

## A Study on the Removal and Fixation of Radionuclides by Coprecipitation with Barite

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Effective sequestering methods are essential for the treatment of the various ions included in radioactive waste water at the Fukushima Daiichi Nuclear Power Plant and general radioactive wastes, in particular for highly soluble elements such as strontium ( $\text{Sr}^{2+}$ ) and selenium ( $\text{SeO}_4^{2-}$  and  $\text{SeO}_3^{2-}$ ). Here, to develop a technique for effective removal of various elements from aqueous solutions, we focus on coprecipitation of various elements into barite ( $\text{BaSO}_4$ ) due to its unique characteristics such as (i) extremely low solubility, (ii) incorporation of numerous elements because of the large ionic radii of the substituted ions, (iii) high density compared to other minerals, which is an advantage for rapid sedimentation, and (iv) high crystal stability under wide ranges of pH, redox potential, temperature and pressure conditions.

In this study, the uptake of various ions by the barite coprecipitation method was examined to elucidate the mechanism, using the distribution coefficient's dependence on ionic radius, and employing extended X-ray absorption fine structure (EXAFS) spectroscopy, and quantum chemical calculation. This revealed immobilization of various trace elements within the lattice of the barite. The ionic radius dependence (Fig. 1) revealed that the distribution coefficient (Kd) was maximized for ions with similar ionic radius to that of the  $\text{Ba}^{2+}$  ion. As a result, the Kd value of  $\text{Sr}^{2+}$  was found to be relatively large, which is not the case for its coprecipitation by calcite (Fig. 1). The EXAFS results (Fig. 2) clearly showed that the local structure of  $\text{Sr}^{2+}$  in barite is very similar to that of  $\text{Ba}^{2+}$  in barite, which reinforces the substitution of  $\text{Sr}^{2+}$  at the  $\text{Ba}^{2+}$  site in barite with the large Kd value. However, the 1<sup>st</sup> neighboring Sr-O distance is smaller than that of Ba-O by 0.16 Å, which is similar to the difference in ionic radii between  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . Such a difference in size causes distortion of the local structure around the incorporated ion, which is responsible for the dependence of Kd on ionic radius. Similar results were also suggested by a stability analysis of ions incorporated in barite based on quantum chemical analysis (Fig. 2). These results provide a basis for developing effective application of removal and fixation of various ions by coprecipitation with barite.

The coprecipitation method with barite was optimized by examining various factors controlling effective removal mainly for Sr and Se, such as pH,

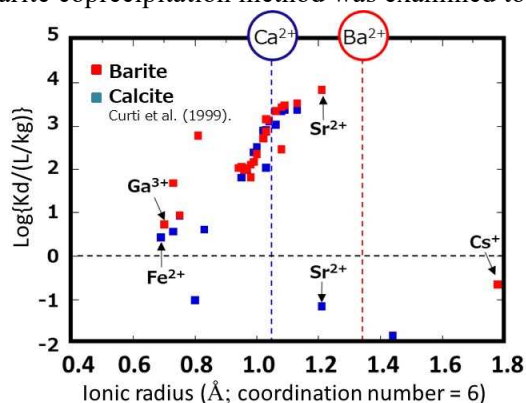


Fig. 1. Ionic radius dependence of distribution coefficient (Kd) of coprecipitation of various ions into barite and calcite.

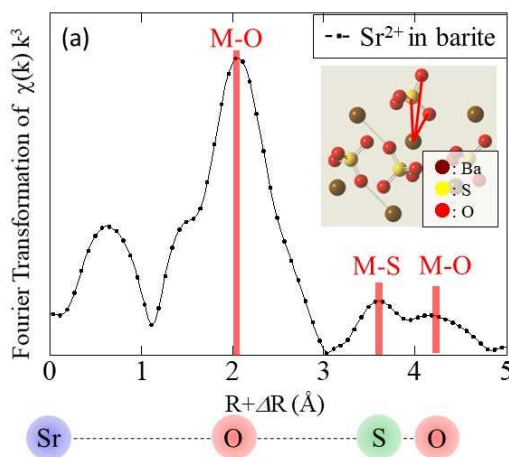


Fig. 2. Sr K-edge EXAFS spectrum in k space of Sr incorporated into barite.

saturation state, ionic strength, competitive ions such as  $\text{Ca}^{2+}$ , and the  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio in the initial aqueous solution (Fig. 3). Their uptakes by barite were found to be dependent on pH, saturation state, and  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio in the initial aqueous solution among the above, showing that most of the aqueous Sr and Se can be removed from the aqueous solution by adjusting these parameters. On the other hand, the effects of ionic strength and competitive ions were negligible, suggesting the effectiveness of its application in their removal of from seawater. As for the addition of  $\text{Ca}^{2+}$ , it was

suggested that the presence of  $\text{Ca}^{2+}$  within barite causes distortion of the barite lattice, which improves (i) incorporation of selenite ion into the structure and (ii) the ion-exchange reaction of  $\text{Sr}^{2+}$  with the  $\text{Ca}^{2+}$  initially contained in the barite. Finally, the uptake of cations and anions was found to increase and decrease, respectively, with an increase in the  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio. As a result, high removal efficiency from seawater (more than 90%) was achieved for Sr and Se, showing that barite is a reliable material for removal of various ions.

We also developed more practical methods for barite coprecipitation. In particular, we paid lots of attention to the concentration of  $\text{Ba}^{2+}$  ions remaining in the solution after the coprecipitation treatment because of the toxicity of barium compounds aside from  $\text{BaSO}_4$ . Thus, a two-step coprecipitation method was developed here consisting of (i) removal of anions under high  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio conditions and (ii) subsequent removal of cations under low  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio conditions by the addition of sodium sulfate in the first and second steps, respectively. This method solved the toxicity problem of  $\text{Ba}^{2+}$  and achieved simultaneous removal of various ions as a practical method that can be applied to treatment of various waste waters, even on a commercial basis.

Considering final disposal of radionuclides such as into the geosphere, which is being promoted by various countries, stability of barite over a longer time scale should be confirmed. From this point of view, its disposal after solidification with other media would be effective. As for barite, solidification by aluminosilicate (geopolymer) would be appropriate, since barite can be dissolved by the presence of high concentrations of carbonate ion in adjacent water, which can result when a Ca-based cement is used. Our preliminary results showed that a solidified material consisting of barite and geopolymer exhibits low porosity and high pressure-resistance. Thus, it is possible that barite, which stably incorporates various radionuclides, can be directly subjected to solidification with geopolymer, followed by geological disposal.

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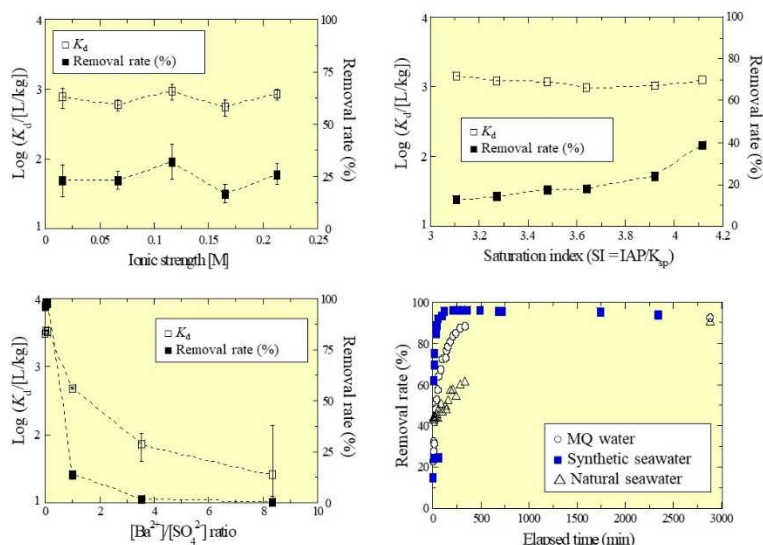


Fig. 3. Distribution coefficient ( $K_d$ ) and removal rate for  $\text{Sr}^{2+}$  in barite coprecipitation system at various ionic strength (a), saturation index (b), and  $[\text{Ba}^{2+}]/[\text{SO}_4^{2-}]$  ratio (c). Removal ratios (%) of  $\text{Sr}^{2+}$  in MQ water, synthetic seawater (SW), and natural SW systems were also shown in (d).