

Chemical Speciation of Boron in the Calcium Carbonate Precipitates

Kazuki Kobayashi, and Yohey Hashimoto

Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koganei-shi, Tokyo 184-8588 Japan

Wastewater containing the natural product of boron contaminates rivers and groundwater. Under the Water Pollution Control Law, since boron is specified as a toxic substance, it is necessary for the company to treat wastewater exceeding the standard value. In order to improve boron removal processing technology, various feasibility experiments were carried out, and the various adsorbents and flocculants for boron removal were developed [1]. There is a need for innovative removal technologies that can be realized on a commercial basis.

Hot-Springs drainage is raised as a representative one which exceeds an environmental-standards value. In addition to boron, Hot-Springs drainage composes of the sediments from calcium carbonates contains, and it has been reported that boron is taken into the sediments [2]. However, the mechanism of how boron co-precipitates with calcium carbonate remains unknown. The purpose of this study is to verify the effect of boron species on the coprecipitation mechanism of boron in calcium carbonate, the amount of boron coprecipitation, and the morphology of calcium carbonate. Different experimental conditions were set up in the presence of different boron species (boric acid, borate ion, polyboric acid) by varying the boron concentration with a pH meter. The ratio of boron species coprecipitated with calcium carbonate as well as the concentration sites was determined by NEXAFS spectroscopy.

We conducted the spontaneous precipitation experiment of the boron to calcium carbonate, keeping the pH adjusted to 8, 10, or 12. Boric concentrations were 0, 1, 5, 10, 20, 35, 50, 75 or 100 mM. We carried out the NEXAFS measurements of the obtained precipitates at boron K-edge by the total electron yield mode at BL-11, Ritsumeikan University SR center.

The spectrum of boron K-edge NEXAFS contains three characteristic peaks [3, 4]. The peak observed at 194 eV (peak A) is derived from trigonal boron (IIIB), which is originated from the 1 s electron transition to the vacant 2 p_z orbital of the BO₃ group. The peak observed at 197-200 eV (peak B) belongs to tetrahedral boron (IVB), which is originated from the 1 s electron transition to the vacant σ^* orbital of the BO₄ group. The broad peak observed at around 200 eV reflects the effects of both IIIB and IVB. H₃BO₃, Borax, and Datolite are standard samples containing 100%, 50% and 0% of IIIB, respectively. However, the signal of IIIB was detected in Datolite which is a mineral which consists of only IVB(s). Since Datolite is a natural mineral, the different coordination number

of boron is contaminated. For the boron K-edge NEXAFS spectrum of the precipitate, both peaks A and B are observed regardless of the boron concentration and pH. This indicates that calcium carbonate incorporates IIIB and IVB regardless of the boron species contained in the solution.

References

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