Removal of strontium from aqueous solutions using scallop shell powder

Fumihiro MIHARA¹, Yuta SHUSEKI¹, Sanae TAMURA², Koiehi UI³, Kenta KIKUCHI⁴, Atsuo YASUMORI⁵, Shinichi KOMABA⁶, Mika FUKUNISHI⁶, Yasuo KOGO⁵, Yasushi IDEMOTO¹ and Ken TAKEUCHI¹,²,⁷

¹Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278–8510, Japan
²Liberal Arts in Oshamambe, Faculty of Industrial Science and Technology, Tokyo University of Science, 102–1 Tomino, Oshamambe-cho, Hokkaido 049–2514, Japan
³Department of Chemistry and Biological Sciences, Faculty of Science and Engineering, Iwate University, 4–3–5 Ueda, Morioka 020–8551, Japan
⁴Frontier Materials and Function Engineering, Graduate School of Engineering, Iwate University, 4–3–5 Ueda, Morioka 020–8551, Japan
⁵Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, 6–3–1 Niiyuku, Katsushika-ku, Tokyo 125–8585, Japan
⁶Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 12–1 Funagawara-cho, Ichigaya, Shinjuku-ku, Tokyo 162–0826, Japan

It is important to efficiently remove radioactive substances contained in polluted waters before they are discharged from nuclear power plants. In particular, there is an urgent need for the development of technology that can adsorb radioactive Sr²⁺, but there are currently no inexpensive Sr²⁺ adsorbents with low environmental burden. We found that scallop shell powder adsorbs Sr²⁺ in aqueous solutions at various initial concentrations. In this study, to obtain fundamental knowledge of the mechanism of Sr²⁺ removal using waste scallop shell, we analyzed the removability of Sr²⁺. Scallops showed the same capacity to remove Sr²⁺ at a high initial concentration (≥0.50 g/dm³) as the reagent CaCO₃, but clear differences in removability occurred at a low initial concentration (0.010 g/dm³), where scallop shell proved to be superior. In addition, scallop shell powder had slit-shaped pores and a specific surface area of 4.3 m²/g. Measurement of the adsorption isotherm in the low concentration aqueous solution showed that Sr²⁺ removal occurred by chemisorption; the adsorbed Sr is present on the surface of the scallop shell powder particles.

Key-words: Scallop shell, Adsorption, Strontium, Calcium carbonate, Radioactive elements, Water treatment

1. Introduction

Processing of the ~1 million tons of contaminated water currently accumulated around the Fukushima Daiichi Nuclear Power Plant has stagnated.¹ The efficient removal of radioactive substances such as Cs⁺ and Sr²⁺ are necessary for processing to proceed. Residual Sr²⁺ is particularly dangerous to the human body due to its propensity to replace Ca²⁺ in bones. Studies have attempted Sr²⁺ removal from aqueous solutions by Sr²⁺ adsorption using antimony oxide,² tantalum-doped tungsten oxide,³ and layered potassium titanate.⁴ However, since these adsorbent materials use rare metals, they involve high manufacturing costs and are not suitable for the treatment of large amounts of contaminated water; thus, these methods have not been put to practical use. Hence, in order to treat contaminated water, there is still an urgent need to develop an inexpensive adsorbent with low environmental burden.

One potential adsorbent is recycled scallop shell, which has been utilized previously as a removal agent for harmful substances; for example, as an aldehyde remover,⁵-⁷ volatile organic compounds adsorbent,⁵,⁶,⁸ desulfurization material,⁹,¹⁰ and dephosphorization material.¹¹ It is expected that waste scallop shells, which are currently discarded, can be utilized as raw materials for inexpensive and environmentally friendly agents that remove harmful substances. From this perspective, aim to apply scallop shells for the treatment of contaminated water generated from nuclear power plants. While scallop shell powder...
removes Sr\(^{2+}\) from aqueous solutions, we are yet to elucidate the mechanism by which the powder removes Sr\(^{2+}\). In this report, we attempt to elucidate basic knowledge as to the mechanism of Sr\(^{2+}\) removal by scallop shell powder.

2. Experimental procedures

2.1 Preparation of scallop shell powder

The meat of the scallops was removed from the shells, which were then cleaned to remove any dirt or stains, then air dried at room temperature. The shells (60 g) were crushed for 3 h with a stamp mill (NITTO KAGAKU, AMM-140D) and a further 3 h with an automatic mortar (NITTO KAGAKU, ANS-143). We then analyzed the Sr\(^{2+}\) removability of the obtained powder. The reagent CaCO\(_3\) was used for comparison (Kishida Chemical, Special Grade).

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

SrCl\(_2\)·6H\(_2\)O hydrate (Kishida Chemical, Special Grade) was dissolved in ion exchanged water to prepare a SrCl\(_2\) aqueous solution of a known concentration. The SrCl\(_2\) aqueous solution was stirred, and 3.0 g of scallop shell powder or reagent CaCO\(_3\) powder were added, such that the aqueous solution was stirred, and 3.0 g of scallop shell powder was added to the solution for 15 h at 25°C.

At an initial concentration of \(0.50 \text{ g/dm}^3\) Sr\(^{2+}\), both scallop shell powder and CaCO\(_3\) showed similar Sr\(^{2+}\) removability. However, with an initial concentration less than \(0.50 \text{ g/dm}^3\), the Sr\(^{2+}\) removability of the scallop shell powder was far higher than that of the reagent CaCO\(_3\): at an initial concentration of \(0.10 \text{ g/dm}^3\), the Sr\(^{2+}\) removability of the scallop shell powder was far higher than that of the reagent CaCO\(_3\) still had a residual Sr\(^{2+}\) rate of almost 100%, whereas the residual Sr\(^{2+}\) concentration in the solution with scallop shell powder was below the detection limit of AAS, indicating the superior removability of the scallop shell powder at low initial concentrations.

Figure 2 shows the change over time of the residual rate of Sr\(^{2+}\) concentration in a high-concentration aqueous solution of SrCl\(_2\) (1.1 g/dm\(^3\) Sr\(^{2+}\)), to which the powder was suspended. Measurements were taken by adding 30 g Sr\(^{2+}\) to the solution with Sr\(^{2+}\) concentration of 1.1 g/dm\(^3\), 25°C, concentration of the powder 60 g/dm\(^3\), 15 h suspended.

3. Results and discussion

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

The Sr\(^{2+}\) removability of the reagent CaCO\(_3\) has been previously reported at an initial Sr\(^{2+}\) concentration of 1.1 g/dm\(^3\). Figure 1 shows the Sr\(^{2+}\) removability of both CaCO\(_3\) and scallop shell powder at various initial concentrations, after suspending 3.0 g of powder in 0.050 dm\(^3\) (concentration of the powder 60 g/dm\(^3\)) of a SrCl\(_2\) aqueous solution for 15 h at 25°C.

Figure 2 shows the change over time of the residual rate of Sr\(^{2+}\) concentration in a high-concentration aqueous solution of SrCl\(_2\) (1.1 g/dm\(^3\) Sr\(^{2+}\)), to which the powder was suspended. Measurements were taken by adding 30 g Sr\(^{2+}\) to the solution with Sr\(^{2+}\) concentration of 1.1 g/dm\(^3\), 25°C, concentration of the powder 60 g/dm\(^3\), 15 h suspended.
of powder to 0.50 dm³ (concentration of the powder 60 g/dm³) of solution at 25°C. At this high concentration, there was no significant difference between the Sr²⁺ removability over time of scallop shell powder and CaCO₃.

3.2 Sr present in the scallop shell powder

Since the Sr²⁺ concentration in the aqueous solution was decreasing, we hypothesized that the removed Sr²⁺ was contained in the scallop shell powder. We therefore attempted to identify Sr compounds within the solids using XRD, as shown in Fig. 3.

After suspension, the scallop shell powder had peaks at the same positions as CaCO₃. However, we were unable to identify compounds containing Sr due to the detection limit of the laboratory XRD. Therefore, in order to investigate the presence of trace amounts of Sr compounds, we took measurements with XPS, which is capable of detecting Sr with higher sensitivity (Fig. 4).

Scallop shell was cut into squares weighing 3.0 g using a diamond cutter. This bulk scallop shell sample was added to 0.050 dm³ of an aqueous solution of SrCl₂ (1.1 g/dm³ Sr²⁺) and left for 2 months. To ensure conductivity during XPS measurements, the sample was wrapped in a non-glossy aluminum wheel. The scallop shell has an additional Sr peak after Sr²⁺ removal, showing that it did contain Sr.

3.3 Removal of low concentration Sr²⁺ by scallop shell

Since a previous report mentioned in detail the mechanism of Sr²⁺ removal from an aqueous solution (1.1 g/dm³ Sr²⁺), we decided to focus on a Sr²⁺ initial concentration of 0.010 g/dm³, where there was a significant difference in the Sr²⁺ removability between scallop shell and the CaCO₃. Figure 5 shows the change over time in the Sr²⁺ residual rate in a SrCl₂ aqueous solution with a low initial concentration (0.010 g/dm³ Sr²⁺). The experiment was conducted by adding 3.0 g of powder to 0.050 dm³ (concentration of the powder 60 g/dm³) of aqueous solution at 25°C.

Within about 3 min of suspension, scallop shell powder was able to remove Sr²⁺ to below the detection limit of the AAS (saturated Sr²⁺ adsorption amount of scallop shell powder at 0.010 g/dm³ Sr²⁺ initial concentration is 0.35 mg/g). Despite the fact that there was no difference between the two powders at a high initial Sr²⁺ concentration (1.1 g/dm³), the scallop shell powder demonstrated an entirely different Sr²⁺ removal capability to CaCO₃ at this low initial Sr²⁺ concentration (0.010 g/dm³). Therefore, we considered the possibility that composition of scallop shell powder and CaCO₃ are different.
The results of XRD measurements of the scallop shell powder and the reagent CaCO₃ are shown in Fig. 6. The scallop shell powder was found to have peaks at the same positions as CaCO₃. Thus, the crystal structure of the scallop shell powder and CaCO₃ was the same. Therefore, we theorized that the difference in Sr²⁺ removability was attributable to the microstructure of the powder.

Figure 7 shows SEM observations of the microstructure of scallop shell powder had a large amount of long and narrow particles, whereas CaCO₃ had a different particle shape like a cube. There were no other obvious differences; hence, we investigated the presence or absence of pores by measuring nitrogen adsorption and desorption. Figure 8 shows the nitrogen adsorption–desorption isotherms of scallop shell powder and reagent CaCO₃. The pre-treatment was carried out at 130°C for 2 h and the temperature at the time of nitrogen desorption was 77 K. Hysteresis of the isotherm was observed only for scallop shell powder. According to the classification of international union of pure and applied chemistry, the type of H3 loop is assumed that particles giving rise to slit-shaped pores. It is therefore presumed that the scallop shell powder has slit-shaped pores, and the CaCO₃ has no pores. Hence, it was considered that the scallop shell powder may have a larger surface area than the reagent CaCO₃.

The specific surface area is calculated by the BET method. Scallop shell powder had a specific surface area of 4.3 m²/g, while that of CaCO₃ was 0.14 m²/g. Because the scallop shell powder has pores that are not present in CaCO₃, and because the specific surface area of scallop shell powder is greater than CaCO₃, the removal of Sr²⁺ by scallop shell powder may be through adsorption.

### 3.4 Classification of Sr²⁺ removal by scallop shell powder

The adsorption isotherm of scallop shell powder in an aqueous solution of SrCl₂ is shown in Fig. 9. The Sr²⁺ concentration was regarded as equilibrium after suspension for 15 h. The experiment was conducted by adding 3.0 g of powder to 0.050 dm³ (concentration of the powder 60 g/dm³) of an aqueous solution of SrCl₂ (Sr²⁺ concen-
The isotherm curve for scallop shell powder took a convex upward shape, but for CaCO₃ it was in the form of a downward convex shape. Generally, when the shape of the isotherm is upwardly convex, there is strong interaction between the adsorbent and the adsorbate, and a high possibility of chemisorption. Conversely, a downwardly convex curve implies that there is no interaction between the absorbent and the adsorbate, so it is not possible to say there has been an adsorption phenomenon. Since the graph of scallop shell powder is in the shape of an upwardly convex curve, it is presumed that Sr²⁺ is removed by chemisorption. Since scallop shell powder is highly likely to chemically adsorb Sr²⁺, we tried to identify compounds containing Sr that formed on the surface of the scallop shell powder particles.

**Figure 10** shows the results of using XRD to identify compounds in scallop shell powder that contain Sr after adsorption.

We measured the powders that were suspended in the aqueous solution of SrCl₂ (Sr²⁺ concentration: 0.010 g/dm³) for 15 h each, then filtered and dried. After suspension, the scallop shell powder had peaks at the same positions as for CaCO₃, and we observed no peak attributable to the compound containing Sr. However, there is a possibility that a trace amount of Sr compound is present in scallop shell powder below the amount detectable by the laboratory XRD.

Therefore, we measured the powder adsorbed with Sr²⁺ by TOF-SIMS, which provides higher sensitivity (**Fig. 11**). The powders were suspended in an aqueous solution of SrCl₂ (0.010 g/dm³ Sr²⁺) for 15 h, then filtered and dried. Since scallop shell naturally contains trace amounts of Sr which are present in the ocean, in order to clarify whether or not Sr is adsorbed onto the scallop shell powder, it is necessary to compare the level of Sr in scallop shell powder before and after suspension.

The TOF-SIMS profile of scallop shell powder after suspension [**Fig. 11(b)**] is similar to that of the reagent SrCl₂ [**Fig. 11(c)**] but differs from the profile before suspension [**Fig. 11(a)**]. Thus, the Sr contained in the suspended scallop shell powder is derived from SrCl₂.

### 4. Conclusions

Although Sr²⁺ removal via scallop shell powder is similar to that via CaCO₃ at a high initial Sr²⁺ concentration (>0.50 g/dm³), a clear difference in Sr²⁺ removability appears with a low initial concentration (<0.50 g/dm³), where scallop shell powder was superior. The scallop shell powder was found to have slit-shaped pores and a specific surface area of 4.3 m²/g. Furthermore, the removed Sr²⁺ was found to be present on the surface of the scallop shell powder by chemisorption.

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