Clarification for removal mechanism of Boron using co-precipitation with magnesium hydroxide

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ABSTRACT

Boron is an essential atom in industries, especially in glass industry. However the maximum contaminant levels of boron in water are regulated in several countries because of its toxicity. Ion-exchange resin is commonly used to remove boron from the waste water though it is relatively expensive. In this study, we investigated co-precipitation method using magnesium salt for boron treatment, in order to create cost efficient way to treat waste water. To clarify the mechanism of co-precipitation, we conducted both co-precipitation experiment and adsorption experiment. For both experiments, we carried out three kinds of experimental studies; (i) sorption isotherm formation, (ii) XRD analysis, (iii) NMR analysis to clarify how co-precipitation of boron with magnesium hydroxide occurred.

KEY WORDS: Co-precipitation / Boron / Magnesium / Hydromagnesite

1. INTRODUCTION

Boron is an essential atom in various industries, such as electronics, semiconductor, and glass industries. However, boron has harmful effects against organisms including plants and humans and it has lacked exhaustive control. In accordance with the guidelines for drinking water by WHO [1], the maximum concentration limits are regulated at 10 mg L\(^{-1}\) and 1 mg L\(^{-1}\) for industrial drainage and drinking water individually. In the most of the countries, the concentration range of boron is judged from 0.1 to 0.3 mg L\(^{-1}\), according to the guidelines of WHO [1]. The main specie of Boron in neutral water is boric acid (H\(_3\)BO\(_3\)), which dissociates to tetrahydroxyborate, with a \(pK_a\) of 9.23.

The former study has investigated the treatment of waste water containing boron using sorbent such as MgO and ion-exchange resin [2,3]. However, these treatment methods had problems such as production of lots of sludge and high operating expenses respectively.

In this study, co-precipitation method, which is the common way to treat waste water containing inorganic harmful matters, was investigated to remove boron from the waste water. In our previous study, As(\(V\)) co-precipitation experiment and adsorption experiment with ferrihydrite were conducted to describe sorption isotherm and residues obtained during these experiments were analyzed by XRD, and we confirmed that the comparison of both experimental results was effective to clarify the mechanism of co-precipitation [4,5]. Therefore, we conducted both co-precipitation experiment and adsorption experiment, and the form of the sorption isotherm and the structure of the residues were evaluated.

2. MATERIALS AND METHODS

2.1 Standards and reagents

All chemicals and solutions used in this study were of analytical grade and were purchased from Kanto Chemicals, Inc., Japan. The B and Mg solutions were prepared using B(OH)\(_3\) and Mg(NO\(_3\))\(_2\) \(\cdot\) 6H\(_2\)O. The pH was fixed at pH 10.5 and the ion strength was adjusted to 0.3 using 1 M HNO\(_3\) and KOH. All experiments were conducted at 25°C.

2.2 Co-precipitation experiments

B solution and Mg solution were combined in 0.5 dm\(^3\) of deionized (DI) water to adjust the initial B/Mg molar ratio to the target level, after which the pH and ionic strength were adjusted to the target levels. Then, the suspension was agitated for one hour while the pH was adjusted at 10.5 by addition of few drops of HNO\(_3\) and KOH. After the agitation, the suspension was filtered through 0.1 \(\mu\)m membrane filter. The obtained filtrates were analyzed by ICP-AES (Varian, Inc Vista-MPX) in order to measure the residual concentration of B and Mg.

Following the preceding co-precipitation experimental method, co-precipitation experiments were also conducted at pH 9.5, 10, 10.5, 11 and 12, in order to evaluate the effect of pH against B removal capability.

2.3 Adsorption experiments

In the adsorption experiments, so as to compare the results of adsorption and co-precipitation, Mg
solutions and B solutions were prepared separately in 0.5 dm³ of deionized (DI) water to obtain twice the target concentration of B and Mg. And then, the pH and ionic strength were adjusted to the target levels in the both solutions respectively. Then, the solutions were mixed and the obtained suspension was agitated for one hour while the pH was adjusted at 10.5 by addition of few drops of HNO₃ and KOH. After the agitation, the suspension was filtered through 0.1 μ membrane filter. The obtained filtrates were analyzed by ICP-AES (Varian, Inc. Vista- MPX) in order to measure the concentration of B and Mg as well as co-precipitation.

Following the preceding adsorption experimental method, adsorption experiments were also performed at pH 9.5, 10, 10.5, 11 and 12, in order to evaluate the effect of pH against B removal capability.

2.4 XRD and NMR analysis

The filter residues of co-precipitation and adsorption were analyzed by XRD (RIGAKU, Inc Geiger flex RAD-IX) and NMR (JEOL, Ltd CMX-400). For XRD and NMR analysis, the initial Mg concentration was set at 200 mg dm⁻³ and the initial Mg concentration was varied to adjust the initial B/Mg molar ratio. The filter residue was freeze-dried at -45 °C for 24 hours prior to analysis to avoid crystallization or transformation of the residue.

The powder XRD patterns were obtained using a copper target (CuKα), a crystal graphite monochromator and a scintillation detector. The equipment was operated at 40 kV and 30 mA by step-scanning from 2° to 80° 2θ at increments of 0.02° 2θ and a scan speed of 2°/min. A crystal sample holder was used and the diffractograms were not corrected by background diffraction.

The NMR analysis was conducted with Delta NMR software version 4.3 using a single pulse method. The resonance frequency and the field strength were 128.3 MHz and 9.39 T respectively. A typical experiment involved the acquisition of sampled in 2.0 μs intervals with 1000 scans. The spinning speed was 10 kHz with the relaxation delay of 0.2 s (B¹¹). The B¹¹ chemical shift was referenced to H₂BO₃ solution at 19.5 ppm [8].

3. RESULTS AND DISCUSSION

3.1 Evaluation of the effect of pH

Fig.1 and Fig.2 describe the results of co-precipitation and adsorption respectively when the pH was varied from 9.5 to 12. In these experiments, the initial B concentration was fixed at 100 mg dm⁻³ (9.25 mmol dm⁻³) and the initial B/Mg molar ratio was set at 0.0625 and 0.5. The Mg concentration was changed to achieve the target initial molar ratio from 45.0 to 3600 mg dm⁻³ (1.85-148 mmol dm⁻³).

From Fig.1, it is found that the maximum B removal was achieved at pH 10.5. Under pH 10.5, it is considered that lower B removal was observed because enough amount of precipitation could not be obtained due to the formation of MgB(OH)₄, which is known to be formed as:

\[ \text{Mg}^{2+} + \text{B(OH)}_4^- \leftrightarrow [\text{MgB(OH)}_4]^+ \]

When the pH was over 10.5, B removal may be disturbed because of the competition adsorption with OH⁻.

Fig.2 shows that the highest removal was also achieved at pH 10.5 in adsorption experiment. This indicates that the surface of Mg(OH)₂ had a stronger negative charge at pH 10.5 than at pH9.5 and pH10. On the other hand, B removal was disturbed by the competition adsorption with OH⁻ when the pH was over 10.5.

![Fig.1 Relationship between pH and residual B concentrations in the co-precipitation experiment: initial B concentration 100 mg dm⁻³.](image1)

![Fig.2 Relationship between pH and residual B concentration in the adsorption experiment: initial B concentration 100 mg dm⁻³.](image2)
3.2 Comparison of co-precipitation and adsorption characteristics

Fig 3 shows the relationship between precipitated Mg concentration and residual B concentration both in the co-precipitation method and the adsorption method at pH 10.5. These experiments were carried out when the initial B concentration was fixed at 100 mg dm$^{-3}$ (9.25 mmol dm$^{-3}$). To give an initial B/Mg molar ratio of 0.0625 to 1, the Mg concentrations were changed from 225-3600 mg dm$^{-3}$ (9.25-148 mmol dm$^{-3}$).

Although more B removal was achieved when more dosage of Mg was given at both co-precipitation and adsorption, B was removed more in co-precipitation experiment than adsorption experiment at any given dosage of Mg. The higher removal during the co-precipitation experiments suggests that the co-precipitation of B with Mg(OH)$_2$ involves more than a simple adsorption.

The precipitated Mg concentration was larger at adsorption than at co-precipitation, at any initial B/Mg molar ratio. It is considered that, because Mg(OH)$_2$ was strongly formed before the combining the B solution and Mg solution in adsorption experiments, it is especially difficult for B to attack the surface of Mg(OH)$_2$ to release Mg$^{2+}$ into the suspension$^{[8][9]}$.

![Graph showing Relationship between precipitated Mg concentration and residual B concentration both in the co-precipitation experiment and in the adsorption experiment, at pH 10.5: initial B concentration 100 mg dm$^{-3}$](image)

Fig 3 Relationship between precipitated Mg concentration and residual B concentration both in the co-precipitation experiment and in the adsorption experiment, at pH 10.5: initial B concentration 100 mg dm$^{-3}$.

3.3 Relationship between sorption density and residual B concentration

Fig 4 shows the sorption density of the co-precipitation experiment and the adsorption experiment at pH 10.5. In these experiments, the initial B concentration was fixed at 100 mg dm$^{-3}$ (9.25 mmol dm$^{-3}$) while the Mg concentrations were changed from 225-3600 mg dm$^{-3}$ (9.25-148 mmol dm$^{-3}$) to obtain an initial B/Mg molar ratio of 0.0625 to 1.

B co-precipitation with Mg(OH)$_2$ with a 1-hour reaction time produced a BET-type isotherm whereas B adsorption with Mg(OH)$_2$ with a 1-hour reaction time produced a Langmuir-type isotherm. In previous study, we found that As(V) adsorption with ferrihydrite and aluminum hydroxide, which occurred almost entirely as a result of surface complexation, produced a Langmuir-type isotherm and was not affected by the initial concentration of As(V)$^{[8][10][11]}$. On the other hand, it is found that BET-type isotherm was produced when the As(V) co-precipitation with ferrihydrite and aluminum hydroxide, of which As(V) removal mechanism was almost entirely a production of surface precipitation$^{[8][10][11]}$. From these previous findings, the BET-type isotherm, which was produced in the B co-precipitation experiment with Mg(OH)$_2$, indicates that B removal mechanism of co-precipitation involves more than a simple adsorption. Therefore it is considered that three dimensional B uptakes occurred during co-precipitation because of the production of surface precipitation or the absorption of B into precipitation layers.

When the residual B concentration is over 5 dm$^{-3}$ mmol, the B sorption density showed steep increase as the residual B concentration increased. In this study, high B residual concentration represents low concentration of Mg or a high initial B/Mg molar ratio, because B sorption density was obtained by changing the Mg concentration to adjust the target initial B/Mg molar ratio and fixing the initial concentration of B. Therefore, from this BET-type isotherm, it is considered that three dimensional B uptake occurred at high initial B/Mg molar ratio due to the steep increase of sorption density, while simple adsorption was occurred at low initial B/Mg molar ratio.

![Graph showing Sorption isotherm of B-magnesium hydroxide both in the co-precipitation experiment and in the adsorption experiment, at pH 10.5: initial B concentration 100 mg dm$^{-3}$](image)

Fig 4 Sorption isotherm of B-magnesium hydroxide both in the co-precipitation experiment and in the adsorption experiment, at pH 10.5: initial B concentration 100 mg dm$^{-3}$.
3.4 XRD measurements

Fig. 5 and Fig. 6 show a comparison of XRD spectrum of B co-precipitated residues and which of B adsorbed residues as a function of the initial molar ratio of B/Mg. Co-precipitated experiments were performed at the initial molar ratio from 0.0625 to 1 at pH 10.5, and the initial Mg concentration was fixed at 200 mg dm$^{-3}$ (8.23 mmol dm$^{-3}$) and B concentration varied to achieve the target molar ratio. In both Figures, the residue, which was produced at B/Mg=0, shows several broad peaks and these peak positions entirely correspond with those of Brucite (Mg(OH)$_2$). Because the co-precipitated and adsorbed residues are poorly crystalline, it is difficult to investigate the presence of the boron phases from XRD patterns. However, in As(V) co-precipitation with ferrihydrite and hydroaluminm, we previously found that surface precipitation is produced when its XRD spectrum peak shifts$^{[5,12,13]}$ and we confirmed that the XRD spectrum peak shift could be used to analyze the sorption mechanism of co-precipitation with different initial As/Fe or As/Al molar ratio. Therefore XRD spectrum were investigated for co-precipitated and adsorbed Mg(OH)$_2$ in this study.

In Fig. 5, co-precipitated magnesium hydroxide at initial B/Mg ratio of 0.0625, 0.125 and 0.25 had several broad and weak peaks at the positions which correspond with the peak positions of Mg(OH)$_2$. The correspondence of the peak positions of co-precipitated residues with which of Mg(OH)$_2$ indicates that the production of surface precipitation did not occur, when the initial B/Mg molar ratio was under 0.25. Because those XRD spectrum peaks were broad and weak, it is proposed that B was inserted into Mg(OH)$_2$ layers, which disturbed the crystallization of Mg(OH)$_2$. However, there is a possibility that surface complexation was formed on the surface of Mg(OH)$_2$. XRD spectrum of B adsorbed Mg(OH)$_2$ at different initial B/Mg molar ratios were also investigated and it was found that their spectrum were all the same as the spectrum of Mg(OH)$_2$. However, the peak at 19° became weaker when the initial B/Mg molar ratio increases, which represents that crystallinity of Mg(OH)$_2$ was lower at higher initial B/Mg molar ratio. From this result, it is considered that more B was inserted into the Mg(OH)$_2$ layers and it disturbed the crystallization of Mg(OH)$_2$ when the initial B/Mg molar ratio was higher. This change of crystallinity of Mg(OH)$_2$ indicates the predominant B removal mechanism in adsorption experiment is the absorption of H$_2$BO$_3$ into the Mg(OH)$_2$ layers, though there is a possibility that surface complexation was formed.

On the other hand, XRD spectrum of B co-precipitated Mg(OH)$_2$ shifted from 19°to 16°and to 22°when the initial B/Mg molar ratio increased from 0.25 to 0.4. Because these two peaks at 16° and 22° originate in XRD spectrum of hydromagnesite, it is considered that production of hydromagnesite is promoted as initial B/Mg molar ratio increases. From these results, when the initial B/Mg molar ratio is over 0.4, the mechanism of co-precipitation of B is predominantly production of hydromagnesite which may involves ternary adsorption.

From the broader and weaker peaks in the XRD spectra obtained during the co-precipitation experiments, the precipitates are a mixture of hydromagnesite and B adsorbed Mg(OH)$_2$. Moreover, XRD spectrum peak shift disclosed that the mechanism of co-precipitation of B was changing from adsorption to production of hydromagnesite at B/Mg=0.4, at which the sorption isotherm was changing from a gradual increase to a steep increase.
3.5 NMR measurements

Fig.7 and Fig.8 show a comparison of NMR spectrum of B co-precipitated residues and B adsorbed residues as a function of the initial molar ratio of B/Mg. The residues, which were obtained during co-precipitation and adsorption respectively for XRD measurement, were also used to be analyzed by NMR. H$_3$BO$_3$ was also analyzed by NMR and the result of which was shown in both Fig.7 and Fig.8 as a reference material. Three-coordinated B has broad chemical shift due to the quadrupolar interaction. On the other hand, four-coordinated B has sharp chemical shift near 0 ppm.[13]

It is found that trigonal B was predominant specie in all co-precipitated residues, which indicates that H$_3$BO$_3$ is preferencenly inserted between hydromagnesite layers during co-precipitation experiments and the formation of surface complexation was not profound. When the initial B/Mg molar ratio was under 0.4, H$_3$BO$_3$ was inserted between Mg(OH)$_2$ layers whereas H$_3$BO$_3$ was inserted between hydromagnesite layers when the B/Mg molar ratio was over 0.4. It should be noted that Hydromagennsite has sheet like structure[15][16] and it is considered that more B was inserted into layers than Mg(OH)$_2$, which may cause BET type isotherm.

It is obvious that trigonal B was predominant specie in all adsorbed residues when the initial B/Mg molar ratio was 0.0625. However, when the initial B/Mg molar ratio was larger than 0.5, tetrahedral B increased as the B/Mg ratio increased. The results suggest that, when the initial B/Mg molar ratio is high, surface complexation may be formed as:

≡MgOH+B(OH)$_4$- $\leftrightarrow$ ≡MgB(OH)$_4$+ OH

In adsorption experiment, B was removed by both the formation of surface complexation and absorption between Mg(OH)$_2$ layers while the ratio of the formation of surface complexation increased as the initial B/Mg molar ratio increased.

4. CONCLUSION

In this study, we conducted both co-precipitation and adsorption experiments with wide range of initial B/Mg molar ratios at pH 10.5, in order to discuss the mechanism of B co-precipitation with Mg(OH)$_2$.

From the co-precipitation experiment and the adsorption experiment at pH 9.5, 10, 10.5, 11 and 12, the most B removal was achieved at pH 10.5.

We confirmed that H$_3$BO$_3$ was inserted into the Mg(OH)$_2$ layers when the initial B/Mg ratio was smaller than 0.4. On the other hand, when the initial B/Mg molar ratio was over 0.4, three dimensional B uptake occurred which was caused by the production of hydromagnesite. We believe that more B was absorbed into the hydromagnesite layers than Mg(OH)$_2$ layers because of its sheet-like structure and the mechanism of B co-precipitation with Mg(OH)$_2$ changed when the initial B/Mg molar ratio was 0.4, from absorption into Mg(OH)$_2$ layers to absorption into hydromagnesite layers.
In adsorption experiment, H$_3$BO$_3$ was inserted into the Mg(OH)$_2$ layers at any initial B/Mg molar ratio and the production of hydromagnesite was not detected. However, as initial B/Mg molar ratio increases, the formation of surface complexation is promoted and it was proposed that the mechanism of B adsorption with Mg(OH)$_2$ also changed because of the increase of initial B/Mg molar ratio.

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