Incorporation Behavior of Cesium into Pollucite and the Optimization of Synthesis Method

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Abstract

For removal and long term storage of radioactive cesium ion (Cs⁺) which diffused into the environment by the Fukushima Daiichi Nuclear Power Plant accident, pollucite (POL: Cs₁₆Si₃₂Al₁₆O₉₆·ₙH₂O) which is a cesium containing mineral was synthesized by using a solution containing sodium silicate, sodium aluminate and cesium chloride, and the optimum synthesis condition for Cs⁺ removal and insolubilization was determined. POL synthesis was carried out at 200°C for 24 h, in the Si/Al molar ratio range of 0.5 to 7.0 and in the Cs⁺ concentration range of 10 to 5000 mg dm⁻³. The product was characterized using X-ray diffractometer and scanning electron microscopy. After synthesis of POL, the concentration of Cs⁺ remained in the solution which was not incorporated into POL was determined by using atomic adsorption spectrophotometer. The Cs⁺ dissolution experiment was carried out with the synthesized product in a 0.6 M NaCl solution for 24 h. It was revealed that excellent Cs⁺ removal and insolubilization were confirmed by the formation of POL with Si/Al molar ratio of 2.0 and 2.5 in the mixed solution adjusted to 2500 mg dm⁻³ Cs⁺ concentration. In addition, even in low Cs⁺ concentrations (100 mg dm⁻³), the excellent Cs⁺ removal and insolubilization were achieved with POL having Si/Al molar ratio of 2.0. Moreover, if Si/Al molar ratio was adjusted to be 2.0 to 2.5, Cs⁺ (100 mg dm⁻³ to 2500 mg dm⁻³) could remove effectively and store stably long time.

Keywords: Pollucite, Cesium, Hydrothermal treatment, Removal, Insolubilization

1. Introduction

A large amount of radioactive substances have spread to environment due to the Fukushima Daiichi Nuclear Power Plant accident caused by Great East Japan Earthquake. These radioactive substances still exist at high concentration in cooling water of the nuclear reactor, and they were also deposited around the power plant (in soil, plants, etc.). The main radioactive nuclide in the contaminated substances, were cesium-134 (¹³⁴Cs, half-life: about 2 years) and cesium-137 (¹³⁷Cs, half-life: about 30 years) and the decontamination operations for ¹³⁴Cs and ¹³⁷Cs have been carried out until now. In particular, it is necessary to keep ¹³⁷Cs for 600 to 1000 years¹ until collapse and disappears because of its long half life.

Therefore, insolubilization technique to retaining the removed ¹³⁷Cs for long time is required. Remove of ¹³⁷Cs using zeolites which have a pore size larger than Cs⁺ diameter (mordenite, clinoptilolite, chabasite etc.) has been reported by many researchers²⁻⁷. However, it is difficult to retain Cs⁺ for
long time without dissolution because zeolite is cation exchanger\(^5\). Cs\(^+\) dissolution from the zeolite pores can easily occur by ion exchange with cations in environment water such as sea water which contains cations at high concentration. Pollucite (POL: \(\text{Cs}_6\text{Si}_{12}\text{Al}_{16}\text{O}_{40}\text{nH}_2\text{O}\)), Si/Al molar ratio: 2.0) is one of the zeolite minerals containing Cs\(^+\) ion, and belongs to analcime (ANA: \(\text{Na}_{16}\text{Si}_{32}\text{Al}_{16}\text{O}_{96}\text{nH}_2\text{O}\)) zeolite family\(^4\). The pore size of POL (0.28 nm)\(^6\) is smaller than Cs\(^+\) diameter. Consequently, if Cs\(^+\) was incorporated in POL it can be expected that Cs\(^+\) would be kept unless POL structure collapses\(^9\).

At present, conversion of various material such as natural zeolites, coal fly ash, smectite clay and chemical regents containing Si, Al and Na to POL or ANA by alkaline hydrothermal treatment method has been reported by many researchers\(^2,3,6-9\). However, the optimization of synthesis condition to improve the Cs\(^+\) removal and the solution stability of obtained product have not been reported. In particular, POL synthesis in a low Cs\(^+\) concentration is very important for removal and insolubilization of radioactive Cs\(^+\).

In this study, the optimum Si/Al molar ratio on POL synthesis using chemical regents for Cs\(^+\) removal and insolubilization were determined in the Cs\(^+\) concentration range of 10 to 5000 mg dm\(^{-3}\).

2. Experimental

2.1 Reagents and Preparation of solution

Mixed solutions containing Si and Al for POL synthesis were prepared by dissolving a mixture of sodium silicate and sodium aluminate (Wako Pure Chemicals Industries Ltd., Osaka, Japan) in 500 cm\(^3\) of pure water at 40°C and by stirring for 30 min. The Si/Al molar ratio was adjusted 0.5 to 7.0 while total concentration of Si and Al was maintained at constant. The solution containing Cs\(^+\) was prepared by dissolving cesium chloride (Wako Pure Chemicals Industries Ltd., Osaka, Japan) to be the concentration of 10 to 5000 mg dm\(^{-3}\).

2.2 POL synthesis by hydrothermal treatment

For alkaline hydrothermal treatment, 30 cm\(^3\) of the mixed solutions and 30 cm\(^3\) of CsCl solution were placed in 100 cm\(^3\) Teflon\(^\text{®}\) cups in a stainless steel pressure vessel and heated at 200°C under autogenous pressure for 24 h in a thermostatic oven. POL or ANA was synthesized by alkaline hydrothermal treatment method at 200°C for 24 h according to the method reported previously\(^3,8\). The synthesis condition was set to be Si/Al molar ratio of 0.5 to 7.0 at Cs\(^+\) concentration of 2500 mg dm\(^{-3}\), and to be Si/Al molar ratio of 2.0 at Cs\(^+\) concentration of 10 to 5000 mg dm\(^{-3}\).

After the hydrothermal treatment, the solid-liquid separation was carried out by passing through 0.45 μm pore size membrane filter. The Cs\(^+\) concentration in the solution which was not taken in the POL was determined by using atomic adsorption spectrophotometer (AAS: Varian SpectrAA 220FS) and Cs\(^+\) removal percentage was calculated from difference between the Cs\(^+\) concentration in the filtrate and those in initial solutions and then resultant product was washed several times with pure water. Then dried at 80°C for 24 h in a thermostatic oven. Thus obtained product was characterized by using X-ray diffractometer (XRD: Rigaku Ultima IV) and scanning electron microscope (SEM: Hitachi S-3000N, S-4700).

2.3 Cs\(^+\) dissolution experiment

The obtained product and 0.6 mol dm\(^{-3}\) NaCl solution were put in a centrifuge tube in which the solid-liquid ratio was set to 1:100 and shaken at 25°C for 24 h at 80 rpm with a rolling shaker. The concentration of Cs\(^+\) in the filtrate after contacting was determined by using AAS and the Cs\(^+\) dissolution percentage was calculated from the measurement result.

3. Results and Discussion

3.1 POL synthesis

Figure 1 shows the XRD patterns of the products obtained with the mixed solution adjusted from 0.5 to 7.0 of the Si/Al molar ratio and in the Cs\(^+\) concentration of 2500 mg dm\(^{-3}\) by hydrothermal treatment. The XRD pattern of only POL (ANA) was confirmed in the Si/Al molar ratios at 2.0, 4.0 and 7.0 (Fig. 2c-e). However, at Si/Al molar ratios of 0.5 and 1.0, XRD pattern of cesium sodium aluminum silicate hydrate was slightly detected together with that of POL (ANA) (Fig. 2a, b).

Fig. 1 XRD patterns of the products. Si/Al molar ratio: (a) 0.5, (b) 1.0, (c) 2.0, (d) 4.0, (e) 7.0.
observed at 0.5 and 2.0 of Si/Al molar ratio (Fig. 2a, 2b) and single polyhedron crystallites about 20 μm in size were observed at 4.0 and 7.0 of Si/Al molar ratio (Fig. 2c, 2d). These results indicate that single phase of POL (ANA) can synthesize in the range from 2.0 to 7.0 and the crystalline growth occurs as Si/Al molar ratio is larger.

Figure 2  SEM images of the products with Si/Al molar ratio of (a) 0.5, (b) 2.0, (c) 4.0 and (d) 7.0.

Figure 3 shows the XRD patterns of the products obtained with the mixed solution adjusted from 10 to 5000 mg dm$^{-3}$ Cs$^+$ concentration at 2.0 of the Si/Al molar ratio by hydrothermal treatment. The XRD pattern of only POL (ANA) was confirmed in all Cs$^+$ concentration. The intensity of 15.3° (211) decreased with the increase of Cs$^+$ concentration. This result indicates that phase change from ANA containing Na$^+$ to POL containing Cs$^+$.

Figure 3  XRD patterns of the products. Cs$^+$ concentration: (a) 10 mg dm$^{-3}$, (b) 100 mg dm$^{-3}$, (c) 1250 mg dm$^{-3}$ and (d) 5000 mg dm$^{-3}$.

3.2 Cs$^+$ removal

As shown in Fig. 5, in the case of the Si/Al molar ratio 0.5 to 7.0 and 2500 mg dm$^{-3}$ of Cs$^+$ concentration, the Cs$^+$ removal percentage was more than 90% in the range of Si/Al molar ratio of 2.0 and 2.5. It was showing the most excellent removal ability among the Si/Al molar ratio conditions in this experiment. The Cs$^+$ removal percentage was low at the Si/Al molar ratio of 0.5 and 1.0 because of the formation of cesium sodium aluminum silicate hydrate as shown in Fig. 1. And at the Si/Al molar ratio of 3.0 to 7.0, the Cs$^+$ removal percentages were low because the amounts of POL production were decreased. From these results, it can be expected that Cs$^+$ remove ability can be efficiently at the Si/Al molar ratio of 2.0 and 2.5.

Although the Cs$^+$ removal percentage decreased from 94% to 60% with increasing the Cs$^+$ concentration from 2500 mg dm$^{-3}$ to 5000 mg dm$^{-3}$, POL was explicitly formed (Fig. 3) and Cs$^+$ dissolution percentage was still satisfactorily low (Fig. 6) and therefore, it can be expected that this method is applicable to the solution containing Cs$^+$ higher than 5000 mg dm$^{-3}$ as long as POL was formed.

Both POL synthesized with low Cs$^+$ concentration, i.e. 10 mg dm$^{-3}$ and 100 mg dm$^{-3}$ gave an excellent removal performance of around 90%. Therefore, remove of Cs$^+$ can be expected even at low Cs$^+$ concentration.
3.3 Cs⁺ dissolution

Figure 6 shows the Cs⁺ dissolution percentage of products. The percentage of dissolution was less than 1% in all conditions except for Cs⁺ concentration of 10 mg dm⁻³. In particular, the Cs⁺ dissolution percentage at the Si/Al molar ratio of 2.0 to 3.0 shows about 0.05%. These dissolution percentages were greatly small compared to that of synthetic mordenite which has high Cs⁺ selectivity (more than 10%)². These results indicate the formation of POL which has the pores smaller than Cs⁺ diameter plays a very important role to prevent dissolution of Cs⁺ and the formation can be maintained even in rich Na⁺ solution. The Cs⁺ dissolution percentage was 4% in 10 mg dm⁻³ Cs⁺ concentration.

Therefore, Cs⁺ remove and long-term storage can be expected in Cs⁺ concentration in the range from 100 mg dm⁻³ to 2500 mg dm⁻³.

![Fig. 5 Percentage of Cs⁺ removal.](image)

![Fig. 6 Percentage of Cs⁺ dissolution.](image)

4. Summary

For the excellent Cs⁺ remove and Cs⁺ insolubilization, it was revealed that the optimum Si/Al molar ratio range for POL synthesis is 2.0 and 2.5 in the mixed solution adjusted to 2500 mg dm⁻³ Cs⁺ concentration at 200°C for 24 h. In addition the excellent Cs⁺ remove showed even at a low concentration of 10 to 100 mg dm⁻³ (Cs⁺ removal percentage was about 90%). However, Cs⁺ dissolution percentage was high (4%) in 10 mg dm⁻³ Cs⁺ concentration. If Si/Al molar ratio adjusts to 2.0 to 2.5, Cs⁺ (100 mg dm⁻³ to 2500 mg dm⁻³) could remove and store. Therefore, the optimized in this study POL can be useful for the remove and long-term storage of radioactive Cs⁺.

References