

Strontium-90 immobilization via coprecipitation with respect to calcite in various disposal site conditions

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1. Introduction

In the intermediate to low level radioactive waste disposal facilities, the main component of concrete is calcium hydroxide ($\text{Ca}(\text{OH})_2$). Even though the pore water pH of fresh concrete is mainly 12 or more, as the time increased, the $\text{Ca}(\text{OH})_2$ in cement and concrete can react with carbon dioxide (CO_2) in the air, resulting in calcite (CaCO_3) precipitation, known as carbonation process and lowering the pH [1]. As $\text{Ca}(\text{OH})_2$ reacts with CO_2 and degrades, up to 80% of Ca released from cement reprecipitates into a large amount of calcite [2]. When the calcite is formed, strontium-90 (^{90}Sr) can either substitute to Ca ion or be incorporated within the calcite lattice structure because of its similar radius and charge to Ca. Radioactive Sr is a fission product of uranium and plutonium, and a beta-emitter (half-life: 28.8 year). Due to its high solubility and biological toxicity, it requires special attention [3]. Previous studies used adsorption methods to remove Sr from waste solution. [4]. However, simple surface adsorption has a disadvantage in that the adsorbed Sr can easily be desorbed by other competing ions in various environmental conditions, which is not the case of coprecipitation process. Coprecipitation has the advantage of retaining Sr in the stable mineral structure, especially calcite over the long term. Thus, in this study we tested and showed that Sr coprecipitation in calcite was more effective in Sr immobilization than adsorption under the same conditions.

2. Materials and Methods

2.1 Materials

All solutions for experiment were prepared with ultra-pure water (deionized water, DIW) using a Direct-Q 8 UV system (Millipore SAS, conductivity 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 °C). Strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) to a concentration of 0.0114 mM Sr (1 ppm) was used to be coprecipitated with calcium carbonate. Calcium chloride (CaCl_2 , 99.0 %, Sigma-Aldrich) and sodium carbonate (Na_2CO_3 , 99.5 %, Sigma-Aldrich) were used to prepare calcite precipitates. Sodium hydroxide (NaOH , 98.0 %, SAMCHUN) was used to adjust solution pH. Pure calcium carbonate (CaCO_3 , 99.0 %, Sigma-Aldrich) was also used to perform an adsorption experiment. Sodium hydroxide (NaCl , 99.0 %, Sigma-Aldrich) was used to perform ionic strength (IS) experiment.

2.2 Comparison test of adsorption and coprecipitation preparation

In case of Sr adsorption, chemical CaCO_3 (0.5 g) was reacted with 0.5 mL of 1.14 mM $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ solution in 49.5 mL of alkali solution using 0.1 M NaOH to adjust pH 10.5. In case of Sr coprecipitation, 44.5 mL of 50 mM CaCl_2 solution was mixed with 0.5 mL of 1.14 mM $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ solution first, and then reacted with 5 mL of 500 mM Na_2CO_3 solution to precipitate calcite. After 7 days reaction, supernatants in Sr adsorption and coprecipitation tests were separated by filtration using a 0.20 μm membrane filter (Millipore). Concentrations of Sr were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). In order to accurately determine the Sr concentration on solids, 20 mg of Sr adsorbed and coprecipitated samples were dried and dissolved using 2 M nitric acid at a solid to solution ratio of 0.1 g/50 mL before analysis.

2.3 Ionic strength test preparation

The effect of IS on adsorption and coprecipitation was investigated within the IS range of 0.01-1 M (fixed at pH = 10.5, $[\text{Ca}^{2+}] / [\text{CO}_3^{2-}] = 1.0$, Temperature = Room Temperature) for 7 days. The IS was adjusted using 1 M NaCl solution.

2.4 Desorption test preparation

In order to compare the effectiveness of adsorption and coprecipitation in retaining Sr, desorption experiment was conducted by setting the same molar mass of Sr on the Sr-containing solids using 10 mM NaHCO_3 solution. The sample collection period was 3, 9, 18, 24, 72, 168, 240, and 336hrs.

2.5 Dissolution test preparation

For the dissolution experiment with Sr coprecipitated respect to calcite and pure strontianite (SrCO_3), the 250 mL of 0.1 M of CaCl_2 solution was mixed with 250 mL of 1.14 mM $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ solution. Then, independently prepared 500 mL of 0.1 M Na_2CO_3 solution was mixed with the mixed solution of CaCl_2 and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. The precipitates could be made and they were aged for 3 days at room temperature. Then, the supernatant was separated by the centrifugation and the solid at the bottom was dried in an oven at temperature 80 °C for 24

hr. After that, the Sr-coprecipitated calcite sample was washed using the DIW several times and dried again before use. In order to investigate the release of Sr from solid samples, additional dissolution experiment was conducted using Sr coprecipitated sample and pure strontianite with the same molar mass of Sr. The experiment was conducted at pH 7, 10, and 12. The solution pH was adjusted using 0.1M NaOH in DIW. Buffer solution was used for pH 7 condition to prevent pH change. The sample collection period was 3, 9, 18hrs, and 1, 3, 5, 7, 10, 14, 20, 30, 60, and 90 days. Concentrations of Sr were analyzed using ICP-MS. Characterization of solid samples were conducted by scanning electron microscope and energy dispersive spectrometer (SEM-EDS).

3. Results and Discussion

3.1 Comparison of Sr removal between adsorption and coprecipitation

As a result, in the case of Sr coprecipitation with respect to calcite, it shows a high amount of Sr uptake than simple adsorption on the calcite surface. The results demonstrate that coprecipitation process is capable of removing about 2.6 times more Sr per 1 mg of the solid sample compared to adsorption.

3.2 Effect of IS on Sr removal

Sr is known to form an outer sphere surface complex with holding water molecules. Therefore, when the IS increases, Sr adsorption with forming outer-sphere surface complexes decreases [5]. In the case of adsorption, Figure 1(a) proves that Sr adsorption onto the solid surface diminishes as the IS increase. However, in the case of coprecipitation, even if the IS increases, the amount of Sr removal is not significantly affected because the coprecipitation of the radionuclide is mainly governed by solubility of the primary calcite and the concentration of Sr in solution, as shown in Figure 1(b). When Sr is incorporated into calcite structure, it eliminates water molecules to coprecipitates with respect to calcite [2].

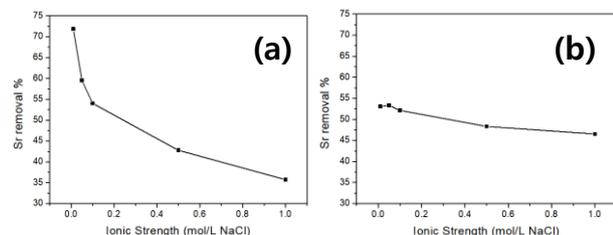


Fig. 1. Removal of Sr as a function of ionic strength changes in (a) adsorption and (b) coprecipitation processes.

3.3 Desorption experiment of adsorption and coprecipitation

The results are presented in Figure 2(a), showing the desorbed Sr masses from both Sr adsorbed and coprecipitated solid samples. The study found that when Sr was adsorbed onto the calcite surfaces, it was easily desorbed and reached equilibrium relatively quickly. However, coprecipitated Sr was considered to be trapped in the main calcite mineral structure and only released Sr amounts depended upon calcite dissolution, resulting in a relatively low initially desorbed Sr concentration. As the time passed, the Sr concentration gradually increased, depending on the calcite solubility over the long term. Additionally, as a result of the released Sr total mass from the adsorbed and coprecipitated solid samples, the adsorbed Sr was released more 1.7 times than the coprecipitated Sr.

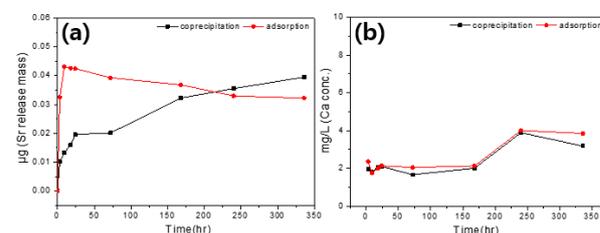
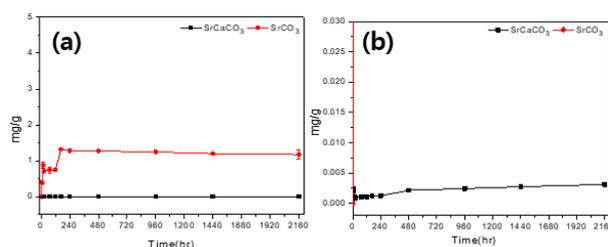


Fig. 2. The mass of Sr desorbed from adsorbed on calcite and coprecipitated calcite (a) and Ca concentration dissolved from adsorbed and coprecipitated solid samples (b).

The concentration of Ca release from both Sr adsorbed and coprecipitated solid samples are shown in Figure 2(b). These findings also confirmed that the initial lower Sr concentration release from coprecipitated solid, as compared to adsorption on calcite, is due to the different Sr removal mechanisms between adsorption and coprecipitation. Sr was trapped within the lattice structure of calcite during coprecipitation, as opposed to being attached to its surface in adsorption. This slower release rate of Sr from incorporated solids leads to a more Sr retention compared to the faster initial Sr release from the adsorbed samples.

3.4 Dissolution experiment of Sr coprecipitated in calcite ($SrCaCO_3$) and pure Strontianite ($SrCO_3$)

Figure 3(a), (c), and (e) show that pure strontianite has more Sr release than $SrCaCO_3$. This result proves the less Sr release and more Sr immobilization by coprecipitation. Figure 3(b), (d), and (f) show the enlarged $SrCaCO_3$ results.



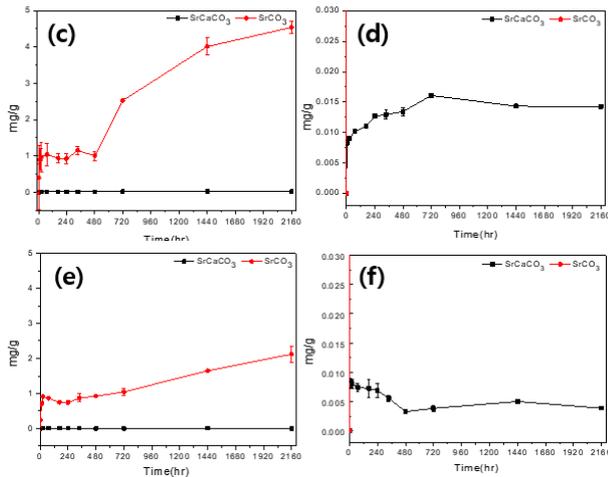


Fig. 3. Sr concentrations released from SrCaCO₃ and SrCO₃ at pH 7 (a), pH 10 (c), pH 12 (e), and enlarged data for Sr concentrations released from SrCaCO₃ at pH 7 (b), pH 10 (d), and pH 12 (f)

3.5 Characterization

In order to verify the effectiveness of coprecipitation in incorporating Sr into the calcite structure, a characteristic analysis was conducted using SEM-EDS. Accelerated charges were applied at 5, 10, and 15 kV to measure the images and chemical properties at deeper location of the samples as the accelerated charges increased. Figure 4 depicts the Sr elemental mapping image of Sr, and as the accelerated charge increases from image (a) to (c), the red colors representative of Sr gradually become more visible and brighten, suggesting that Sr is effectively incorporated inside calcite structure during coprecipitation.

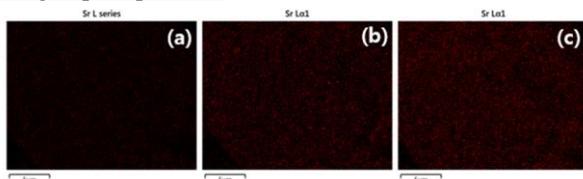


Fig. 4. Sr elemental mapping images of (a) 5kV, (b) 10kV, and (c) 15kV in the same solid sample.

SEM was used for characteristic analysis, and Figure 5(a) shows the Sr-coprecipitated calcite sample (SrCaCO₃) before dissolution at pH 10, while Figure 5(b) shows the SrCaCO₃ sample after 90 days of dissolution. In comparison to Figure 5(a), Figure 5(b) shows etched surfaces and new needle-shaped forms, suggesting that the Sr ions coprecipitated inside the calcite may have formed a new mineral. Figure 5(c) depicts strontianite before dissolution, while Figure 5(d) shows strontianite after dissolution. Since there is no process involving the coprecipitation of Sr in pure strontianite, the mineral dissolves directly, leading to high levels of Sr release, as shown in Figure 3(a), (c), and (e).

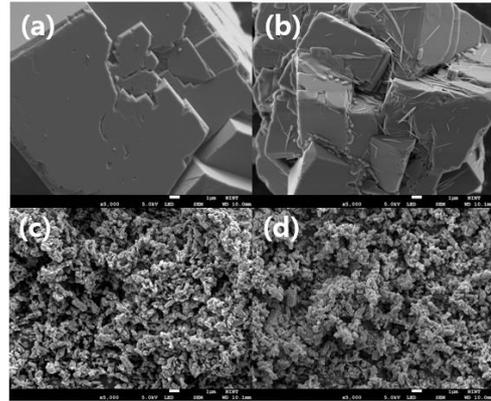


Fig. 5. SEM images (a) SrCaCO₃ before dissolution (b) SrCaCO₃ after dissolution (c) SrCO₃ before dissolution (d) SrCO₃ after dissolution.

4. Conclusions

Unlike simple adsorption on the mineral surface, coprecipitation is incorporated in the mineral lattice structure, so more radioactive waste can be removed and immobilized even at the same condition. Coprecipitated Sr with respect to calcite was released less than that of adsorption, suggesting better immobilization process for a long-term perspective storage. It is expected that the removal or retarding effect of Sr is expected by incorporating Sr in a large amount of calcite formed at adjacent to the disposal sites constructed with cement and concrete materials.

5. Acknowledgments

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