A Novel Recovery Method for Treating Wastewater Containing Fluoride and Fluoroboric Acid

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A new treatment method for wastewater containing concentrated fluoride and fluoroborate ions by hydrothermal treatment were developed. The treatment is an earth-mimetic method to produce natural minerals by hydrothermal treatment with $Ca(OH)_2$ as a mineralizer. Results of various analyses of the precipitate indicated that the recovered minerals were $Ca_2B_2O_5 \cdot H_2O$ (parasibirskite) and CaF_2 (fluorite). By optimizing the conditions, it was possible to recover more than 98 percent of the boron and 99.9 percent of the fluorine from model wastewater samples containing fluoride ($7000\,mg\,L^{-1}$) and fluoroborate ($8000\,mg\,L^{-1}$) ions. Moreover, in the case of fluoroborate ions, the present treatment simultaneously caused the decomposition of the fluoroborate ion, the formation of each minerals, and the preventation of redissolution of parasibirskite. Therefore, the present hydrothermal mineralization treatment with the $Ca(OH)_2$ mineralizer is an effective technique to recover boron and fluorine from wastewater.

Borate ions can be found in wastewaters derived from plating, semiconductor production, metal processing, and glass-manufacturing industries. Discharge of such wastewater into the surface water would cause groundwater pollution. Excess intake of these elements greatly impacts plants, animals, and human bodies.[1,2] In our previous study, we found that the hydrothermal mineralization using $Ca(OH)_2$ as a mineralizer caused the precipitation of a boron-containing mineral.[3] However, it is often the case that actual wastewater contains other ions, especially, fluoride ion. An acceptable limit of fluoride ion in potable water is $1.5\,mg\,L^{-1}$ according to the WHO standard.[4] Also, the quality standard of discharged water with fluoride ions from manufacturing plants has been set at $8\,mg\,L^{-1}$. Additionally, some local governments in Japan tack on stringent standards for discharged water (e.g $0.8\,mg\,L^{-1}$). Therefore, advanced treatment of wastewater containing fluoride is necessary to meet the required regulations. Several defluorination methods for wastewater such as adsorption,[5] chemical precipitation,[6–8] ion exchange,[9,10] and electrochemical method,[11,12] have been intensively investigated. The lime precipitation method is commonly used to remove fluorine from the wastewater. However, this technique cannot in practice, reduce the fluorine concentration in wastewater less than ca. $20\,mg\,L^{-1}$.[6–8] Because the theoretical concentration of fluoride ion eluted from fluorite in water is $16\,mg\,L^{-1}$ at 18 °C. Furthermore, fluoroborate ion is formed by coexistence of the borate and fluoride ions. Fluoroborate ion cannot be removed from the wastewater with both borate and fluoride ions by general chemical precipitation methods because of the extremely high stability of fluoroborate ions. Thus, there is no effective method to remove or recover both boron and fluorine from wastewater containing fluoride or fluoroborate ions. Therefore, a new technique to concurrently recover both boron and fluorine from wastewater containing fluoroboric acid is highly desired.

In this study, a new method to remove fluorine and boron from wastewater containing fluoride and fluoroborate ion by using a novel hydrothermal mineralization technique was investigated. Hydrothermal mineralization uses the earth-mimetic method reported in our previous study.[3] This technique imitates a natural mechanism for forming minerals from various ions in aqueous media under hydrothermal conditions, which was derived from the activity of magma.

Experimental

Hydrothermal Mineralization Treatment. Model wastewaters were prepared by diluting hydrofluoric acid (48 wt %, Wako Pure Chemical Industries, Ltd.), fluoroboric acid (48 wt %, Wako Pure Chemical Industries, Ltd.) into distilled and deionized water. Each of the model wastewaters contain fluoride ion (368 $mmol\,L^{-1}$, F; $7000\,mg\,L^{-1}$) or fluoroborate ion ($92\,mmol\,L^{-1}$, B; $1000\,mg\,L^{-1}$, F; $7000\,mg\,L^{-1}$). Thirty milliliters of these model wastewaters, which contain 11.0 mmol of fluoride ions or 2.76 mmol of fluoroborate ions, were sealed in a pressure vessel lined with a fluorocarbon resin along with 0.5–1.0 g of $Ca(OH)_2$ (6.41–12.8 mmol). Hydrothermal treatment was carried out by placing the vessel in a dry oven controlled over a temperature range of 100–200 °C for 2–48 h. After the hydrothermal treatment, the vessel was cooled in air for 1 h. The precipitates obtained by hydrothermal treatment were collected by using membrane filter (0.2 µm) and dried at 50 °C for 24 h.

Characterization. The precipitates were identified by using X-ray diffraction (XRD: RIGAKU RINT-2500) using Cu Kα radiation. The microstructural observation and qualitative elemental analysis of the precipitates were performed by using scanning

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Table 1. Concentration of F^- in the Model Wastewater before and after the Treatment (F^-; 7000 mg L^{-1}, $Ca(OH)_2$; 0.5 g, 200 °C, 4 h)

	Before treatment	After $Ca(OH)_2$ addition	After hydrothermal mineralization
Concentration of F^-	7000 ppm	18 ppm	N.D.

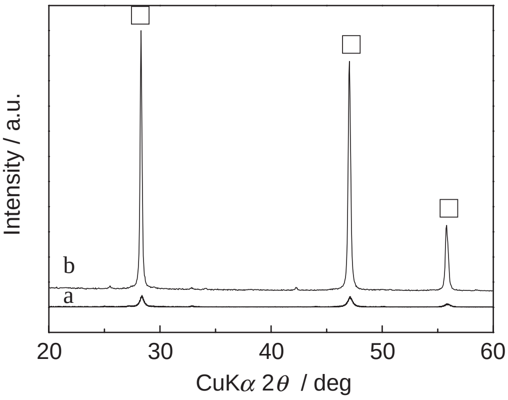

Fig. 1. XRD patterns of the precipitates obtained before and after hydrothermal treatment, a: before the treatment, b: after 4 h. (F^-: 7000 mg L^{-1}, $Ca(OH)_2$: 0.5 g). ○: $Ca(OH)_2$, □: CaF_2.

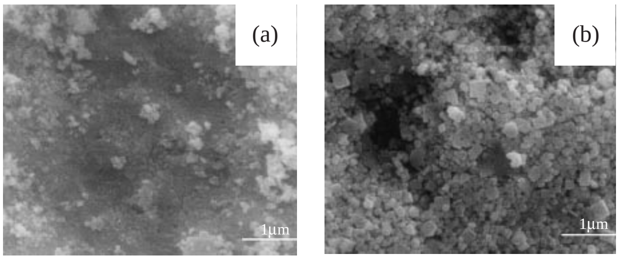

Fig. 2. SEM micrographs of the precipitates obtained (a) before and (b) after the hydrothermal treatment (F^-; 7000 mg L^{-1}, $Ca(OH)_2$; 0.5 g, 200 °C, 4 h).

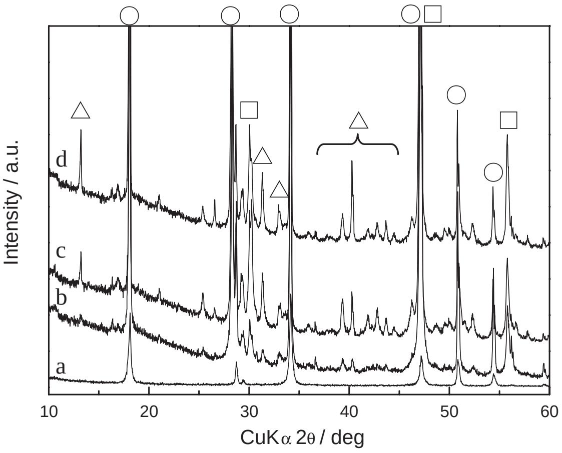

Fig. 3. XRD patterns of the precipitates before and after the hydrothermal treatment. a: before treatment, b: 2 h, c: 10 h, d: 24 h (BF_4^-: 8000 mg L^{-1}, $Ca(OH)_2$: 1.0 g). ○: $Ca(OH)_2$, □: CaF_2, △: $Ca_2B_2O_5 \cdot H_2O$.

electron microscopy (SEM: JEOL, JSM-T20) equipped with energy dispersive X-ray spectrometry (EDS: JED-2140). Quantitative elemental analysis of boron in the solvent, obtained after hydrothermal treatment, was carried out by using the inductively coupled plasma-atomic emission spectrometry (ICP-AES: Perkin-Elmer, Optima3300DV). Concentration of fluoride ion remaining in the treated-water was measured by using ion chromatograph (Shimadzu, CTO-10AC. Mobile phase; Bis-Tris 0.067 wt % and *p*-Hydroxybenzoic acid 0.11 wt % aqueous solution, Column; Shim-Pack IC-A3) with conductivity detector (Shimadzu, CDD-10A).

Results and Discussion

Recovery of Fluorine from Wastewater Containing Fluoride Ion. Table 1 shows the concentrations of F^- in the model wastewater before and after the hydrothermal treatment using 0.5 g of $Ca(OH)_2$ at 200 °C for 4 h. The concentration of fluoride ion before the hydrothermal treatment was 18 mg L^{-1}. This result is similar to that in the previous report.[8] On the other hand, it could not detected after the hydrothermal treatment. This suggested that the fluoride ion in the wastewater was completely consumed to form precipitates under the hydrothermal conditions using $Ca(OH)_2$. Figure 1 shows XRD patterns of the precipitates before and after the treatment, and the diffraction peaks of CaF_2 (fluorite) were observed. However, the concentration of fluoride ion in the treated-water was well below than the concentration, that was calculated using the solubility of CaF_2. In other words, all of the fluoride ions in the model wastewater precipitated as CaF_2 under hydrothermal conditions. Additionally, CaF_2, produced under hydrothermal conditions, may prevent redissolution during the cooling process. Figure 2 shows the SEM micrographs of the precipitates before and after the treatment, and the crystallinity and crystal size of CaF_2 increased dramatically by the hydrothermal treatment. This result is in agreement with the increase in intensity of the X-ray diffraction peaks derived from CaF_2 (Fig. 1). Thus, the recovery of fluorine from wastewater was achieved by decreasing dissolution rate of CaF_2 at room temperature because of a decrease in specific surface area. As well, a minimum amount of $Ca(OH)_2$ required to form CaF_2.

Recovery of Boron and Fluorine from Wastewater Containing Fluoroboric Acid. Figure 3 shows XRD patterns of the precipitates before and after hydrothermal treatment of a fluoroboric acid solution. Only the diffraction peaks of $Ca(OH)_2$ were observed before the treatment (Fig. 3a), indicating that a precipitate containing fluoride ion does not form by the addition of $Ca(OH)_2$ into wastewater containing fluoroborate ion. On the other hand, the diffraction peaks for CaF_2 and $Ca_2B_2O_5 \cdot H_2O$ were observed after the treatment (Figs. 3b, 3c, and 3d), and the intensities of diffraction peaks of $Ca_2B_2O_5 \cdot H_2O$ increased over 24 h. Thus, decomposition of fluoroboric acid took place during the treatment. Figure 4 shows the treatment time dependence of the B and F concentrations in waste-

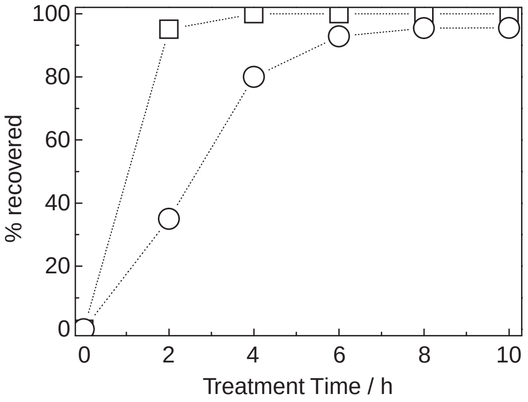

Fig. 4. The percent recovered of B and F in the treated-water versus the treatment time at 150 °C (BF_4^-: 8000 mg L^{-1}, $Ca(OH)_2$: 1.0 g). ○: B, □: F.

water treated at 150 °C. The significant enhancement in the recovered yield of fluorine was observed at 2 h, and recovery was complete by 4 h. On the other hand, the recovered yield of boron was only 30 percent at 2 h, and gradually increased. The recovery of F and B occurred by forming CaF_2 and $Ca_2B_2O_5 \cdot H_2O$ in the same manner as in the case of wastewater containing fluoride or borate ion only. It is thought that F^-/$B(OH)_4^-$ ions are generated from the thermal decomposition of BF_4^- at the initial stage of the treatment. The decomposition of BF_4^- was completed by 4 h, after which the mineralization of boron and fluorine occurred.

Figure 5 shows the B and F concentrations in the treated-water versus the treatment time in the temperature range of 100 to 200 °C. Treatment time required for the removal of B and F greatly decreased with an increase in treatment temperature. The optimal conditions to recover both F and B from model wastewater containing 8000 mg L^{-1} of fluoroborate ion were 200 °C and 36 h. The concentrations of the ions treated

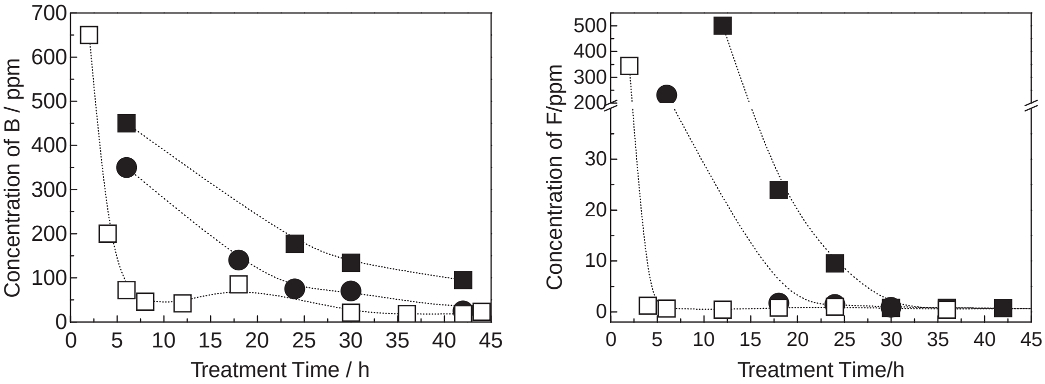

Fig. 5. Concentration of borate (a) and fluoride ions (b) in the treated-water versus treatment time (BF_4^-: 8000 mg L^{-1}, $Ca(OH)_2$: 1.0 g). ■: 100 °C, ●: 150 °C, □: 200 °C.

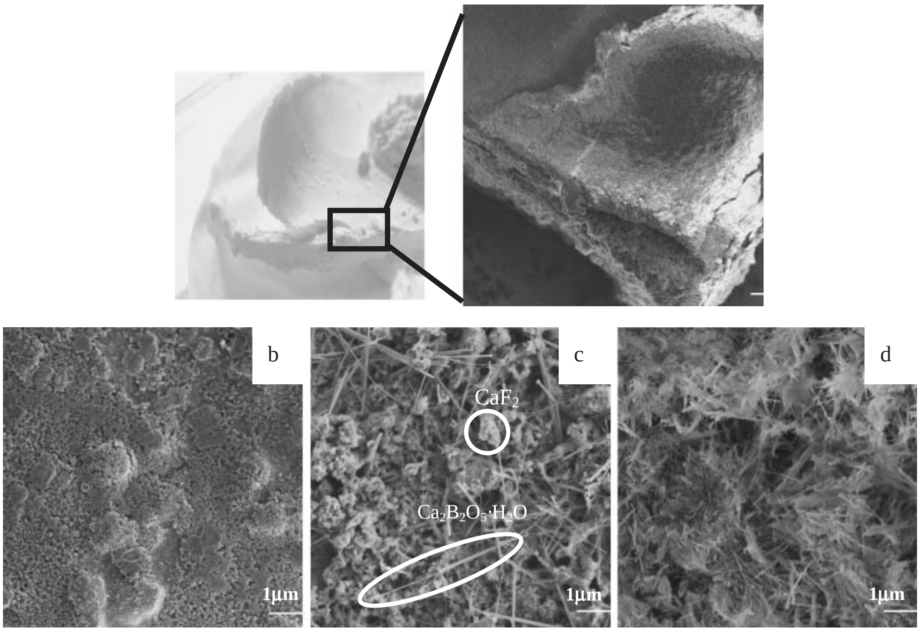

Fig. 6. SEM micrographs of the precipitates obtained by the hydrothermal treatment. a: over view of precipitate, b: first layer, c: second layer, d: third layer (BF_4^-: 8000 mg L^{-1}, $Ca(OH)_2$: 1.0 g, 150 °C, 24 h).

under these conditions were 0.3 mg L^{-1} of F and 20 mg L^{-1} of B, respectively, and the percents recovered were more than 99.9 and 98%, respectively. It was already shown that the boric acid in the model wastewater was precipitated as $Ca_2B_2O_5 \cdot H_2O$ by using hydrothermal mineralization in our previous study.[3] However, amounts less than 100 mg L^{-1} could not be isolated without H_3PO_4, because of redissolution of the precipitate during the cooling process. On the other hand, the concentration of boron in the treated-water was ca. 5 mg L^{-1} by using H_3PO_4. H_3PO_4 caused the formation of hydroxylapatite on the surface of precipitate containing $Ca_2B_2O_5 \cdot H_2O$ and $Ca(OH)_2$. The particle would grow on the $Ca_2B_2O_5 \cdot H_2O$ and residual $Ca(OH)_2$. Therefore, the encapsulation of $Ca_2B_2O_5 \cdot H_2O$ prevented redissolution of $Ca_2B_2O_5 \cdot H_2O$ by preventing contact with H_2O. However, the boron concentration in the case of fluoroboric acid solution was reduced to ca. 20 mg L^{-1} without the redissolution inhibition reagent H_3PO_4. The difference between present and previous studies is only coexistence of fluoride ion or not. In other words, CaF_2 in the treated-water affects the recovery yield of boron.

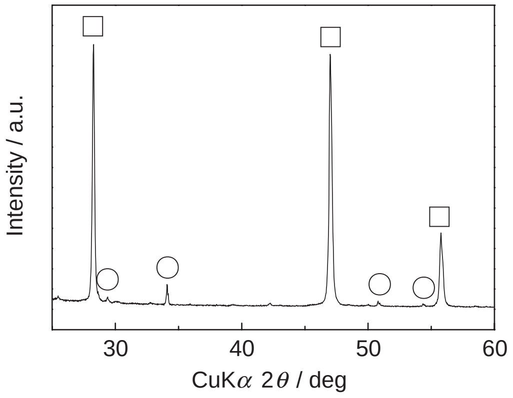

Fig. 7. XRD pattern of the suspended particle obtained by hydrothermal mineralization treatment at 200 °C for 6 h. BF_4^-; 92 mmol L^{-1} (B; 1000 mg L^{-1}, F; 7000 mg L^{-1}). ○: $Ca(OH)_2$, □: CaF_2.

Mechanism of Boron and Fluorine Recovery. SEM micrographs of the precipitate obtained by the hydrothermal treatment are shown in Fig. 6. Three layers were observed in the overview micrograph (Fig. 6a). From XRD analysis, it was found that the compounds included in this system were $Ca(OH)_2$, CaF_2, and $Ca_2B_2O_5 \cdot H_2O$ (cf. Fig. 3d). Quantitative analysis by EDS showed the upper layer (Fig. 6b) was CaF_2, the middle layer (Fig. 6c) was a mixture of CaF_2 and $Ca_2B_2O_5 \cdot H_2O$, and the bottom layer (Fig. 6d) was a mixture of $Ca_2B_2O_5 \cdot H_2O$ and residual $Ca(OH)_2$. Very fine particulates were suspended in the model wastewater after hydrothermal treatment at 200 °C for more than 4 h. The amount of the particulates seemed to gradually decrease over 8 h with an increase in the treatment time and completely settled out after 20 h. Figure 7 shows the XRD pattern of the suspended particles, and they were determined to be CaF_2. Therefore, the decomposition of BF_4^- was complete in ca. 4 h, and subsequently, fine particles of CaF_2 formed in the model wastewater. Finally, they settled out slowly over 20 h. The formation of a bottom layer of residual $Ca(OH)_2$ and $Ca_2B_2O_5 \cdot H_2O$ began in the time range of 2–4 h and was complete in 8–10 h by heterogeneous nucleation of $Ca_2B_2O_5 \cdot H_2O$ on the surface of $Ca(OH)_2$. After that, the suspended CaF_2-coated $Ca_2B_2O_5 \cdot H_2O$ because of the slow sedimentation rates. Figure 8 shows

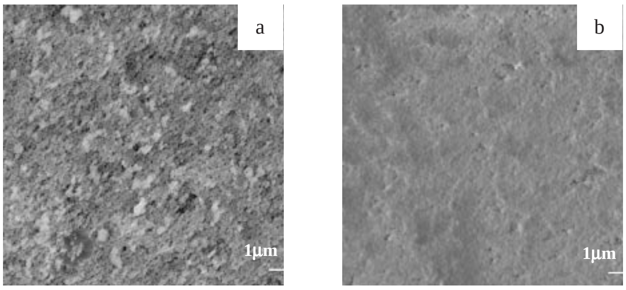

Fig. 8. SEM micrographs of the CaF_2 particles obtained by hydrothermal treatment at 200 °C. a: 8 h, b: 30 h.

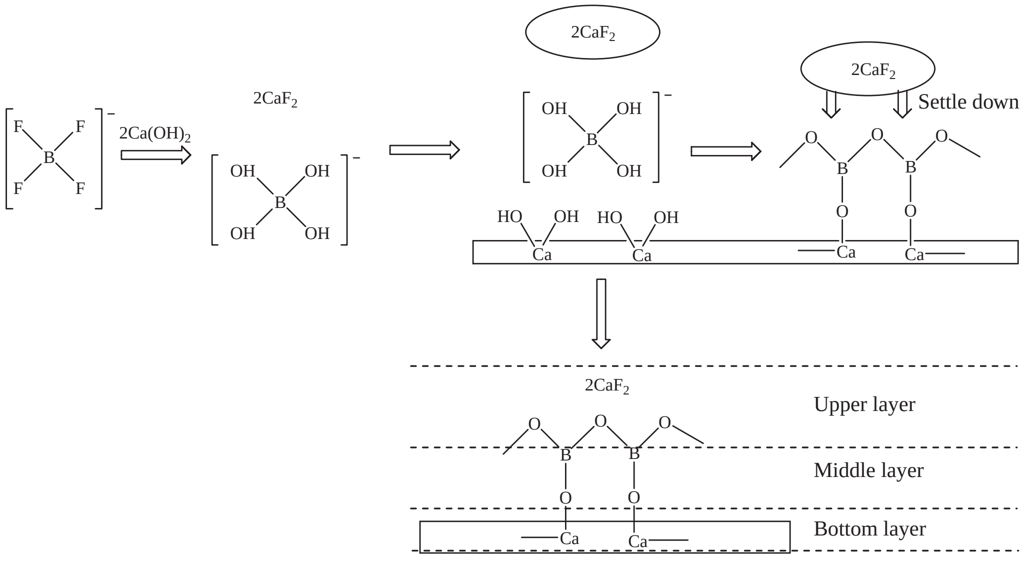

Fig. 9. A schematic diagram of the reaction mechanism for the recovery system of fluorine and boron during the hydrothermal mineralization.

the SEM micrographs of CaF_2 particles obtained by using the hydrothermal treatment at 200 °C for 8 and 30 h. Precipitates obtained at 200 °C for 30 h formed a very dense layer (Fig. 8b) compared with those for 8 h (Fig. 8a). Possibly, this dense layer plays a role in inhibiting the redissolution of $Ca_2B_2O_5 \cdot H_2O$ into aqueous media by coating the precipitate surface. The schematic diagram of the mechanism for this recovery is shown in Fig. 9. This mechanism is different from that for hydroxylapatite. Therefore, resource recovery of boron and fluorine was achieved by precipitating them as CaF_2 and $Ca_2B_2O_5 \cdot H_2O$, respectively, from fluoroboric acid solution by using hydrothermal mineralization without a precipitation reagent, such as phosphoric acid.

Conclusion

Hydrothermal mineralization treatment was successfully used to recover fluorine and boron as CaF_2 and $Ca_2B_2O_5 \cdot H_2O$, respectively, from model wastewater containing fluoride and fluoroborate ions. The percents recovered of fluorine and boron, respectively, were 99.9 and 98% from model wastewater containing 8000 $mg\,L^{-1}$ of fluoroboric acid without an agent to prevent redissolution, such as hydroxylapatite. As the results of investment, redissolution preventation agent in this system was fluorite, which was simultaneously produced during the hydrothermal mineralization treatment. Additionally, percents recovered for this treatment depended only on the solubility of products ($Ca_2B_2O_5 \cdot H_2O$ and CaF_2), and not on the initial concentration of treated ions, such as fluoride and fluoroborate ion. Therefore, the present treatment is useable for actual wastewater.

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