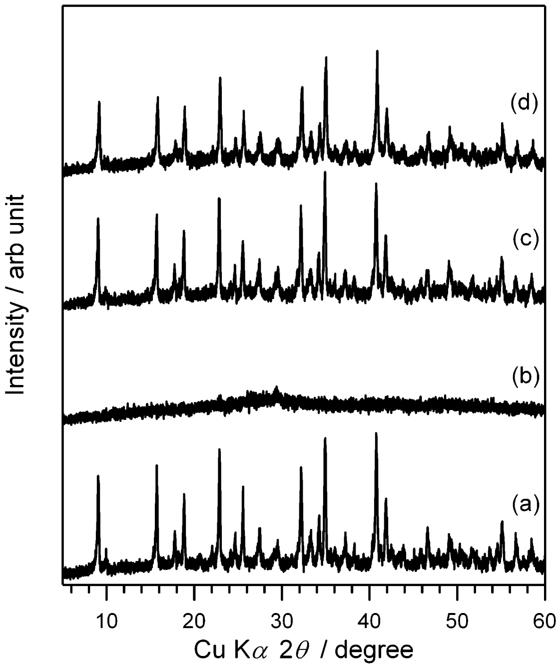

Figure 1. XRD patterns of the ettringite (a), metaettringite (b), borate-uptake ettringite (c), and borate-uptake metaettringite (d).

FE-SEM observation shows a needle-like morphology of the ettringite entangled with each other (Figure 2a). The particles were approximately 2–6 μm in length and 80–800 nm in diameter. After the 16 h of heat treatment at 175 °C, the fine needle-shaped ettringite was agglomerated to form nodules (Figure 2b).

The adsorption kinetics of borate on ettringite and metaettringite was measured at room temperature. A solution (94 ppm) of borate was prepared from a H_3BO_3 solution (Kanto Chemical Co., Inc.). The pH of the prepared borate solution was 6.2. Samples of 3 g were dispersed in 100 mL of the dilute solution for different time periods (5–240 min). The solid particles from the mixtures were separated by filtration. The concentration of residual borate in the filtrates was determined using an ICP atomic emission spectrometer.

The variation of borate adsorption as a function of time is shown in Figure 3. The kinetic curves show that the equilibrium

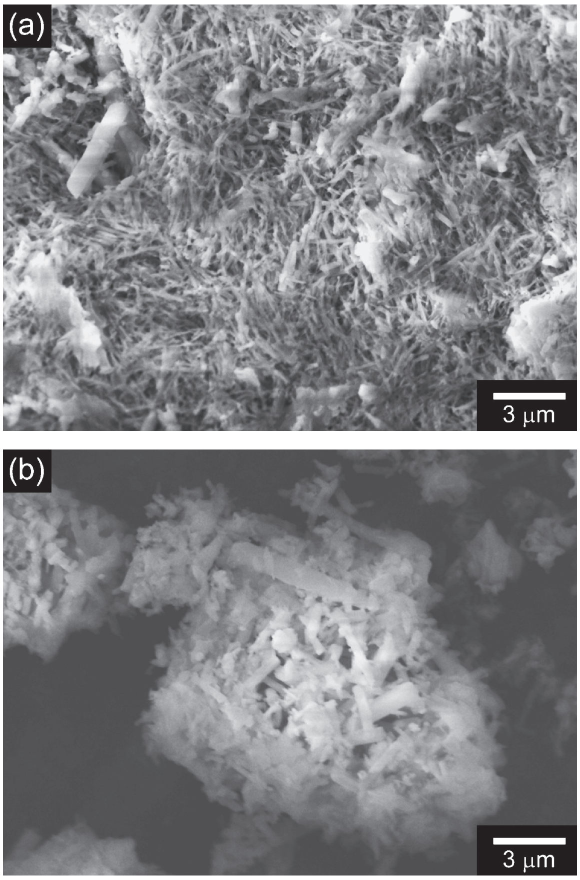

Figure 2. FE-SEM images of the ettringite (a) and metaettringite (b).

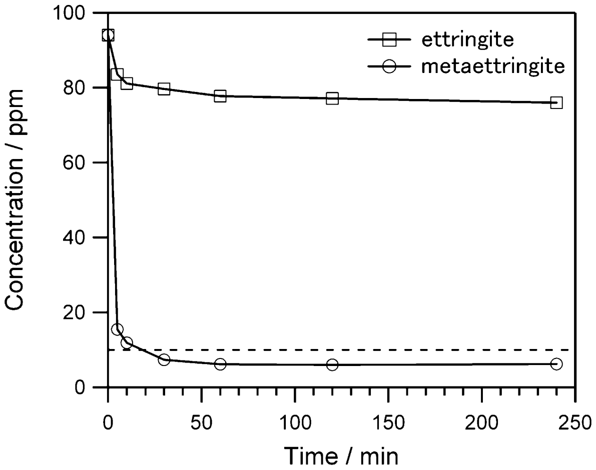

Figure 3. Concentration changes of borate due to adsorption by the ettringite and the metaettringite as a function of time. The dotted line in figure shows the maximum permissible concentration of boron in Japan.

times and adsorption capacities of the ettringite and the metaettringite are quite different. Using the ettringite as adsorbent, the borate concentration exhibits an initial step at 10 min, after which it decreases gradually until 240 min. The concentration of borate after 240 min was 76 ppm. For the metaettringite, the borate concentration decreased rapidly at the initial 5 min and after that decreased slowly until 60 min. After that the concentrations were almost constant, and the concentration after 240 min was 6 ppm. The final concentration at 240 min for the metaettringite was lower than the environmental standards of industrial wastewater in Japan. When using 1 g of the metaettringite as adsorbent in the 94 ppm borate solution (100 mL), the final concentration after 240 min was 16 ppm. To meet the environmental standards, 3 g of the metaettringite was found to be necessary for 100 mL of the solution. The borate adsorption amounts at 240 min by the ettringite and the metaettringite were 0.60 and 2.93 mg-B/g-adsorbent, respectively. The metaettringite was found to have approximately five times higher adsorption capacity than the ettringite in the removal of borate. The adsorption capacity of the metaettringite is higher than the reported data in the literature: 13.0 mg-B/g-adsorbent (pH 11, 90 °C);[16] 20.9 mg-B/g-adsorbent (pH 2.0, room temperature).[17] Both adsorbents are calcium-based adsorbents for boron removal from water.

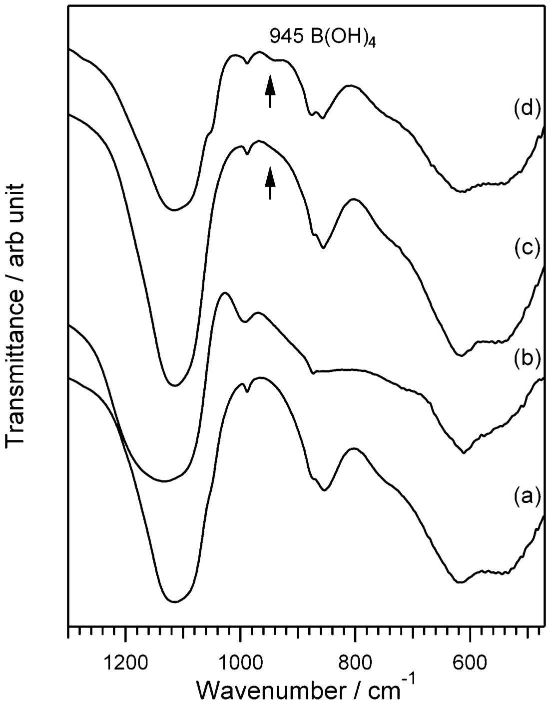

Figure 4. FT-IR spectra of the ettringite (a), metaettringite (b), borate-uptake ettringite (c), and borate-uptake metaettringite (d).

Figure 4 shows the IR spectra of the ettringite, metaettringite, and their borate-uptake samples at 240 min. The IR spectrum for ettringite (Figure 4a) agreed well with the reference.[18] The IR spectrum of the borate-uptake metaettringite showed a weak adsorption peak at 945 cm^{-1} assigned to $B(OH)_4$ vibration (Figure 4d).[19] This result indicated that the borate is adsorbed on the metaettringite as $B(OH)_4^-$ state. The IR spectrum of the borate-uptake ettringite showed feeble adsorption peak characteristic of $B(OH)_4$ vibration (Figure 4c). This is due to the small amount of borate adsorbed to the ettringite.

The pH values after 240 min of the solution for the ettringite and the metaettringite were 9.6 and 10.5, respectively. The pH increase from the initial pH value of 6.2 is considered to be due to OH^- ions released from the samples. According to the dissociation equilibrium of borate in the aqueous phase, the dominant form of boron under the pH condition in this study is $B(OH)_4^-$. This is consistent with the FT-IR measurements (Figures 4c and 4d).

The XRD pattern of the borate-uptake ettringite showed characteristic peaks of ettringite (Figure 1c). The ettringite structure consists of columns of $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}^{6+}$ with the intercolumn space (channels) occupied by SO_4^{2-} and H_2O molecules. The SO_4^{2-} is substitutable for other oxyanions, and this property has been applied to adsorb oxyanions such as CrO_4^{2-}, AsO_4^{3-}, and SeO_3^{2-}.[13,14] In this study, the ettringite adsorbed borate through the substitution of SO_4^{2-} by $B(OH)_4^-$; this exchange took place only in the surface layer.[15] Interestingly, the XRD pattern of the borate-uptake metaettringite also showed characteristic peaks of ettringite (Figure 1d). The metaettringite has a property to recrystallize to ettringite phase by rehydration.[11] It can be considered that the ion exchange of sulfate ions for borate ions in metaettringite occurs during the recrystallization through hydration. This ion exchange would occur in the intercolumn space inside the particle as well as the surface layer. Therefore, the borate adsorption amount of the metaettringite was much higher than the ettringite. Considering the borate adsorption mechanism, the metaettringite adsorbent could be reusable. This is because only approximately 5% of SO_4^{2-} was exchanged for $B(OH)_4^-$ after 240 min.

In conclusion, the metaettringite showed approximately five times higher adsorption capacity for borate than the ettringite. The metaettringite recrystallized to the ettringite phase in the borate solution while involving $B(OH)_4^-$ in the structure.

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