In Situ Solid/Liquid Separation Effect for High-Yield Recovery of Boron and Fluorine from Aqueous Media Containing Borate or Fluoroborate Ions

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Detoxification of polluted water and resource recovery of boron and fluorine by using a sampling-type hydrothermal mineralization treatment apparatus was investigated. The hydrothermal mineralization treatment is a geomimetic treatment, which recovers natural minerals from aqueous media under hydrothermal conditions. As a result, hydrothermal mineralization treatment for aqueous solutions containing borate or fluoroborate ions, followed by separation of the reaction solution from precipitate, effectively reduced boron and fluorine concentration in solution, and parasibirskite ($Ca_2B_2O_5 \cdot H_2O$) and fluorite (CaF_2) formed in high yields. Both the boron and fluorine concentration after the treatment for 2 h at 150 °C was 4 mg dm^{-3} regardless of its initial concentration (5–3000 mg dm^{-3}) and the ionic species ($B(OH)_4^-$ or BF_4^-). Therefore, the hydrothermal mineralization treatment by using a sampling-type apparatus should be an effective method to detoxify the wastewater and ground water containing these ions and recover these ions as reusable mineral.

Boron is distributed widely in the environment mainly as boric acid. The largest boron source in the world exists in Turkey, where boron contamination in water is a common environmental problem.[1] The excess intake of boron has a strong impact on plants, animals, and human bodies. For example, the tolerable limit of boron for citrus and some agricultural crops is 2 or 3 mg dm^{-3}. Its recommended content in drinking water is 0.3 mg dm^{-3} in the European Union.[2,3] Recently, the quality standard for discharged water with boron from manufacturing plants has been set at 10 mg dm^{-3} in Japan.[4] On the other hand, boric acid is an important industrial resource and is widely used in many kinds of the manufacturing processes, such as in semiconductor, ceramic, and plating processes. Thermal power plants also discharge wastewater containing hazardous analogues of the borate ion. Wastewater containing several hundred to thousand mg dm^{-3} of boron is generated from these industrial processes.

Removal and detoxification methods for wastewater containing borate ion has been widely investigated by using adsorption,[5–8] membrane,[9–12] electro-coagulation,[13] and combinations of these methods.[10] However, there is no method for removing boron effectively in aqueous media and recovering it as reusable resources. Additionally, it is often the case that wastewater containing boron discharged from several industries includes fluoride ions, and thus, fluoroborate ion is produced by the reaction of borate and fluoride ions. Conventional detoxification methods, e.g., co-precipitation or lime precipitation, cannot be applied to such wastewater,[14,15] because these ions are very stable in aqueous solutions. Furthermore, there is an acceptable limit of fluorine in water based on its toxicity. Japanese standard of discharged water is 8 mg dm^{-3}, whereas WHO standard of potable water is 1.5 mg dm^{-3}.[16] Therefore, an effective removal technique for boron and fluorine from aqueous solutions containing borate or fluoroborate ions is strongly desired.

Most natural minerals have relatively low solubility, and certain minerals exhibit negative solubility curve to water with an increase in temperature. It is thought that they are formed under hydrothermal conditions caused by the activity of magma in nature. Hydrothermal mineralization is a geomimetic mineral precipitation technique, in which polluted water is hydrothermally treated with a mineralizer. In our previous study, we have investigated the precipitation recovery of borate and fluoroborate ions as reusable natural minerals as well as the detoxification of the polluted solution by hydrothermal mineralization method.[17,18] As a result, it has been shown that the borate ion in aqueous media can be precipitated as parasibirskite ($Ca_2B_2O_5 \cdot H_2O$) when treated at 130–150 °C by using ordinary batch-type treatment vessel (Fig. 1A). However, the boron concentration in the treated water was ca. 100 mg dm^{-3}, which is higher than the quality standard of water. The cause of this result has been attributed to the redissolution of parasibirskite during the cooling process. In order to reduce the boron concentration, H_3PO_4 has been added to prevent the redissolution of parasibirskite by coating the surface of precipitates with calcium hydroxyapatite and to block the contact of $Ca_2B_2O_5 \cdot H_2O$ with H_2O. As a result, boron concentration could be reduced to ca. 4 mg dm^{-3} after 12 h treatment. However, contamination with phosphorus compounds, such as hydroxyapatite, in the precipitate inhibit the reuse of the mineral as an industrial resource. Reuse of boron from this precipitate would require the dissolution of minerals into acidic solution, such as sulfuric acid, to form a concentrated, aqueous boric acid solution. In other words, the hydroxyapatite coating inter-

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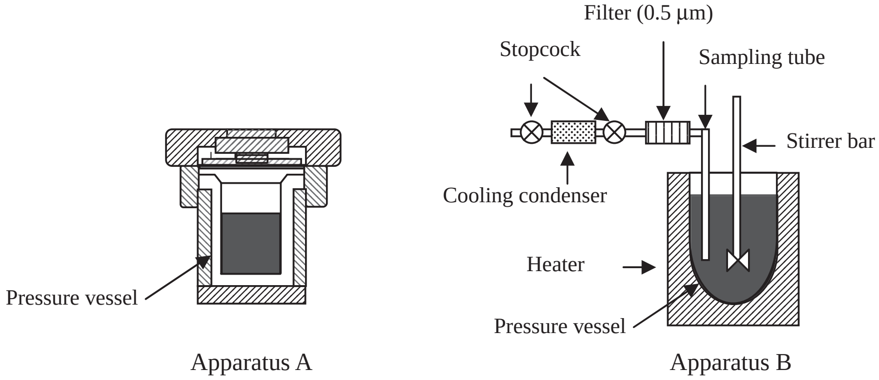

Apparatus A Apparatus B

Fig. 1. Schematic diagram of the ordinary (apparatus A) and sampling-type (apparatus B) hydrothermal treatment apparatuses.

feres with the dissolution of the parasibirskite. Additionally, the optimum treatment time to reduce the boron concentration to less than the standard for discharged water is too long (12 h), which is due to the formation reaction of hydroxyapatite and crystal growth. Thus, a method to inhibit the redissolution of formed mineral that does not use phosphorus acid is desirable. We think from the above results that the solubility of parasibirskite under hydrothermal conditions is lower than that at room temperature. Therefore, a method to separate the precipitates from the reaction solution in quasi-equilibrium under hydrothermal conditions would be effective to reduce the boron concentration in treated water.

Experimental

Sampling-Type Hydrothermal Treatment Apparatus. The sampling-type hydrothermal treatment apparatus, shown in Fig. 1 (apparatus B) was used to separate the precipitate form the solution in quasi-equilibrium state under hydrothermal conditions. The suspended product was pushed into the sampling tube by its own vapor pressure, and the precipitates were then separated from suspension by using a metal filter with 0.5 μm mesh. After that, the samples were immediately cooled down to room temperature in a cooling condenser. Treatment time was fixed from the time to turn on the power of heater. Temperature inside the pressure vessel was at 150 °C after heating for 1 h. An ordinary pressure vessel (apparatus A), shown in Fig. 1, was used in order to determine the effectiveness of apparatus B.

Preparation of Samples. Model wastewaters were prepared by dissolving B_2O_3 or diluting hydrofluoric acid (Wako Pure Chemical Industries, Ltd.) into distilled and deionized water. The boric acid solutions contained 45.5–273 mmol dm^{-3} (500–3000 mg dm^{-3}) of boron and the fluoroboric acid solutions contained 45.5 mmol dm^{-3} (500 mg dm^{-3}) of boron and 182 mmol dm^{-3} (3500 mg dm^{-3}) of fluorine.

Sampling-Type Hydrothermal Treatment. Model wastewaters (60 mL) were sealed in a pressure vessel with $Ca(OH)_2$ (0.2–6.0 g, 2.7 or 81 mmol, respectively) as the mineralizer. The temperature was controlled using a DZ1000 temperature controller (CHINO Corporation). Simple solubility tests were carried out by sealing a water (60 mL) and 1.0 g of single-phase parasibirskite, which was synthesized by using ordinary batch-type hydrothermal treatment apparatus, in the pressure vessel.

Ordinary Batch-Type Hydrothermal Treatment. Model wastewaters (30 mL) were sealed in a pressure vessel lined with a fluorocarbon resin along with $Ca(OH)_2$ 1.0 or 3.0 g, 13 or 40 mmol, respectively. Hydrothermal treatment was carried out by placing the vessel in a dry oven controlled at 150 °C for 2–6 h. After hydrothermal treatment, the vessel was cooled in air for 1 h. The precipitates and solvents obtained by hydrothermal treatment were collected by using a membrane filter (0.2 μm).

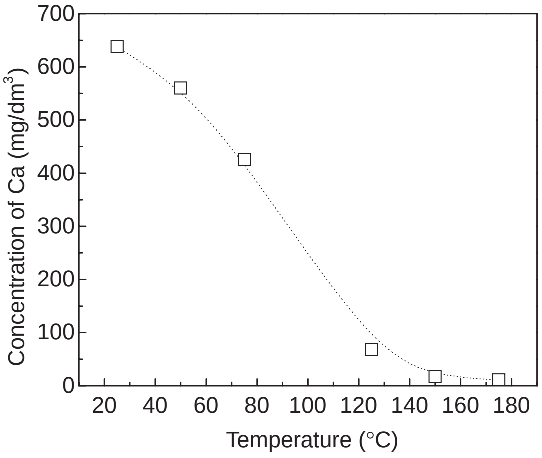

Fig. 2. Dependence of the $Ca(OH)_2$ solubility on the temperature in aqueous solution. The holding time of each temperature is 2 h.

Analytical Method. Quantitative elemental analysis of boron in the solvent, which was obtained after hydrothermal treatment, was carried out by using inductively coupled plasma-atomic emission spectrometry (ICP-AES: Perkin-Elmer, Optima3300DV). Concentration of fluoride ion and fluoroborate ion remaining in the treated-water was measured by using an ion chromatograph (Shimadzu, CTO-20AC. Mobile phase; $NaHCO_3$ 0.1008 wt % and Na_2CO_3 0.0064 wt % aqueous solution, Column; Shim-Pack IC-SA2) with a suppressor (Shimadzu, HIC-10Asp, type 312) and a conductivity detector (Shimadzu, CDD-6A).

Results and Discussion

Firstly, we examined the solubility of $Ca(OH)_2$ under hydrothermal conditions. It is well known that it decreases with an increase in the temperature under atmospheric pressure. Figure 2 shows the variation in the solubility of $Ca(OH)_2$ in the autoclave in the temperature range of 25 to 175 °C, which was measured by using apparatus B. Solubility of $Ca(OH)_2$ decreased gradually with an increase in the temperature, and the concentration of Ca^{2+} was lower than 20 mg dm^{-3} at

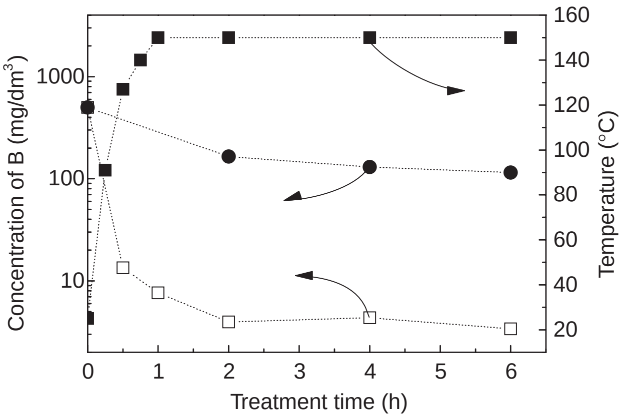

Fig. 3. Dependence of boron concentration on treatment time. B concentrations in aqueous media before the treatment were 500 mg dm^{-3}, and □: using sampling-type apparatus B ●: using apparatus A; ■: temperature of apparatus B. All the treatments were carried out with 6.0 g $Ca(OH)_2$.

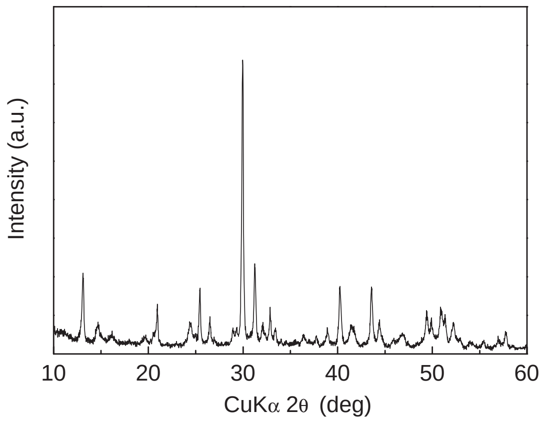

Fig. 4. XRD pattern of the precipitate obtained by the treatment for 3 h with 1.0 g of $Ca(OH)_2$ mineralizer at 150 °C using the apparatus B. All diffraction peaks are correspond to $Ca_2B_2O_5 \cdot H_2O$.

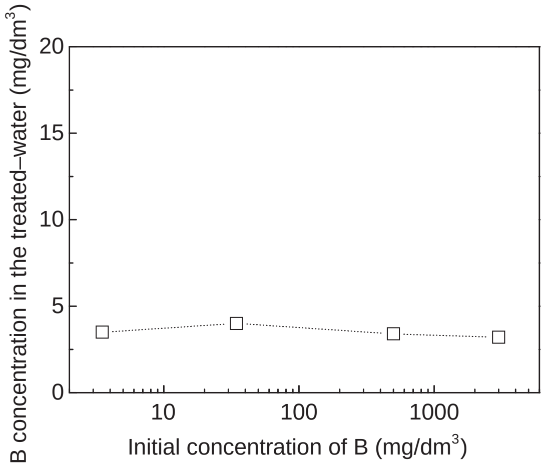

Fig. 5. Initial concentration dependence of the boron concentration in the treated-water. Sample: 60 mL, $Ca(OH)_2$: 6.0 g, Treatment temperature: 150 °C, Treatment time: 4 h.

temperatures more than 125 °C. These results indicated that apparatus B can be used to separate the reaction solution and the precipitate under hydrothermal conditions.

Figure 3 shows the result of hydrothermal mineralization treatment for the model wastewater containing 500 mg dm^{-3} of borate ion with $Ca(OH)_2$ mineralizer at 150 °C by using apparatus A and B. The boron concentration decreased, and parasibirskite ($Ca_2B_2O_5 \cdot H_2O$) was simultaneously formed during the treatment. XRD pattern of the precipitate obtained by this treatment using apparatus B is shown in Fig. 4. The mineral formed during the hydrothermal mineralization treatment was $Ca_2B_2O_5(H_2O)$, which was the same product in both apparatus A and B. In our previous study, parasibirskite also formed by heterogeneous nucleation on the surface of $Ca(OH)_2$ when apparatus A was used.[17] However, the boron concentration after the treatment by using apparatus A was more than 100 mg dm^{-3} even with a longer treatment time, because parasibirskite redissolved during the 1 h cooling process.[17] On the other hand, residual boron concentration in the water treated by using apparatus B was lower than 4 mg dm^{-3}. This result supports that redissolution of parasibirskite occurs during the cooling process. Simple solubility tests of parasibirskite under hydrothermal and ordinary temperature and pressure conditions were carried out by using sampling-type apparatus B. As a result, boron concentration under ordinary temperature and pressure conditions was 210 mg dm^{-3}, and under hydrothermal conditions (150 °C), it was 130 mg dm^{-3}. This result indicates the solubility of parasibirskite decreases with increase of temperature. However, the boron concentration is higher than the aqueous solution after hydrothermal mineralization treatment for boron-containing water with $Ca(OH)_2$ at 150 °C (see Fig. 3). On the other hand, the boron concentration in the solution with parasibirskite and excess amount of $Ca(OH)_2$ at 100 °C was 40 mg dm^{-3}. These results suggest that the precipitation of $Ca(OH)_2$ is required as a medium for controlling the dissolution behavior of parasibirskite, because formation of parasibirskite under hydrothermal conditions occurs on the surface of $Ca(OH)_2$ by heterogeneous nucleation.[17] Furthermore, the boron concentration after the treatment was not influenced by varying the initial concentration of boron. Detailed description of initial concentration dependence is shown in Fig. 5. The boron concentration in the treated-water is independent of the initial concentration, i.e., it depends only on the solubility of $Ca_2B_2O_5 \cdot H_2O$ under hydrothermal condition. This boron concentration in treated-water is lower than the standard of discharged water of Japan. Therefore, the separation of precipitate from solvent under hydrothermal condition enables effective recovery of boron and simultaneous detoxification of polluted water. This result also suggests that the boron concentration after the treatment does not depend strongly on the amount of $Ca(OH)_2$ as long as an adequate amount is added to form parasibirskite. It was confirmed that the recovery rate of boron was barely decreased at all by changing molar ratio of B:$Ca(OH)_2$ from 0.01 to 0.6. In addition, the total treatment time (1–2 h) required for the reduction of boron concentration down to less than 10 mg dm^{-3} was shorter by using apparatus B than that by using apparatus A, which needed treatment time more than 12 h. This result

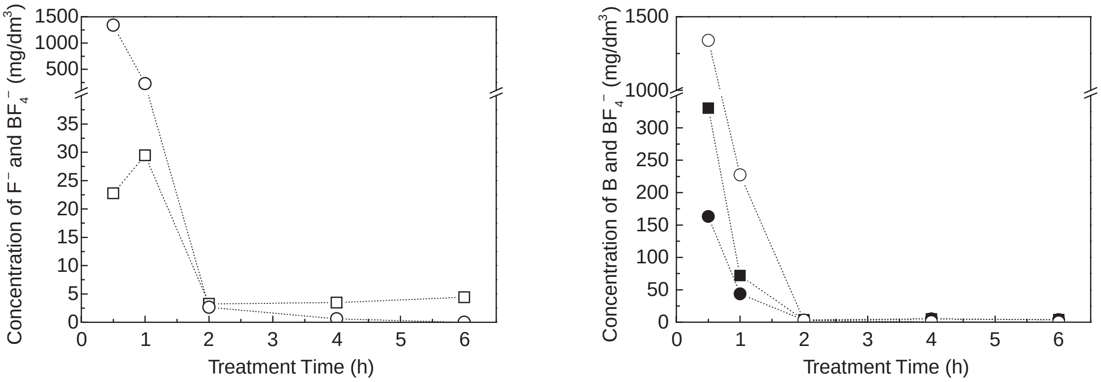

Fig. 6. Dependence of the boron, borate ion and fluoroborate ion concentration treated against model wastewater containing fluoroborate ion on the treatment time. (a): Concentration of F^- (□) and BF_4^- (○), (b): Concentration of B (■), BF_4^- (○) and B exist as borate ion (●). Treatment temperature: 150 °C, $Ca(OH)_2$: 2.0 g, BF_4^-: 4000 mg dm^{-3}.

suggests the detoxification and resource recovery are accomplished immediately when the treatment temperature of apparatus B reaches 150 °C. On the other hand, the boron concentration when apparatus A was used gradually decreased and it took more than 12 h to decrease appreciably (see Fig. 3). It is expected that the decrease in the boron concentration over a longer treatment time by using apparatus A causes the crystal and/or grain growth of parasibirskite. The difference in treatment time between apparatus A and B is responsible for that the redissolution rate of parasibirskite, which must be controlled by the grain and/or crystal size in the high-pressure vessel. To improve in the recovery yield in the case of apparatus A with longer treatment time, the parasibirskite was separated from solution before reaching the equilibrium state, because the redissolution rate of parasibirskite is slow due to crystal and/or grain growth. In contrast, the crystal and/or grain growth of the precipitate is not be required in case of apparatus B, because parasibirskite is separated from the reaction suspension under hydrothermal conditions. Therefore, it is concluded that the separation of precipitate from reactive aqueous solution is effective for a prompt detoxification of wastewater polluted by boric acid and the recovery of boron as reusable resource.

Results of the hydrothermal mineralization treatments in aqueous solutions containing 4000 mg dm^{-3} of fluoroborate ion (B: 500, F: 3500 mg dm^{-3}) with $Ca(OH)_2$ at 150 °C by using apparatus B are shown in Fig. 6. A steady state of the residual concentrations of boron and fluorine was attained after a treatment time of 2 h and both boron and fluorine concentrations were ca. 4 mg dm^{-3}. This result shows that the hydrothermal mineralization treatment is also applicable to the fluoroborate ion. Residual concentration of fluoroborate ion drastically decreased from the beginning of the treatment, and it was not detected after 2 h. Borate and fluoride ions were detected along with a decrease in fluoroborate ion concentration. It is expected that the fluoroborate ion decomposes under alkali, high-temperature and high-pressure conditions, and the decomposition is complete for 2 h. The residual boron concentration after treatment for 1 h was 75 mg dm^{-3}, which is higher than that of the treatment at same treatment condition against aqueous media containing borate ion (see Fig. 3), which may be caused by the decomposition of the fluoroborate ion. The formation of parasibirskite, that is reduction in boron concentration, should occur on the surface of $Ca(OH)_2$, followed by decomposition reaction of fluoroborate ion. In addition, 20–30 mg dm^{-3} of fluoride ion was observed, and it increased with an increase in the treatment time from 0.5 to 1 h. This fluoride ion concentration is higher than the calculated value from the solubility of CaF_2 at 25 °C (17 mg dm^{-3}). The solubility of CaF_2 has been shown to decrease with an increase in temperature in our previous study.[18] Thus, it was anticipated that the precipitation of fluoride ion would occur as soon as the fluoroborate ion decomposed. The excess amount of F^- generated by decomposition of fluoroborate ion in a short period is greater than the amount of Ca^{2+} (ca. 10 mg dm^{-3}), as shown in Fig. 2. It is expected that the rate controlling factor to form CaF_2 is not the reaction between Ca^{2+} and F^-, but the dissolution process of $Ca(OH)_2$ and diffusion of dissolved Ca^{2+}. Therefore, the F^- concentration increased between 0.5 and 1 h.

Conclusion

We investigated the detoxification of polluted water containing borate or fluoroborate ions and the resource recovery of boron and fluorine by using a sampling-type hydrothermal treatment apparatus. As a result, effective recovery of boron and fluorine from aqueous solution containing both borate and fluoroborate ions was achieved in a shorter amount of time through in situ solid/liquid separation under quasi-equilibrium hydrothermal conditions. We obtained important information about the decomposition of fluoroborate ion and formation of fluorite by measuring the solubility of $Ca(OH)_2$ under hydrothermal conditions. Therefore, the hydrothermal mineralization treatment by using a sampling-type apparatus would be effective method to detoxify the wastewater and ground water containing these ions and recover these ions as recyclable mineral. These results suggest that a large amount of wastewater containing boron and fluorine can be treated more effectively in a shorter amount of time by using flowing-type hydrothermal apparatus.

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