Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11434

58 (2017) 435–441
January

Boron removal from wastewater via coagulation sedimentation with ettringite: an experimental and mechanism study

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Received 23 December 2015; Accepted 9 May 2016

ABSTRACT

Boron compounds that are largely being used in industrial processes may pose health risks to humans and animals due to unpredictable emissions to the environment. Nowadays, the boron (including its compounds) emission standard in Japan requires a more thorough removal of boron from all effluents than previously. Compared with other novel technologies, the coagulation process using ettringite as a purifying agent is known to be more economically effective, but the sophisticated water treatment method and mechanism have rarely been described. In this study, we wanted to clarify the boron removal mechanism by batch tests followed with measurement and data analyses on boron, calcium, aluminum, and sulfate in both the liquid and solid phases. Results indicate that increasing the pH from 10 to 13 enhances the removal of boron and also changes the amount of calcium, aluminum, and sulfate (sulfur and oxygen) in both phases. The mechanism suggested is that in aqueous solutions at high pH, OH^- can drive a few sulfate and tetrahydroxy aluminate ions out of the boro-ettringite. Other measurements further detected the presence of two similar materials of boro-ettringite in precipitates that were formed at different pHs and observed to actually be mixtures.

Keywords: Wastewater; Boron removal; Ettringite; Coagulation sedimentation

1. Introduction

Boron exists mainly in the form of boric acid or borate salts with concentrations of 5–150 mg/kg in natural soils [1] and an average level of 4.5 mg/kg in seawater [2]. Boron is an useful component for many industries [3]. It is used in manufacturing glass via raw materials, that is, borax [4], and as a key ingredient in some chemicals such as wood preservative agents [5], abrasive compounds [6], and flame retardants [7]. Boron is also one kind of the most important micro-nutrients for plants and animals [3, 8]; however, excessive intake will inhibit the growth of both plants and animals [9, 10]. Actually, of all plant nutrient elements, boron has the narrowest range between deficient and toxic soil/solution concentrations [11]. Moreover, there are slight differences between published data for adequate intake levels for the health benefits of boron [8]. The World Health Organization (WHO) has provided a guideline for the boron concentration in drinking water to be less than 0.5 mg/L, using the tolerable daily intake value of 0.16 mg/kg/d and the daily drinking water consumption of 2L for 60 kg adults and the source allocation of 10% [12], whereas in the European Union regulations, the guideline is 1 mg/L [13]. The United States of America still does not have a national standard regarding an acceptable amount of boron in drinking water. Several state guidelines are as follows: California, 1 mg/L; Wisconsin, 0.9 mg/L; Florida, Maine, and New Hampshire, 0.63 mg/L; and Minnesota, 0.6 mg/L [14]. Besides, the U.S. Environmental Protection Agency (EPA) has issued a higher drinking water equivalent level, that is, 3.0 mg/L [15]. Japan revised its water pollution control act emissions standards in 2001, 2011, and 2014. The Japanese national effluent standards [16] regarding

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Presented at the 2015 International Environmental Engineering Conference (IEEC 2015) October 28–30, 2015, Busan, Korea.

boron and its compounds in fresh waters (in non-coastal areas) and seawater (in coastal areas) are currently set at 10 and 230 mg/L, respectively.

Landfill leachate and hydrothermal waters are two important boron emission sources, and boron concentrations have been reported to range between tens of mg/L (landfill leachates) and 1,000 mg/L (hydrothermal waters) [17, 18]. So far, there have been many technologies developed for treatment of water and wastewater with different levels of boron [19]. These technologies are capacitive deionization [20], double-layered hydroxides [21], electrocoagulation [22, 23], chemical precipitation [24], ion exchange [25], reverse osmosis [18, 26–28], nanofiltration [18, 27], adsorption [17, 29], liquid-liquid extraction [30], and electrodialysis [31]. Of these methods, chemical coagulation is known to be one of the most inexpensive methods [22].

Ettringite is known as a hydrous calcium aluminum sulfate mineral with an empirical formula: $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$. Its affinity for boron is crucial for boron removal from water/wastewaters [32–34], and the coagulation, adsorption, and replacement play important roles. This characteristic has also been found in hydrocalumite [32], metaettringite [34, 35], and other analogs [36–38] for various toxic constituents [32, 39–41]. However, although a few studies have been reported, the development of systematic and practical applied methods and an understanding of the mechanism for boron removal have rarely been described. For example, Kudo and Sakata [39] improved the boron removal by addition of $CaSO_4$ into the boron-containing wastewaters, but their work neither discussed the mechanism on which the removal process was based on nor described the composition of the precipitates. In conducting the efficient and cost-effective treatment of boron-containing wastewaters, this study was designed to clarify the removal mechanism by batch tests, followed with measurement and data analyses. Unlike previous studies, all the chemical reagents essential for the formation of ettringite were added sequentially into wastewaters, and after the desirable pH was reached, B, Ca, Al, and SO_4^{2-} in both liquid and solid phases were investigated to identify a reasonable mechanism.

2. Principle, materials, and experimental methods

2.1. Principle

The formation of ettringite is simply described in Eq. (1):

$$Al_2(SO_4)_3\cdot 16H_2O + Ca(OH)_2 + 10H_2O \rightarrow Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O \quad (1)$$

which is actually an equilibrium [42]:

$$Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O \rightleftharpoons 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O \quad (2)$$

The solubility product constant, $K_{sp,ettringite}$ is $[Ca^{2+}]^6[Al(OH)_4^-]^2[SO_4^{2-}]^3[OH^-]^4[H_2O]^{26}$). Perkins and Palmer reported a mean $\mathrm{Log}K_{sp,ettringite}$ to be –44.9 ± 0.32 (at 25°C). High $[Ca^{2+}]$, $[Al(OH)_4^-]$, $[SO_4^{2-}]$, and the solution pH contribute to the formation of ettringite.

Ettringite shows an anion displacement ability due to the SO_4^{2-}, and the boron removal process is expressed in Eq. (3) [43].

$$Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O + B(OH)_4^- \rightarrow Ca_6Al_2(B(OH)_4)_{2\text{–}4}(OH,O)_{12}\cdot 26H_2O \quad (3)$$

In the present study, boron removal was carried out by onsite formation of boro-ettringite under high solution pH, rather than by anion displacement which used pre-prepared ettringite [38]. We can consider that the former way will lead to a faster boron removal than the latter, and that it should be described as follows:

$$Al_2(SO_4)_3\cdot 16H_2O + Ca(OH)_2 + B(OH)_4^- + 10H_2O \rightarrow Ca_6Al_2(B(OH)_4)_{2\text{–}4}(OH,O)_{12}\cdot 26H_2O \quad (4)$$

High levels of $[B(OH)_4^-]$ would favor the formation of boro-ettringite. Taking into account the dual benefits of engineering and economic aspects, we should conduct fast and large boron removal with small amounts of water purifying reagents.

2.2. Materials

A synthetic boron-containing wastewater was employed in this study. It was prepared by dissolution of 70 mg of $B(OH)_3$ in 1 L of distilled water in a 1-L polyethylene (PE) beaker and stirring with a stirrer at 25°C for more than 10 min. $B(OH)_3$ and other chemicals including $Al_2(SO_4)_3\cdot 16H_2O$ (first class grade), $Ca(OH)_2$ (95%, special grade) and NaOH (special grade) were provided by Wako Pure Chemical Industries, Ltd., Japan. Distilled water was applied throughout the whole experiment.

2.3. Experimental

The experiment was started by adding 6.166 g of $Al_2(SO_4)_3\cdot 16H_2O$ into 1 L of pre-prepared synthetic wastewater and electromagnetically stirring until complete dissolution. Then, 4.117 g of $Ca(OH)_2$ was slowly added and stirred constantly for a period of 30 min to form a white suspension. It is noteworthy the amount of $Ca(OH)_2$ added was much greater than the solubility (1.6 at 20°C). After the volume of the suspension was accurately measured, the total contents of B, Ca, Al, and SO_4^{2-} were estimated to be 1.13, 55.6, 36.0, and 54.1 mmol/L, respectively. Table 1 also shows the chemical composition of aqueous suspensions used in this study. The subsequent experiment was carried out by batch method, in which a volume of 100 ml of boron solution was moved separately into a series of 200-ml PE beakers and then the pH of aqueous suspensions was adjusted to values close to 10, 10.5, 11, 11.5, 12, and 13, respectively, within the 25%wt NaOH aqueous solution. Here, to accurately measure the solution pH with a minimum deviation of ±0.01, a specially crafted alkali-resistant electrode was employed. The solution pH was adjusted at least twice and the obtained aqueous suspensions were allowed to stand for more than 24 h. During the period of standing, all the aqueous suspensions were strictly isolated from the air to prevent CO_2 from being dissolved. After confirming the pH of the aqueous suspensions, the solid–liquid

Table 1
Chemical composition of aqueous suspensions used in this study

Chemical formula	g/mol	g	Elements and ingredients	mol/L
$B(OH)_3$	61.83	0.06998	B	1.13×10^{-3}
$Ca(OH)_2$	74.09	4.117	Ca	5.56×10^{-2}
$Al_2(SO_4)_3\ 16H_2O$	342.15	6.1654	Al	3.60×10^{-2}
			SO_4^{2-}	5.41×10^{-2}

phases were carefully separated with a centrifuge, followed by separating the supernatants with 1-µm ADVANTEC filter paper and keeping the precipitates in a dryer under ambient temperature for more than one week. All the filtered supernatants were kept until the analyses were completed respectively on the B, Ca, and Al by inductively coupled plasma – mass spectrometry (Agilent 8800) and on the SO_4^{2-} by an ion chromatography system (Metrohm 883 Basic IC Plus). The microstructures of the precipitates were observed with an electron probe microanalyser (EPMA, JEOL JXA-8530F), X-ray diffractometer (XRD, Bruker D8 Discover) and scanning electron microscope (SEM, JEOL, IB-09020CP).

3. Results and discussion

3.1. B, Ca, Al, and SO_4^{2-} in aqueous phases

After confirmation of the formation of stable aqueous suspensions with stirring at different pHs close to 10.0, 10.5, 11.0, 11.5, 12.0, and 13.0, respectively, followed by solid–liquid separation, the supernatants were filtrated and kept at 4°C until the next analyses. Results obtained are shown in Fig. 1 to demonstrate the changes in the concentrations of B, Ca, Al, and SO_4^{2-} in aqueous phases with pH, and also the extent of boron removal. As can be seen, the B removal increased nearly linearly with the pH value, and exceeded 98% near the pH of 13. This occurred mainly because in this study, boron ions present in the aqueous suspensions were far less than Al(III), Ca^{2+} and SO_4^{2-} based on the stoichiometric ratio for the formation of boro-ettringite, namely, $Ca_6Al_2(B(OH)_4)_{2-4}(OH,O)_{12}{\cdot}26H_2O$. The vast majority of boron ions were firmly fixed in the formed boro-ettringite, which was confirmed to be a mixture of various forms of ettringite and other substances such as $CaSO_4$ and $Ca(OH)_2$. The concentration of Ca^{2+} ions ($[Ca^{2+}]$) also decreased and finally stabilized at quite a low level as the pH-value was higher than 11.5, indicating that more and more Ca^{2+} ions (nearly 100% as shown in Fig. 1(b)) were fixed in the boro-ettringite. It should be mentioned that Al and SO_4^{2-} showed significantly different performances from those of B and Ca^{2+}. That is, with the pH value being higher than 11.5, more Al(III) and SO_4^{2-} ions turned to dissolve into the aqueous phases. It is speculated they were constantly substituted by hydroxide ions.

It is believed there may be several processes underway at the same time in the aqueous suspensions.

First of all, it should be mentioned that because $Ca(OH)_2$ was added to be several times greater than the solubility (4.0×10^{-4}), a certain amount of slightly soluble $CaSO_4$ would also have been formed. Based on the solubility product constant ($K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = 4.93 \times 10^{-5}$ (25°C) [44]), $[Ca^{2+}]$, and $[SO_4^{2-}]$ should be inversely proportional with each other.

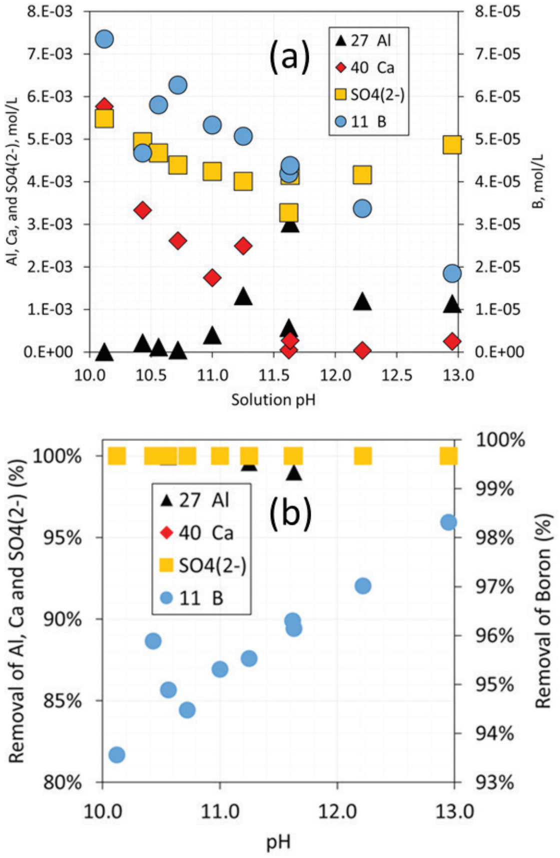

Fig. 1. The pH-dependence of concentrations and removal rates of B, Al, Ca and SO_4^{2-}.

Secondly, Al(III) exists in a variety of chemical species and displays both acidic properties and basic properties. The dissociation processes of $Al(OH)_3$ in aqueous phases are expressed in Table 2. Thus, the ranges of existence of all the species Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$, and $Al(OH)_4^{-}$ are calculated and given in the distribution diagram as Fig. 2(a) which clearly shows the only major form of Al(III) is $Al(OH)_4^{-}$ as the pH value is higher than 8.

Thirdly, H_3BO_3 is dissociated by three steps with increasing pH (Table 2). Based on these reactions, the distributions of H_3BO_3, $H_2BO_3^{-}$, HBO_3^{2-}, and BO_3^{3-} are calculated and shown in Fig. 2(b). It can also be observed that in the aqueous solution with increasing pH from (9) 10 to 12, $H_2BO_3^{-}$ becomes the major species. As the pH is moved higher than 11, HBO_3^{2-} starts to increase more and more until after pH13, BO_3^{3-} soon became the major species. By making a direct comparison in Figs. 2(a) and 2(b), both of which show pH-dependent distributions of Al(III) and B(III), we get a clear understanding of the aqueous phases with the pH value ranging from 10 to 13. It therefore becomes easy to discuss what is shown in Fig. 1.

The whole experiment can be described to take place in two stages with the pH value ranging from 10 to 13. The first stage involves the formation of ettringite, boro-ettringite and some other products like $CaSO_4$ from Ca^{2+}, SO_4^{2-}, $Al(OH)_4^{-}$, and $H_2BO_3^{-}$ through several processes shown

Table 2
Dissociation equations and constants of $Al(OH)_3$ and H_3BO_3 in water (25°C)

(1) $Al(OH)_3$ [45]	
$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$	$K_{1a} = 10^{-5.00}$
$Al(OH)^{2+} + H_2O \rightleftharpoons Al(OH)^+ + H^+$	$K_{2a} = 10^{-5.29}$
$Al(OH)^+ + H_2O \rightleftharpoons Al(OH)_3^0 + H^+$	$K_{3a} = 10^{-6.40}$
$Al(OH)_3^0 + H_2O \rightleftharpoons Al(OH)_4^- + H^+$	$K_{4a} = 10^{-5.98}$
(2) H_3BO_3	
$H_3BO_3^0 \rightleftharpoons H_2BO_3^- + H^+$	$K_{a1} = 5.8 \times 10^{-10}$
$H_2BO_3^- \rightleftharpoons HBO_3^{2-} + H^+$	$K_{a2} = 4 \times 10^{-13}$
$HBO_3^{2-} \rightleftharpoons BO_3^{3-} + H^+$	$K_{a3} = 4 \times 10^{-14}$

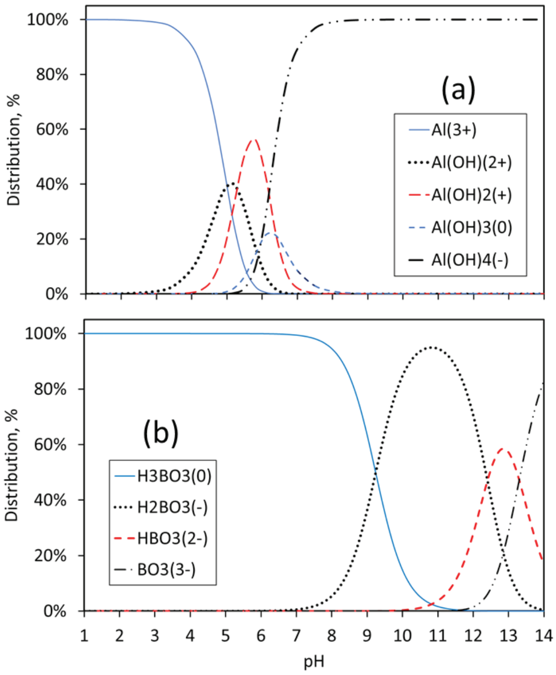

Fig. 2. The pH-dependence of Al and B species in aqueous solutions.

in Table 2. Fig. 1(b) shows that more than 93% of chemical materials added into the aqueous suspensions at the beginning of the experiment existed in solid phases. Importantly, it can be concluded that $H_2BO_3^-$ is more likely to form the ettringite rather than present in the aqueous phases of the suspensions. During the second stage, in which the pH was further increased, the concentrations of Al(III) and SO_4^{2-} anions significantly increased. This indicates that small parts of Al(III) and SO_4^{2-} anions were being gradually substituted by a growing number of OH^- molecules. At this moment, the B(III) species present in the aqueous phase would be HBO_3^{2-} and/or BO_3^{3-}. Generally speaking, whether HBO_3^{2-} or BO_3^{3-} is highly charged and prefers to be kept in precipitates. This, to some extent, would promote boron removal from wastewaters. Therefore, it is concluded by this experimental study that boron (i.e., boric acid here) can easily be removed from boron-containing wastewaters due to the formation of boro-ettringite as the pH is raised higher than 10. If the acidity of aqueous suspensions is further decreased by the addition of NaOH (as an OH^- source), the removal of boron will be greatly enhanced. It is noteworthy that the amounts of chemicals, including $Al_2(SO_4)_3{\cdot}16H_2O$, $Ca(OH)_2$ and NaOH, in this study required for the efficient and cost-effective treatment of boron-containing wastewaters should be further optimized in a quantitative way.

3.2. Ca, Al, S (SO_4^{2-}), and O in precipitates

To understand the suggested mechanism of B removal through the formation of boro-ettringite, an electron probe micro analyzer (EPMA) was employed to non-destructively determine the chemical compositions of solid samples. A wavelength-dispersive X-ray spectrometer (WDS) was used to isolate the X-rays of interest for quantitative analysis. Fig. 3 shows an example of spectroscopy actually measured, and the X-ray dispersive signals as to Ca, Al, S, and O can be clearly observed.

Table 3 gives the mass percent compositions (%) of all elements (except for B due to its low level), which were obtained by normalizing and then averaging the results measured at 5 spots on the surfaces of dried samples. It can be seen that the results of Al and S are consistent with that observed with respect to aqueous phases, whereas those of Ca and O seem slightly different. Specifically, the contents of both Al and S elements tended to decrease as the pH was raised higher than 11 and reached quite a low level at pH 12.95. These results indicated certain amounts of Al and S-containing ions were driven into the aqueous phase by more and more OH^- anions. As shown in Fig. 2, the only species of Al is the $Al(OH)_4^-$ and that of S is SO_4^{2-}. On the other side, it is noteworthy that the content of the O element increased with increasing pH. It is believed there is an exchange between OH^- (present in the aqueous phase) and SO_4^{2-} anions (in a precipitate). Adding OH introduces more than enough O atoms to offset the reduced O atoms due to the loss of SO_4^{2-}, resulting in a net increase in the amount of O atoms in precipitates at high solution pH. Moreover, no significant change of total Ca was determined.

3.3. XRD and SEM analyses

To further confirm the mechanism previously proposed, precipitate samples were also analyzed with XRD and SEM techniques.

Fig. 4 illustrates the XRD pattern of the sample No. 1 formed at pH 10.12 (No. 1 shown in Table 3) as an example, confirming the presence of $Ca_6Al_2B_4O_6(OH)_{18}{\cdot}30H_2O$ and $Ca_6Al_2(B(OH)_4)_{3.8}(OH)_{14.2}{\cdot}20H_2O$, with both having quite similar chemical compositions with the early reported boro-ettringite, that is, $Ca_6Al_2(B(OH)_4)_{2\text{–}4}(OH,O)_{12}{\cdot}26H_2O$. Therefore, it can be concluded that the precipitation samples obtained in this experimental study are actually mixtures, which may contain the unsubstituted ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$), conventional boro-ettringite and its analogues, some other substances such as $CaSO_4$ and even a small amount of incompletely dissolved $Ca(OH)_2$.

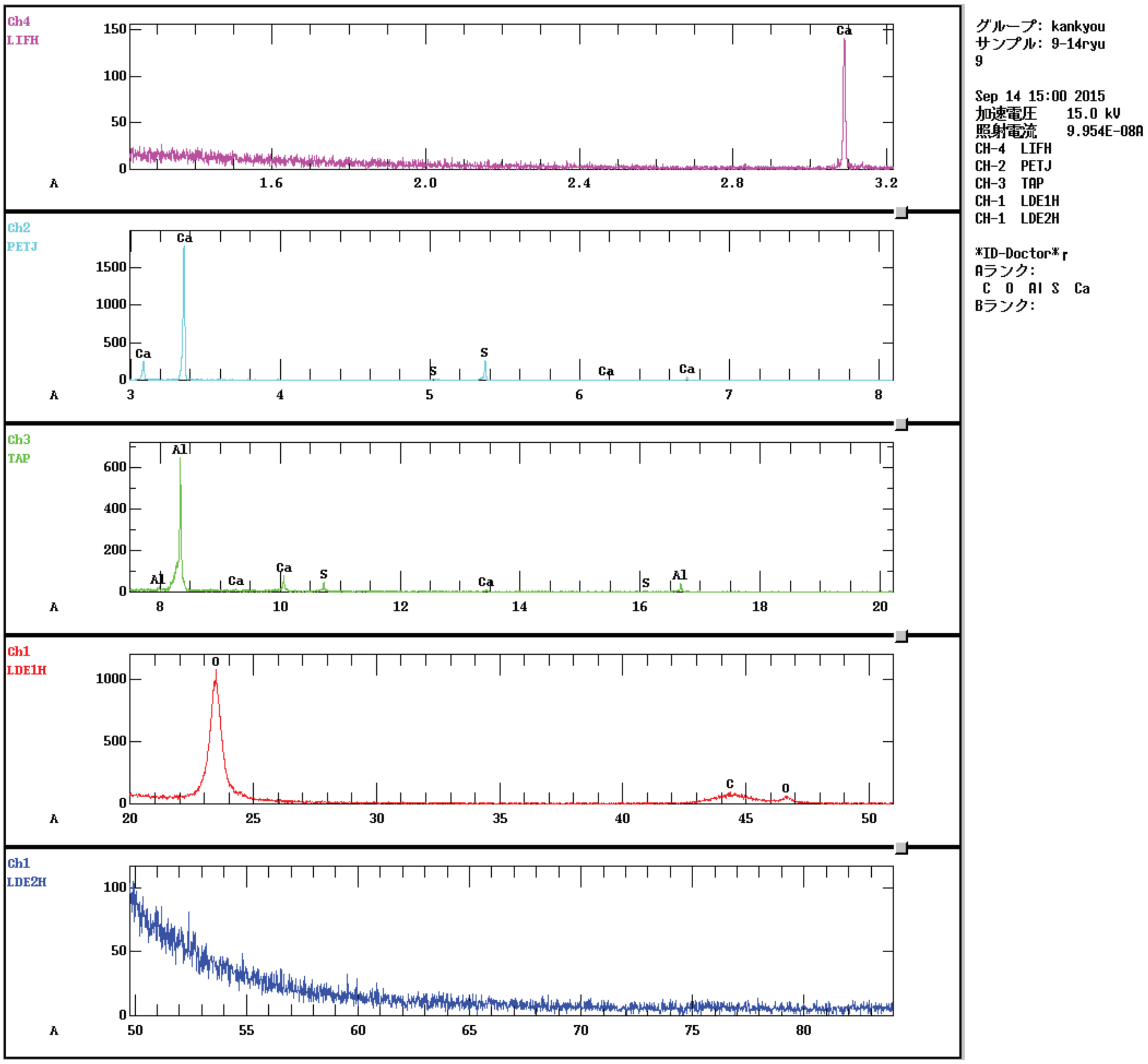

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Fig. 3. An example of quantitative elemental analysis (in which the sample obtained at pH 11 is used and shown as No. 4 in Table 3) using WDS in EPMA.
Note: Here, the horizontal axis represents wavelength (Å) and the vertical one does the X-ray intensity (count).

Table 3
Mass percent compositions (%) of precipitates determined using WDS in EPMA

No.	1	2	3	4	5	6	7
pH	10.12	10.43	10.72	11.00	11.62	12.22	12.95
Ca	33.081	33.336	32.671	31.999	31.487	30.195	32.143
	(33.511–32.757)	(34.318–32.587)	(33.357–31.181)	(35.752–30.029)	(33.322–29.429)	(31.083–29.761)	(33.574–30.396)
Al	7.547	7.756	8.005	7.269	7.195	6.596	6.325
	(7.925–7.107)	(8.306–7.021)	(8.349–7.731)	(8.015–6.362)	(7.888–6.593)	(6.898–6.118)	(7.221–4.691)
S	11.601	11.827	11.893	10.311	11.287	9.860	8.844
	(12.019–11.267)	(12.236–11.577)	(12.264–11.553)	(11.082–9.508)	(12.115–10.531)	(10.103–9.287)	(9.908–6.862)
O	47.771	47.081	47.431	50.421	50.031	53.348	52.688
	(48.449–47.249)	(48.499–45.737)	(49.535–46.313)	(52.911–45.420)	(53.446–46.675)	(54.195–52.016)	(58.051–49.419)

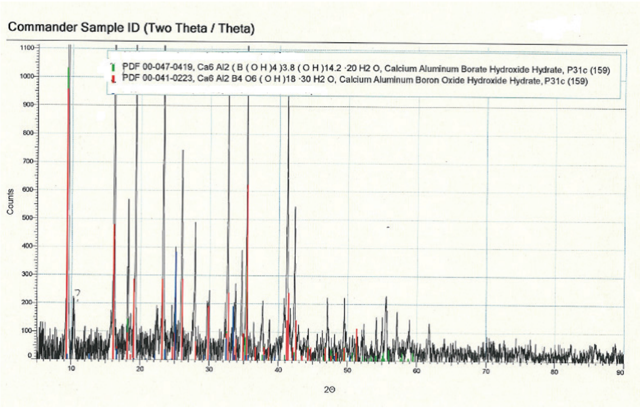

Fig. 4. XRD pattern of sample No. 1 obtained at pH 10.12 (shown in Table 3).

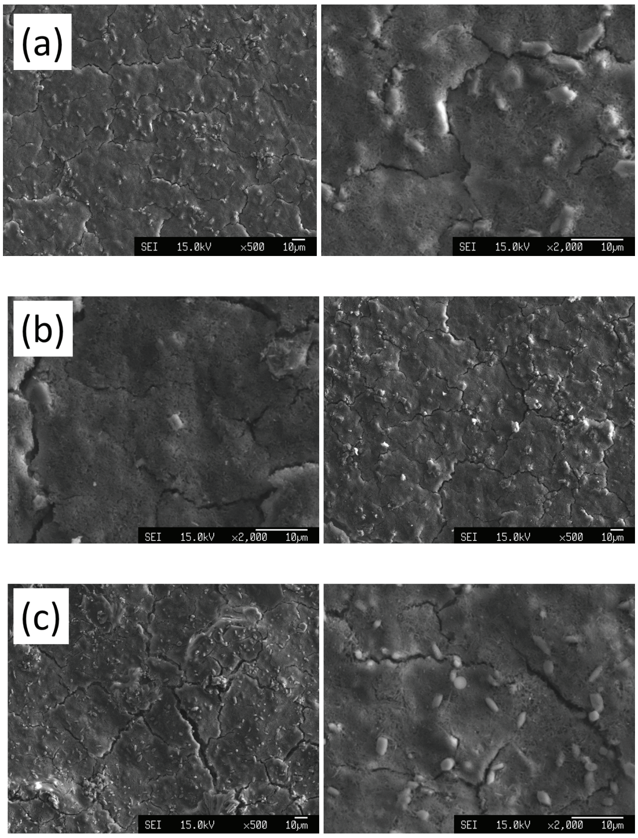

Fig. 5. SEM images of precipitation samples obtained at (a) pH 10.12 (corresponding to the sample No. 1 in Table 3), (b) 11.00 (No. 4), and (c) 12.95 (No. 7), respectively.

SEM images of the precipitation samples obtained at pH 10.12 [(a) No. 1 shown in Table 3], 11.00 [(b) No. 4] and 12.95 [(c) No. 7], respectively, are also shown in Fig. 5. Although the images on the left side with a resolution (×500) show the formation of highly homogeneous mixtures, the images on the right side with a slightly higher resolution (×2,000) do show the presence of a very small amount of tiny crystals, which can be attributed to the incomplete dissolution of excess $Ca(OH)_2$.

4. Conclusion

B is a vital trace mineral required for the normal growth and health of the human body. Various boron compounds are being widely used in industrial processes, thus posing potential health risks to humans and animals due to unpredictable emissions to the environment. Nowadays, the boron (including its compounds) emission standard set out in the revised Japan Water Pollution Act requires a more thorough removal of boron in all effluents (e.g., landfill leachates and hydrothermal waters) than previously. In this study, we clarified the boron removal mechanism by batch tests followed with measurement and analyses on B, Ca, Al and SO_4^{2-} in aqueous and Ca, Al, S, and O in solid phases. Results indicate that increasing the solution pH from 10 to 13 enhances the removal of B (boric acid) and also changes the distributions of Ca, Al, and SO_4^{2-} (S and O) in both phases. The mechanism is suggested that in aqueous solutions at high pH, OH– anions can drive certain amounts of SO_4^{2-} and $Al(OH)_4^-$ out of the boro-ettringite. The XRD and EMPA analyses confirmed the presence of two similar materials of boro-ettringite in precipitates, which were obtained at different pHs and found to be mixtures of different morphologies of the same materials.

Acknowledgements

We would like to express our sincerest gratitude to (1) Yoshioka Lab, Tohoku University, Japan; (2) Technical Division, School of Engineering, Tohoku University, Japan; Kawada laboratory, Graduate School of Environmental Studies, Tohoku University, Japan; and (3) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan, for their kind supports during the implementation of the experiment and analyses of samples.

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