## **1–4** How to Effectively Remove lodate from Solutions?

- Coprecipitation of lodate with Barite (BaSO<sub>4</sub>) Was Evaluated at a Molecular Level -





**Fig.1-7 Design of IO**<sub>3</sub><sup>-</sup> **coprecipitation with barite** We add BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> into a solution containing iodate by adjusting the  $[Ba^{2+}]/[SO_4^{2-}]$  molar ratio. Barite is rapidly precipitated, and iodate is effectively removed from solution even in the presence of competitive anions in solution.

Radioactive iodine (<sup>129</sup>I) is of great concern owing to its high environmental mobility and long-term radiotoxicity (<sup>129</sup>I: halflife =  $1.6 \times 10^7$  years). In the environment, iodine exists in two oxidation states (-1, +5), and it is mostly dissolved in natural water and radioactive liquid wastes as iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>). To date, the formation of AgI is the only method available for I<sup>-</sup> removal, and there is no effective method for removing IO<sub>3</sub><sup>-</sup> from contaminated natural water and waste liquid. In the present study, we developed a new technique for removing radioactive IO<sub>3</sub><sup>-</sup> from aqueous solutions by using barite (BaSO<sub>4</sub>). Although a variety of toxic and/or radioactive elements in the cationic form and selenium (Se) oxyanions can be removed from aqueous solutions by coprecipitation with barite, the removal of IO<sub>3</sub><sup>-</sup> had not been investigated yet.

Barite is rapidly precipitated by mixing BaCl<sub>2</sub> aqueous solution in Na<sub>2</sub>SO<sub>4</sub> aqueous solution (= coprecipitation). A diagram of IO<sub>3</sub><sup>-</sup> coprecipitation with barite is shown in Fig.1-7. This study investigated the coprecipitation of IO<sub>3</sub><sup>-</sup> with barite and found that IO<sub>3</sub><sup>-</sup> can be effectively removed by this method. The main parameter affecting iodate removal is the [Ba<sup>2+</sup>]/[SO<sub>4</sub><sup>2-</sup>] molar ratio in the initial aqueous solution. Results showed that iodate was effectively removed from the aqueous solution by coprecipitation when the [Ba<sup>2+</sup>]/[SO<sub>4</sub><sup>2-</sup>] ratio was high. Extended X-ray absorption fine structure analysis also indicated that the incorporated IO<sub>3</sub><sup>-</sup> was strongly bound to the crystal lattice of barite by the substitution of the SO<sub>4</sub><sup>2-</sup> site in the structure when the IO<sub>3</sub><sup>-</sup> concentration was low. It is believed that the charge compensation problem due to the substitution of IO<sub>3</sub><sup>-</sup> for SO<sub>4</sub><sup>2-</sup> was achieved by the substitution of Na<sup>+</sup> for the nearest Ba<sup>2+</sup>

Fig.1-8 Comparison of iodate removal between barite and Mg–AI layered double hydroxide (LDH)

The  $K_d$  values of iodate for barite and Mg-AI LDH in the presence of Cl<sup>-</sup> ions are estimated. The  $K_d$  of Mg-AI LDH decreased with increasing competitive Cl<sup>-</sup> concentration, while that of barite was nearly independent of the Cl<sup>-</sup> concentrations.

because Na<sup>+</sup>, which was not detected in the barite prepared without  $IO_3^-$ , was detected in the  $IO_3^-$ -bearing barite  $(2IO_3^- + 2Na^+ \Leftrightarrow Ba^{2+} + SO_4^{2-})$ .

Subsequently, we investigated the influence of competitive anions on IO<sub>3</sub><sup>-</sup> removal efficiencies by comparing with adsorption on hydrotalcite-like Mg-Al layered double hydroxide (LDH). Mg-Al LDH is a well-known inorganic layered mineral with a high anion exchange capacity, and the anion is intercalated into interlayer spaces. Many papers have reported on the removal of anionic contaminants by LDH. Fig.1-8 shows the distribution coefficient ( $K_d$ ) of IO<sub>3</sub><sup>-</sup> for barite prepared under the optimum condition and that for the Mg-Al LDH with and without the addition of NaCl in the initial aqueous solution. Kd is the ratio of concentrations of a solute (in this case, IO3-) between a liquid phase and a solid phase (barite or Mg-Al LDH). The higher the  $K_{d}$ , the higher is the selectivity of the solute to the solid phase. The  $K_d$  of Mg-Al LDH decreased with increasing competitive Cl<sup>-</sup> concentration, while that of for barite was nearly independent of the Cl<sup>-</sup> concentrations. At an initial Cl<sup>-</sup> concentration of 10 mmol  $L^{-1}$ , the  $K_d$  of barite was two orders of magnitude greater than that of Mg-Al LDH. Hence, the coprecipitation method using barite performs better than the conventional adsorption method using LDH for IO<sub>3</sub><sup>-</sup> removal when competitive anions are present. IO3- was also effectively removed from aqueous solutions in the presence of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, which are also environmentally common anions. Coprecipitation with barite will be a promising tool for removing radioactive IO3<sup>-</sup> from various aqueous solutions contaminated with IO3-.

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Reference

Tokunaga, K. et al., Effective Removal of Iodate by Coprecipitation with Barite: Behavior and Mechanism, Chemosphere, vol.266, 2021, 129104, 10p.