Influence of amorphous calcium carbonate on strontium ion removability from aqueous solution

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The Fukushima nuclear power plant accident caused an outflow of pollutants. Thus, precautionary measures must be taken by using preventive materials for the deterrence of such accidents. Herein, we aimed to develop inexpensive materials that can remove radioactive elements from an aqueous solution. We found that powders obtained from milling scallop shells, which were discarded in large quantities, removed Sr²⁺ from aqueous solutions. The Sr²⁺ removability of the scallop shell powder improved with milling time, indicating the influence of increase in the specific surface area on Sr²⁺ removability. Despite of the same specific surface area, the scallop shell powder exhibited higher Sr²⁺ removability than that of the unmilled CaCO₃. Differential scanning calorimetry evaluation for the investigation of factors other than the specific surface area revealed that the milled scallop shell powder contained amorphous calcium carbonate. Moreover, we synthesized amorphous calcium carbonate and found that it exhibited 60-times higher Sr²⁺ removability than that of crystalline calcium carbonate. We concluded that the amorphous structure of calcium carbonate significantly affects the Sr²⁺ removability from aqueous solutions. It was hypothesized that amorphous calcium carbonate removes Sr²⁺ by incorporating Sr²⁺ into the structure during crystallization in an aqueous solution.

Key-words : Adsorbent, Pollution water, Calcium carbonate, Scallop shell, Amorphous structure

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1. Introduction

Japan is located where the North American, Eurasian, Pacific, and Philippine Sea plates collide, resulting in frequent earthquakes. In recent years, very large earthquakes of magnitude 6 or more occurred, such as the Hokkaido Iburi Eastern earthquake, the Northern Osaka earthquake, and the Kumamoto earthquake, which have led to many missing people and deaths. Among them, the 2011 Tohoku Pacific Ocean earthquake was a disaster that gained international attention. The Fukushima Daiichi nuclear power plant accident occurred due to the tsunami caused by this earthquake, due to which contaminated water containing radioactive elements such as ⁹⁰Sr and ¹³⁷Cs got released from the facility. As of November 2018, there are 9 reactors that are in operation, 28 that are not in operation, and 23 that are scheduled to be decommissioned. In order to prevent the outflow of pollutants similar to that occurred after the Fukushima nuclear accident, a protective wall which can adsorb radioactive elements can be created to enclose reactors during operation and decommissioning. For this purpose, many preventive materials are required, and the materials must be able to remove radioactive elements efficiently at low cost.

The removal of metal ions using antimony oxide and tantalum doped tungsten oxide has been reported, however, these adsorbents use rare metals which are expensive, so are difficult to be used for preventive materials. Therefore, we focused on calcium carbonate to develop materials that can remove radioactive elements at low cost. It has been reported that calcium carbonate can adsorb harmful substances such as aldehydes and VOCs. In
addition, calcium carbonate is harmless to the human body and abundant on the earth, making it an attractive protective material for the 60 nuclear reactors in Japan.

It has been demonstrated that scallop shell powder from industrial waste, whose main component is calcium carbonate, can remove Sr\(^{2+}\) from aqueous solutions. However, the Sr\(^{2+}\) removal mechanism has not been clarified, so it has not been put into practical applications. The purpose of this study was to obtain detailed basic knowledge about the Sr\(^{2+}\) removal mechanism of scallop shell powder.

2. Experimental procedure

2.1 Materials

We used scallop shell and CaCO\(_3\)-A, B, C (Ube Materials CS·3N-D, 3N-C, 3N-A) to evaluate Sr\(^{2+}\) removability. The milling process was conducted with a stamp mill (Nitto ANS-143). The amount charged to the mill was 60 g, and the atmosphere for milling was dry at room temperature.

A CaCl\(_2\)-NaCO\(_3\)-NaOH aqueous solution reaction was used to synthesize amorphous CaCO\(_3\) [Synthesized Amorphous Calcium Carbonate (S-ACC)]. To adjust the pH during synthesis, 0.10 mol dm\(^{-3}\) NaOH solution was added to 0.10 mol dm\(^{-3}\) NaCO\(_3\) prior to the addition of 0.10 mol dm\(^{-3}\) CaCl\(_2\). The reaction was carried out at 0 °C. After the solution became cloudy, the colloidal material was filtered, washed with acetone, cooled to 0 °C, and dried for 24 h in drier.

2.2 Evaluation of Sr\(^{2+}\) removability

I took place all of evaluation of Sr\(^{2+}\) removability using 1.0 g of scallop shell or CaCO\(_3\) powder. I was added it to a SrCl\(_2\) solution and stirred (Sr\(^{2+}\) concentration: 10 mg·dm\(^{-3}\), volume: 0.050 dm\(^3\)). Approximately 3.0 mdm\(^3\) of solution was sampled using a syringe with a filter (ADVANTEC, pore size 0.20 μm). The solution was analysed with an atomic adsorption photometer (Thermo, iCE3000) to obtain the Sr\(^{2+}\) concentration of the samples.

2.3 Method for analysis of scallop shell powder

We used BELSORP-miniX (MicrotracBEL) to obtain the specific surface area for each powder. Pretreatment was performed at 120 °C for 3 h, and N\(_2\) adsorption isotherms were obtained and evaluated. Differential scanning calorimetry (DSC, Thermo plus EVO2 DSC8231) was conducted to evaluate the amorphized CaCO\(_3\) present in the milled scallop shell powder. The sample weight was 10 mg, the reference sample was Al\(_2\)O\(_3\), the set temperature was 30 to 500 °C, and the heating rate was 10 °C/min. The S-ACC was evaluated using an X-ray diffractometer (XRD, Rigaku RINT-2000, Cu K\(_x\))

3. Results and discussion

3.1 Sr\(^{2+}\) removability of scallop shell powder

To evaluate the Sr\(^{2+}\) removability of scallop shell powder (mill time 3 h) and CaCO\(_3\) (mill time 0 h), each powder was suspended in a 10 mg·dm\(^{-3}\) aqueous solution of SrCl\(_2\), and the Sr\(^{2+}\) concentration of the solution was analyzed.

The Sr\(^{2+}\) adsorption amount of the unmilled CaCO\(_3\)-A at 30 min was 0 mg·g\(^{-1}\), whereas the Sr\(^{2+}\) adsorption amount of the milled scallop shell powder was 0.40 mg·g\(^{-1}\). We hypothesized that the presence or absence of the milling treatment influenced the ability of CaCO\(_3\) to remove Sr\(^{2+}\). Therefore, as a result of milling the CaCO\(_3\)-A for 3 h and evaluating Sr\(^{2+}\) removability (Fig. 1), the amount of Sr\(^{2+}\) adsorbed by the milled CaCO\(_3\)-A was 0.41 mg·g\(^{-1}\). Compared to the result of scallop shell powder, the difference was 0.010 mg·g\(^{-1}\), indicating that it has the same ability to remove Sr\(^{2+}\). From these results, we concluded that the milling treatment had an effect on the Sr\(^{2+}\) removability of CaCO\(_3\).

3.2 Effect of milling treatment on Sr\(^{2+}\) removability of scallop shell powder

To evaluate the effect of milling treatment on the Sr\(^{2+}\) removability of scallop shell powder, we measured the Sr\(^{2+}\) removability of scallop shell powder with different milling times (Fig. 2). As the milling treatment time was extended, the Sr\(^{2+}\) removability of scallop shell powder improved; at a milling time of 5 h, Sr\(^{2+}\) removability was about 36 times higher than that of unmilled scallop shell.
To explore this factor, Table 1 shows the results of measuring the specific surface area of scallop shell powder for milling times of 1, 3 and 5 h. Since the specific surface area increased as the milling time was extended, we hypothesized that this could affect the Sr\(^{2+}\) removability of scallop shell powder. In order to evaluate the influence of the specific surface area, Fig. 3 shows the results of the Sr\(^{2+}\) removability of unmilled CaCO\(_3\)-A, B, C with different specific surface areas, and scallop shell powder milled for 3 h.

The specific surface areas are summarized in Table 1. CaCO\(_3\)-A, B, and C improve Sr\(^{2+}\) removability as the specific surface area increases, and the adsorption amount per unit area was 3.0 \(\times 10^{-2}\) mg m\(^{-2}\) (standard deviation: 0.80 \(\times 10^{-2}\) mg m\(^{-2}\)). On the other hand, the scallop shell powder milled for 3 h showed 2.7-times higher Sr\(^{2+}\) removability despite the specific surface area being equivalent to that of CaCO\(_3\)-C. From these results, we considered that the increase of specific surface area and other factors affect the Sr\(^{2+}\) removability of milled scallop shell powder.

### Table 1. Specific surface area measurement of scallop shell powder and CaCO\(_3\)

| Samples name | Specific surface area/m²·g\(^{-1}\) |
|--------------|-----------------------------------|
| Scallop 1.0 h | 2.6                               |
| Scallop 3.0 h | 6.3                               |
| Scallop 5.0 h | 8.9                               |
| CaCO\(_3\)-A  | 0.40                              |
| CaCO\(_3\)-B  | 0.87                              |
| CaCO\(_3\)-C  | 6.6                               |

Fig. 3. The Sr\(^{2+}\) removability of CaCO\(_3\) with different specific surface area and scallop shell powder. CaCO\(_3\)-A (milling time 0 h), CaCO\(_3\)-B (milling time 0 h), CaCO\(_3\)-C (milling time 0 h), Scallop shell powder (milling time 3.0 h).

3.3 Amorphization of CaCO\(_3\) by milling treatment

It is reported that CaCO\(_3\) can be partially amorphized by dry milling.\(^9\) In this study, we considered that CaCO\(_3\) amorphized by the milling treatment affects the Sr\(^{2+}\) removability of scallop shell powder. We used DSC to measure the existence of amorphous structures in scallop shell powder (mill time: 3 h) and CaCO\(_3\)-C (mill time: 0 h) (Fig. 4). Although the endothermic and exothermic peaks could not be confirmed with the unmilled CaCO\(_3\)-C, the scallop shell powder had an endothermic peak due to evaporation of water contained in the powder at around 100 °C, and an exothermic peak due to crystallization at around 300 °C. So, the milled scallop shell powder contained amorphous structures.

Based on the results of Fig. 4, the Sr\(^{2+}\) removability was measured after heating the scallop shell powder (mill time: 3 h) and CaCO\(_3\)-C (mill time: 0 h) at 400 °C, where the exothermic peak had decreased (Fig. 5). CaCO\(_3\)-C showed no change in Sr\(^{2+}\) removability with or without heat treatment, but the scallop shell powder decreased Sr\(^{2+}\) removability by 35% when heat treated. We considered that CaCO\(_3\) partially amorphized by the milling treatment was recrystallized by heat treatment at 400 °C, and the Sr\(^{2+}\) removability decreased by crystallization of the amorphous structure.

3.4 Sr\(^{2+}\) removability of amorphous CaCO\(_3\)

In order to evaluate the influence of the amorphous
structure of CaCO₃ on Sr²⁺ removability, we S-ACC. XRD and DSC were used to confirm whether the powder was S-ACC (Figs. 6 and 7).

From these data, the peak was not confirmed. Two halo patterns were shown around 30° and 45°, and the exothermic peak accompanying crystallization was confirmed at 380 °C, therefore, we confirmed the powder was S-ACC.⁹ The results from evaluating the Sr²⁺ removability using S-ACC are show in Fig. 8. Also, to compare Sr²⁺ removability, crystalline CaCO₃-C (mill time: 0 h) and scallop shell powder (mill time: 5 h) were used. S-ACC has considerably higher Sr²⁺ removability than those of crystalline CaCO₃ and scallop shell powder, and 60-times higher Sr²⁺ removability than that of crystalline CaCO₃. From these data, it was confirmed that the amorphous structure of CaCO₃ has a major influence on Sr²⁺ removability. To confirm the Sr²⁺ removal mechanism of S-ACC, the shape of S-ACC after stirring in SrCl₂ aqueous solution and ion-exchanged water was observed by a scanning electron microscope (SEM) (Fig. 9).

From the SEM observation, S-ACC looked like the calcite shape of CaCO₃ after stirring in each aqueous solution.¹⁰ As a result of XRD measurements to identify the structure of each powder (Fig. 10), we found that both were crystallized and exhibited a calcite structure. Moreover, the CaCO₃ peak with Sr shifted to a low degree, indicating that the lattice constant increased and imply that Sr²⁺ is in the structure. From these results, we considered that S-ACC has high Sr²⁺ removability because Sr²⁺ was incorporated into the structure when crystallized from an aqueous solution.

4. Conclusions

We found that CaCO₃ could not remove Sr²⁺ from an aqueous solution, but the scallop shell powder could. As a result of exploring this factor, it was found that the milling treatment had an effect on the Sr²⁺ removability of scallop shell powder, and that the increase in the specific surface area and CaCO₃ amorphization due to the milling treatment were important factors. The effect of the amorphous structure of CaCO₃ on the Sr²⁺ removability was evaluated using S-ACC. The amorphous structure of CaCO₃ had 60-
times higher Sr$^{2+}$ removability than that of crystalline CaCO$_3$. S-ACC was speculated to have high Sr$^{2+}$ removability because it can incorporate Sr$^{2+}$ into its structure when the amorphous structure is crystallized in an aqueous solution.

Fig. 10. XRD patterns of the S-ACC after suspension in aqueous solution. (a) S-ACC after Sr$^{2+}$ removed, (b) S-ACC suspended in ion exchanged water ▼: The peak of the calcite of CaCO$_3$.

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