



## Interfacial effects of MgO in hydroxylated calcined dolomite on the co-precipitation of borates with hydroxyapatite

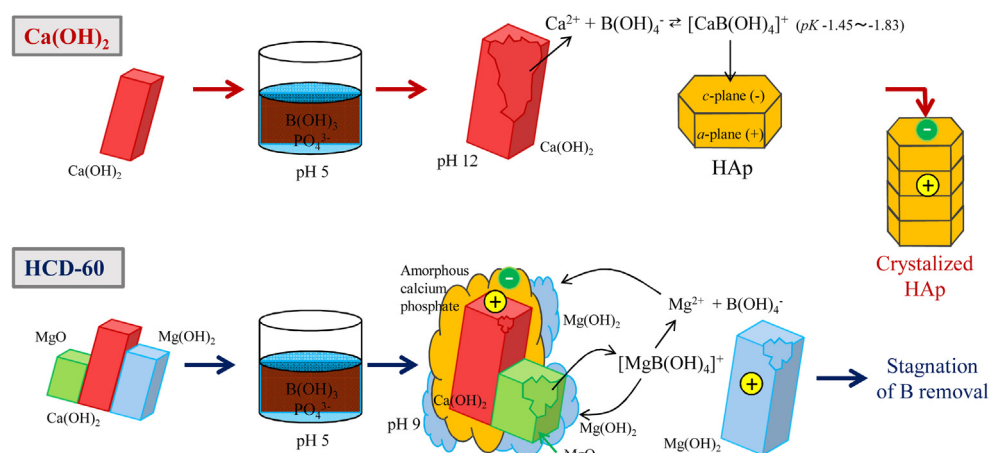


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### GRAPHICAL ABSTRACT



### HIGHLIGHTS

- MgO in HCD delayed coprecipitation rate borate with apatite.
- Hydroxylation of MgO causes to cover the surface of  $\text{Ca(OH)}_2$ .
- TEM images showed delay of HAp crystallization with HCD-60.
- Zeta potential suggested  $\text{Mg(OH)}_2$  coverage on  $\text{Ca(OH)}_2$ .

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### ABSTRACT

Hydroxylated calcined dolomite (HCD) is used as a mineralizer to immobilize borates by co-precipitation with hydroxyapatite (HAp). HCD sometimes includes appreciable quantities of MgO depending on the degree of hydroxylation of the calcined dolomite. In this work, the interfacial effects of MgO in HCD on the removal kinetics of borates were examined using  $\text{Ca(OH)}_2$  and HCDs with different degrees of hydroxylation. As the fraction of MgO phases within the HCD increased, the borate immobilization rate stagnated because the formation of hydroxyapatite (HAp) was inhibited. This effect arose from the interaction of boric acid ( $\text{H}_3\text{BO}_3$ ) with the MgO in HCD, followed by hydroxylation to cover the  $\text{Ca(OH)}_2$  surfaces with newly formed  $\text{Mg(OH)}_2$ . In the presence of borate, the unstable intermediate  $[\text{MgB(OH)}_4]^+$  complex was formed through ligand-promoted dissolution of MgO in the HCD.  $^{11}\text{B}$  NMR spectra revealed that the stagnation in immobilization of tetragonal boron ( $^{14}\text{B}$ ) species was observed for up to 45 min,

<sup>11</sup>B-NMR  
Co-precipitation

accompanied by the suppression of HAp formation. TEM images of the HCD suggested that Ca(OH)<sub>2</sub> was partially associated with MgO and Mg(OH)<sub>2</sub> phases within the HCD and hydroxylation of MgO led to a thin covering of the surface of Ca(OH)<sub>2</sub> with the newly formed gel phases comprising Mg(OH)<sub>2</sub>/H<sub>3</sub>BO<sub>3</sub> that hinders the dissolution of Ca(OH)<sub>2</sub>. However, when MgO was completely hydroxylated in the HCD this delay was not observed. This was supported by zeta potential measurements on the solid residues during co-precipitation. The results suggest that the degree of hydroxylation of the calcined dolomite in HCD markedly influences the co-precipitation kinetics of borates in industrial water treatment.

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## 1. Introduction

Boron (B) is utilized in many industries for the production of semiconductors, ceramics, borosilicate glasses, detergents, and pharmaceuticals [1], and is also naturally discharged in high concentrations by some hot springs and mine waters. Excess concentrations of boron and its compounds in industrial waste represents a public health risk and damages ecosystems because it can slow reproduction and is toxic by uptake through the gastrointestinal and respiratory tracts [2]. The toxicity of boron-based compounds is still a matter of some debate because they are emergent contaminants and therefore maximum concentration limits are inconsistent between different countries [3]. The World Health Organization defines maximum concentration limits of 10 mg L<sup>-1</sup> for B in industrial discharges and 1 mg L<sup>-1</sup> for B in drinking water [4].

The conventional methods for treatment of effluent and wastewater containing boron species are widely reviewed [5–8]. The treatment methods used for the removal of boron from solutions include coagulation–electrocoagulation [9,10], adsorption [11–13], ion exchange [14], electrodialysis [15,16], membrane filtration after complexation [17], and the use of B selective resins containing diols as B complexing agents [18]. Of these options, the removal of B through the use of adsorption processes and ion exchange systems are the most effective treatment methods. Unfortunately, conventional processes such as sedimentation, precipitation followed by sedimentation, coagulation, and adsorption remove little or no B from wastewater with low B concentrations such as sewage [19]. Conventional methods also suffer from slow reaction rates, production of large quantities of waste sludge, and relatively high costs [3].

Co-precipitation with hydroxyapatite (HAp, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) has been investigated as an alternative for the removal of borates from very dilute solutions [20]. The reaction facilitates the simultaneous removal of the target pollutants with phosphates because they have very low solubility products ( $K_{sp}$  for HAp = 10<sup>-126</sup> at 25 °C) [21]. Apatites (Ap) with the general formula [Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, or Cl)] are suitable materials to accommodate a variety of pollutants including cationic species, halogen, and oxoanionic species in their structure by co-precipitation using lime as a Ca source. Because of their low solubility products, apatites are also utilized as ion-exchangers for radioactive waste sequestration, storage, and disposal. Some Mg minerals are also found in natural lime resources. A representative example is dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] and Hydroxylated calcined dolomite is sold commercially for soil and groundwater remediation. In our previous reports [22] hydroxylated calcined dolomite (HCD), in which Mg species coexist with Ca(OH)<sub>2</sub>, showed enhanced removal of fluoride (F<sup>-</sup>) by precipitation of calcium fluorophosphate. It was concluded that Mg(OH)<sub>2</sub> and MgO functioned as adsorbents for the newly formed amorphous calcium fluorophosphate which prevented adhesion to Ca(OH)<sub>2</sub> and this was supported by transmission electron microscopy (TEM) observations.

In this work, borate was chosen as a target for removal from the aqueous phase and the effect of MgO phases in HCDs on the kinetics of the co-precipitation of borate with HAp using HCD as a Ca source was investigated. The Mg components have a variety of stoichiometries in lime resources and a scientific understanding of the role of the quantity of Mg in the removal of borate was therefore desirable from a practical standpoint. We have interpreted the mechanism of the interfacial effect of MgO components in HCD on the removal of borate by considering the parallel reactions of Ca(OH)<sub>2</sub> dissolution, precipitation of HAp, and hydroxylation of MgO in HCD, using powder X-ray diffraction (XRD), <sup>11</sup>B NMR spectroscopy, TEM, and zeta potential measurements combined with a knowledge of aqueous chemistry.

## 2. Methods and materials

All solutions were prepared in ultrapure water. All chemicals were special grade and obtained from Wako Pure Chemical Industries, Ltd (Osaka, Japan). Aqueous H<sub>3</sub>BO<sub>3</sub> solution (2.40 mM) was prepared in the presence of (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> (16.0 mM). In some experiments 0.53–5.02 mM Mg<sup>2+</sup> ions were added to the solutions in the form of Mg(NO<sub>3</sub>)<sub>2</sub>.

HCDs, which were used as the Ca sources in this work, were produced by calcination of dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) at 1000 °C for 2 h, followed by hydroxylation by Yoshizawa Lime Industry, Co. Ltd (Tokyo, Japan). Ca(OH)<sub>2</sub> (Wako, special grade) was also used as a reference Ca source. The HCDs were characterized by powder XRD and it was found that the mineralogical phases in HCD consisted of Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, CaCO<sub>3</sub>, and MgO [22]. Samples were labelled by their hydroxylation degrees and the samples with Mg(OH)<sub>2</sub> contents of 60% and 100% were named HCD-60 and HCD-100, respectively. Compositional quantification was conducted according to JIS K9011 [23]. Briefly, the total Ca and Mg concentrations were initially determined by EDTA titration after acid-decomposition. The carbonate content was then determined by CO<sub>2</sub> volumetric measurement after decarbonation using HCl and it was assumed that the resulting CO<sub>2</sub> came entirely from CaCO<sub>3</sub> in the samples. The hydroxyl group contents were estimated by subtracting the CO<sub>2</sub> contents from the ignition mass loss. The Ca(OH)<sub>2</sub> content was calculated by subtracting the amount of Ca in CaCO<sub>3</sub> from the total Ca content. The Mg(OH)<sub>2</sub> content was calculated by subtracting the hydroxyl groups of Ca(OH)<sub>2</sub> from the total hydroxyl group content. Finally, the MgO content was estimated by subtracting the Mg(OH)<sub>2</sub> content from the total Mg content.

The BET specific surface areas of Ca(OH)<sub>2</sub>, HCD-60 and HCD-100 were measured by an MX-6 surface analyzer (Bel Japan Inc., Toyonaka, Japan) using 99.99% N<sub>2</sub> gas and a seven-point method.

The Ca sources, referred to as mineralizers, Ca(OH)<sub>2</sub> (0.18 g), HCD-60 (0.32 g), and HCD-100 (0.29 g) were added to 40 mL of the solutions described above to equalize the molar quantities of Ca(OH)<sub>2</sub> whilst maintaining a P/Ca molar ratio of 0.3, which corresponds to half of the theoretical value for HAp. Only the Ca(OH)<sub>2</sub> content was used to calculate the quantity of added mineralizer because CaCO<sub>3</sub> is poorly soluble in alkaline solution and therefore

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