Study for the Formation of Sponge-like Ion Exchanger Containing Sodium-form Synthetic Mica and Its Cesium Adsorption Characteristics

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(Manuscript received April 2, 2018, accepted August 29, 2018)

Abstract

As an adsorbing material for recovering cesium from radioactive contaminated water, a sponge-like compound was synthesized using sodium-form synthetic mica (Na-TSM) as an ion exchanger which does not contain lithium and is inexpensive and readily available. The cesium adsorption ratio from aqueous solutions was 80% or higher in low cesium concentration region and the desorption ratio was less than 5%. It suggests that synthesized sponge-like material is much adapted as cesium adsorbent.

Keywords: ion exchange, cesium adsorbent, sodium-form synthetic mica

1. Introduction

The unprecedented earthquake disaster that hit eastern Japan on March 11, 2011 has raised many problems even seven years thereafter. Among them, the environmental pollution caused by accidents at Fukushima Daiichi Nuclear Power Plant is a grave situation, and there are many inhabitants who have not yet returned due to the seriousness of the pollution. The problem of contamination by radioactive substances can be roughly divided into two. One is the problem of the nuclear power plant itself. The other is the local pollution by spread radioactive materials. Focusing on contaminated water, the authors consider two factors. Firstly, seawater injected for cooling the nuclear reactor just after the accident became a large amount of contaminated water at the nuclear power plant. Secondly, the groundwater flowing down to the sea from mountainside became also contaminated water as it passed through the polluted area. These contaminated waters are stored in tanks, and beautiful forests were transformed to forests of tanks with an increasing amount of contaminated water. Tokyo Electric Power Co. is working on the contaminated water countermeasures following the three mottoes; “Remove”, “Do not approach” and “Prevent leak”1). As for “Remove” among them, a multi-nuclide removal equipment, ALPS, has been introduced and tests are underway for full-scale operation. Before introducing contaminated water into ALPS, it is necessary to remove cesium and strontium. For such a purpose, cesium adsorption apparatus such as KURION and SARRY are used. In these devices, the key collecting material is mainly zeolite and a lot of research has been conducted regarding recovery of cesium2–6). Meanwhile, in areas where radioactive substances were spread, decontamination was carried out at many public facilities and individual housing in order to reduce air dose below the standard, leading to the generation of contaminated water. It is mandatory to recover contaminated water, to remove cesium before discharge to sewers and to serve methods for passing through sandbags using zeolite and filtering after coagulation sedimentation, etc.

The authors’ research regarding buffer materials in the geological disposal of spent nuclear fuel reported that sodium taeniolite had high total cesium-ion adsorption capacity and sodium-form synthetic mica, Na-TSM, had high ion-exchange selectivity for cesium ion7). Na-TSM belongs to the same tetrafluoride mica group as sodium taeniolite but does not contain lithium. In layered clay minerals, interlayer interchangeable cations are generally involved in ion-exchange phenomenon. In Na-TSM, the exchange occurs between interlayer sodium and external cesium ions. However, ion-exchange sites are not only interlayer zones but other sites are also involved8). When these substances are utilized as buffer materials, their powder form is not a matter but rather a merit because it is meant to fill the gaps.

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Nonetheless, in this study, the purpose is to recover the clay mineral itself after absorbing target ions from contaminated water and allow the treated water below environmental standards to be discharged to ordinary sewage, etc. If the clay mineral was powder, it should be filtered. Therefore, molding in some way is indispensable to easy operation. The authors started molding of sodium taeniolite because it has high total cesium adsorption capacity rather than of its selectivity. In the attempts to granular and to form film, the authors succeeded in molding by taking advantage of the hydrophobicity of poly(vinylidene fluoride), gave the name “sponge-like form” to the product and reported its ion-exchange properties. In this method, recovery ratio is 95.4% when the initial concentration of reactant was 1.0 mmol/L which is similar to that of the powder could be obtained with a sponge-like form. But because sodium taeniolite contains lithium and the price of lithium jumped dramatically up as lithium-ion secondary battery has become widespread, the cost of sodium taeniolite has become higher. Moreover, there is no example of practical application or sale in the market. For that reason, the authors aimed at molding into sponge-like form by replacing sodium taeniolite to Na-TSM. However, when synthesizing with the same formulation as sodium taeniolite, soft sponge-like product could not be formed with Na-TSM. Also failure of Na-TSM was observed during the ion-exchange experiments and satisfactory ion-exchange ratio could not be attained. Therefore, this paper reports the method of molding a sodium-form synthetic mica into sponge-like form and its cesium adsorption ability.

2. Experimental

Materials Ten% gel form of Na-TSM obtained from Topy Industrial Co., Ltd. was washed several times with ultrapure water (purified by PURIC Z-II, Organo). Sediment particles after approximately 30 min leaving at rest were collected and dried at room temperature. The binder was poly(vinylidene fluoride) (PVF) and N,N-dimethylacetamide (DMA) was used as the solvent for PVF. Both were of special reagent grade.

Method PVF of 0.1 g or 0.2 g was taken in a 30-mL beaker and was dissolved in 2 mL DMA. Na-TSM of 0.1 g or 0.2 g was added there and was thoroughly stirred with a glass rod until a uniform mixture. Ultrapure water was poured slowly along the inner wall of the beaker. PVF-Na-TSM aggregate was floated and was recovered, rinsed with ultrapure water, and dried at room temperature. The powder X-ray diffractometer Ultima IV (Rigaku Corporation, Japan) equipped with monochromatized Cu Kα radiations, λ = 0.1541 nm, was used for the characterization of the materials as prepared above. All ion-exchange experiments were carried out by batch method. Cesium chloride aqueous solution of 20 mL prepared to a predetermined concentration was taken in a plastic container, a sponge-like Na-TSM was added and the container was continuously stirred for 24 h on a rotary shaker. After the reaction, the supernatant was filtered through a 0.45-μm filter and the concentration of cesium in the supernatant was measured by atomic absorption spectrophotometry (Hitachi Z-2300, Hitachi High-Technologies).

The sponge-like Na-TSM obtained after ion exchange described above was dried in the air without rinsing. Ultrapure water of 20 mL was taken in a plastic container and the dried sample was added. Reaction and measurement were carried out under the same conditions as the ion-exchange experiment.

3. Results and Discussion

Table 1 shows the amounts of materials used for each sponge. The sponge prepared with the same formulation as sodium taeniolite was described as “Former Sponge”. Photographs of sponge-like Na-TSMs synthesized with the amounts listed in Table 1 are shown in Fig. 1. Both Sponge A and Sponge B had less shrinkage after drying than Former Sponge and presented a fluffy feeling. The difference from Former Sponge is the mass ratio of Na-TSM: PVF, which is 1 : 1 for Sponge A and Sponge B whereas that for Former Sponge is 2 : 1. At this ratio Sponge A and Sponge B could be molded into sponge-like Na-TSM similar to sponge-like sodium taeniolite. In general, the uptake of water molecules into the interlayer of smectite is up to two layers for sodium taeniolite and ten layers for Na-TSM.

When ultrapure water is added to Na-TSM/PVF/DMA mixture, Na-TSM is apter to swell than sodium taeniolite. During the dry process, the shrinkage of interlayer spacing is larger than sodium taeniolite because dehydration is more. At same time, PVF also diminishes following the contraction between layers. As a result, the sponge became smaller such as Former Sponge as seen in Fig. 1. This phenomenon could be partly explained by the fact that the contraction of the sponge was improved by decreasing the ratio of Na-TSM. Sponge A and Sponge B differed in thickness due to the difference in the amount of

| Table 1 | Prescriptions of each sponge |
|---------|-----------------------------|
| Raw material | Former Sponge | Sponge A | Sponge B |
| Na-TSM | 0.2 g | 0.1 g | 0.2 g |
| PVF | 0.1 g | 0.1 g | 0.2 g |
| DMA | ca. 2 mL | ca. 2 mL | ca. 2 mL |

Na-TSM: sodium-form synthetic mica
PVF: poly(vinylidene fluoride)
DMA: N,N-dimethylacetamide
PVF because beakers of the same size were used. Because the amount of DMA was fixed to 2 mL and PVF dissolving in 2 mL DMA was limited to 0.2 g, it was impossible to make a larger sponge. However, the authors believe that a larger sponge can be formed by increasing the amounts of solvent and PVF.

Table 2 shows the results of ion-exchange experiments with each sponge-like Na-TSM for some cesium chloride initial concentrations with the result of powder Na-TSM\(^7\) and sponge-like sodium taeniolite\(^9\). Adsorption ratios were calculated as follows.

\[
\text{Adsorption ratio} = \frac{\text{initial concentration} - \text{concentration of supernatent after ion-exchange reaction}}{\text{initial concentration}} \times 100
\]

Contrary to expectation from powder form, sponge-like Na-TSM showed higher adsorption ratio compare with sponge-like sodium taeniolite. The amounts of cesium were 0.02 mmol, 0.10 mmol and 0.20 mmol, respectively, in 1, 5 and 10 mmol/L solutions. Generally, the cation-exchange capacities (CEC) of smectite-type clay minerals are from 60 to 150 meq/100 g. Therefore, assuming that the CEC of Na-TSM used is 100 meq/100 g, the theoretical capacities of 0.1 mmol are obtained for Sponge A and 0.2 mmol for Sponge B. In order to obtain higher ratio of adsorption, the use of an ion exchanger with larger CEC is required with respect to the amount of cesium in the reaction solution.

Comparing Sponge B and powder Na-TSM, it can be seen that the adsorption ratio decreased as a result of molding. In Na-TSM, interlayer sodium ion underwent ion exchange for cesium ion in the reaction solution with excluding the interlayer water and the interlayer distance shrinked\(^7\). Figure 2 shows the XRD patterns of Sponge B, Sponge B in wet condition, powder Na-TSM and PVF sponge. The interlayer spacing for Na-TSM of anhydrous form, single-layered form and double-layered form are 9.56 Å, 12.34 Å and 15.17 Å, respectively\(^11\). Sponge B has 11.77 Å for the interlayer spacing of Na-TSM that means Na-TSM is hydrated in sponge-like form. Although it swells in the water because Sponge B/wet has 13.98 Å for the interlayer spacing of Na-TSM, swelling is diminished if it is compared to powder Na-TSM. Therefore

| initial concentration/mmol dm\(^{-3}\) | Sponge A | Sponge B | powder Na-TSM\(^7\) | Sponge-like sodium taeniolite\(^9\) |
|--------------------------------------|----------|----------|---------------------|-------------------------------|
| 1.0                                  | A 86.1   | 97.0     | 100.0               | 95.4                          |
| 3.0                                  | A 3.38   | 2.58     | —                   | —                             |
| 5.0                                  | A 33.9   | 86.7     | —                   | —                             |
| 10.0                                 | A 17.8   | 2.06     | —                   | —                             |
| 10.0                                 | A 15.0   | 61.0     | 74.7                | 44.7                          |
| 10.0                                 | D 22.2   | 5.83     | —                   | —                             |

A: adsorption ratio, D: desorption ratio.

Amount of Na-TSM, Sponge A: 0.1 g, Sponge B: 0.2 g, powder Na-TSM: 0.2 g.
Amount of sodium taeniolite: 0.2 g.
interlayer sodium ion is difficult to move and adsorption ratio decreases. This effect is weaker in Sponge B than that in Sponge A. One of the plausible reasons may be the bulk of the sponges. Due to the difference in the amount of PVF, Sponge B was larger and the inside area was wider than that of Sponge A. Therefore, even if the compounding ratio of PVF and Na-TSM is the same, it could be assumed that Na-TSM is more uniformly dispersed, good contact is established with the reaction solution to carry out ion exchange; however, this point needs further verification.

The results of the desorption experiment are shown in Table 2. Desorption ratio is calculated as follows.

\[
\text{Desorption ratio} = \frac{\text{Desorption amount}}{\text{Adsorption amount}} \times 100
\]

With reaction solutions of 5 mmol/L and 10 mmol/L, the desorption ratios on Sponge A are higher than that of other samples. This result suggests the higher adsorption ratios contribute to the lower desorption ratios. In such sponge-like Na-TSMs, the desorption ratios are less than 5%, therefore a sponge-like Na-TSM after use can safely be stored even if in contact with moisture of the level of environmental water.

4. Conclusion

Sponge-like Na-TSM was successfully molded using poly(vinylidene fluoride) as a binder. It exhibited a somewhat higher recovery ratio compared with the sponge-like sodium taeniolite. Furthermore, the desorption experiment demonstrated that the desorption ratio of cesium is less than 5% in the used sponge-like Na-TSM with high adsorption ratio, suggesting that a sponge-like Na-TSM is useful as cesium recovery material.

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