REMOVAL OF Cs$^+$ USING ZEOLITE RHO

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Abstract

Radioactive Cs$^+$ in water needs to be removed to prevent health problems in humans and animals. After the Fukushima nuclear power plant explosion, Cs$^+$ has been removed by ion-exchange using zeolites such as Chabazite and Mordenite. To reduce the amount of contaminated zeolite waste, more efficient zeolite is needed. Zeolite RHO is a zeolite with a low Si/Al ratio, and a high ion-exchange capacity is expected. Thus, zeolite RHO was prepared using the conventional hydrothermal synthesis method and characterized by X-ray diffraction (XRD), adsorption/desorption isotherm of nitrogen, and elemental analysis by X-ray fluorescence (XRF) and inductively-coupled plasma spectroscopy (ICP). Removal of Cs$^+$ was performed batch-wise in water and artificial seawater. Zeolite RHO showed promising Cs removal ability even in artificial seawater.

1. Introduction

Zeolites have been used as catalysts and adsorbents based on their acid-base properties and micro-porous and crystalline structure[1)-3)]. Another important feature of zeolite is its ion-exchange ability, and A-type zeolite has long been used in detergents to remove divalent cations such as Ca^{2+} in hard water[4,5)]. Since the 2011 earthquake off the Pacific coast of Tohoku and the explosion at the Fukushima nuclear power plant, zeolites such as Chabazite and Mordenite have been used to remove radioactive elements such as Cs$^+$ and Sr^{2+} from water[6,7)]. The capacity to exchange cations is closely related to Si/Al molar ratio of zeolite as follows: as the Si/Al ratio decreases, the ion-exchange capacity increases. The aperture or window size also influences the ion-exchange ability. Thus, based on the amount of zeolite waste, zeolites with a low Si/Al ratio and a sufficient window size are preferable. The typical Si/Al ratios for Chabazite and Mordenite are approximately 2 and approximately 10, respectively.

Zeolite RHO (hereafter, RHO) has a low Si/Al ratio of approximately 3.5, and this suggests a comparatively high ion-exchange capacity[8,9)]. RHO has three-dimensional pore system[10)] and its window, which is made of eight-membered oxygen rings, is 3.6 Å, and is sufficiently large for the diffusion of Cs$^+$. Thus, RHO may be a promising zeolite to remove Cs$^+$.

In this study, we prepared RHO using the conventional hydrothermal method, which was characterized by XRD, nitrogen adsorption/desorption isotherm, and elemental analyses. Cs removal in water and artificial seawater was studied and the ability of RHO to remove Cs$^+$ was compared with those of Chabazite and Mordenite.

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2. Experimental

2.1 Preparation of zeolite RHO[11]

Into 2.73 g of distilled water in a polytetrafluoroethylene beaker, 1.39 g of crown ether (18-crown-6) was added. Into this solution, 1.88 g of 50 wt% CsOH (Cs: 6.30 mmol), 0.67 g of NaOH (Na: 16.8 mmol), and 1.72 g of sodium aluminate (Al: 21.0 mmol) were added. The mixture was refluxed at 80 °C for 30 min under stirring at 300 rpm, which resulted in a clear solution, and this was cooled to room temperature. Here, 21.0 g of colloidal silica (LUDOX®HS-30, Merck Japan, Si: 105 mmol) was added dropwise at a rate of 1 mL/min under stirring at 800 rpm. The composition of the starting solution was $Na_2O:Cs_2O:Al_2O_3:SiO_2:18\text{-}Crown\text{-}6:H_2O$ = 1.8:0.3:1:10:0.5:100. After stirring for 24 h, the solution was transferred into a Teflon® vessel and sealed. This vessel was held in a stainless steel autoclave and heated at 110 °C for 3 d. After the hydrothermal synthesis, the vessel was cooled to room temperature and the mixture was centrifuged. The solid product was washed with distilled water, dried at 70 °C overnight, and finally calcined at 500 °C for 3 h. Thus, Na,Cs-RHO was obtained. To prepare K-RHO, Na,Cs-RHO was ion-exchanged with 2 M KCl solution at 60 °C for 6 h.

2.2 Characterization

The crystalline structure was analyzed using XRD (RINT2000, Rigaku Corp., Japan) at 40 kV and 20 mA. The specific surface area was calculated based on the nitrogen adsorption/desorption isotherm measured using a Belsorp-mini (MicrotracBel, Corp., Japan) and by the Brunauer-Emmet-Teller (BET) method. The samples were pretreated in a nitrogen flow at 150 °C for 1 h. Elemental analysis (Si and Al) was performed using inductively coupled plasma atomic emission spectrometry (ICPS-7150, SHIMADZU Corp., Japan) after dissolving the sample in hydrofluoric acid. Elemental analysis for Na, K, Cs, Si, and Al was performed using XRF (XRF-1800, SHIMADZU Corp., Japan).

2.3 Removal of Cs^+

The desired concentration of aqueous Cs solution was prepared with CsCl and distilled water. Into 50 mL of solution, a 50 mg portion of K-RHO was added and stirred for a fixed period at room temperature. The concentration of Cs^+ before and after the ion-exchange was measured using a polarized Zeeman atomic absorption spectrophotometer (Z-2010, Hitachi High Technologies, Japan). To study the influence of co-existing cations, artificial seawater containing appropriate amounts of Na^+, K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} was prepared.

3. Results and Discussion

3.1 Properties of zeolite RHO

XRD patterns of prepared zeolites are shown in Fig. 1. The XRD pattern of the as-prepared zeolite was consistent with that of reported Na,Cs-RHO[10]. Thus, a phase-pure zeolite

RHO was obtained. When Na^+ and Cs^+ cations were exchanged with K^+, peak shifts to higher angles and a relative peak intensity change were observed. This suggests that the position of T-atoms (Si and Al) had changed slightly.
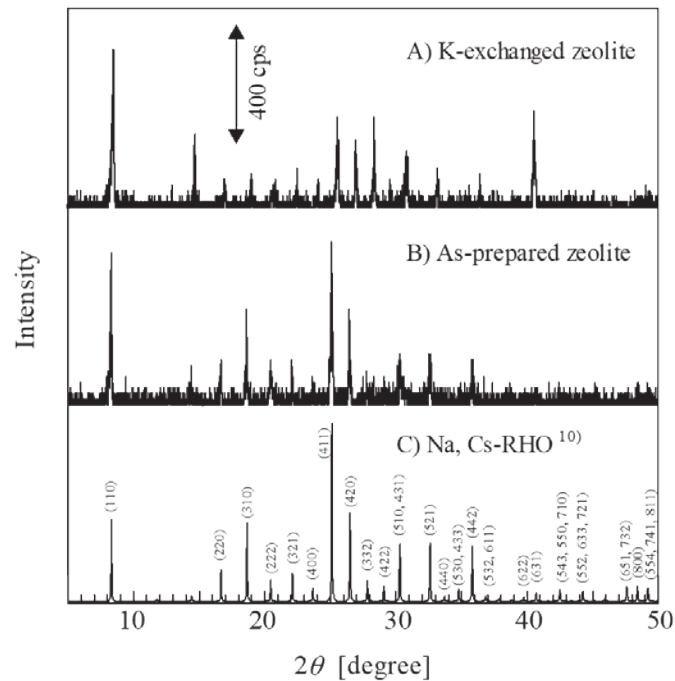

Fig. 1. XRD patterns of as-prepared zeolite and K-exchanged zeolite
Conditions: Cu Ka, 40 kV, 20 mA

The nitrogen adsorption/desorption isotherm is given in Fig. 2. Adsorption at $p/p_0 \simeq 0$ suggests the existence of micropore. The adsorption at high p/p_0 results from spaces between particles. The BET-specific surface area was calculated to be 93.5 m^2/g.
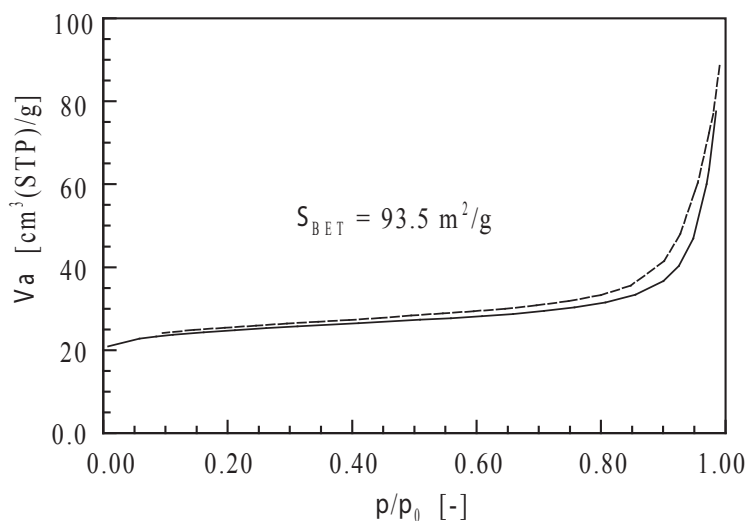
Fig. 2. Nitrogen adsorption/desorption isotherm for K-RHO

Results for the elemental analyses by XRF and ICP are presented in Table 1. The amount of exchangeable cation and aluminum should coincide with each other, and this was confirmed in Table 1. The total amount of Na and Cs in Na,Cs-RHO was approximately 17 mol%, while the amount of Al was 20 mol%. For K-RHO, the amount of K was 18 mol%, while that of Al was 19 mol%. The Si/Al molar ratios by XRF and ICP were the same, within experimental error. The Si/Al molar ratio in the initial preparation solution was 5.0 and that of the obtained RHO was about 3.4, which suggests that not all the Si was included in the zeolite obtained. A Si/Al molar ratio of 3.4 was small among known zeolites, which seems to indicate a high ion-exchange capacity for Cs^+. Typical Si/Al molar ratios for Chabazite and Mordenite[12] are approximately 2 and approximately 10, respectively, and these values are similar or higher than that of RHO, which suggests a preferable ion-exchange capacity of RHO to the zeolites used to remove Cs^+ and Sr^{2+}.

Table 1. Composition of zeolite RHO by XRF and ICP analyses

Zeolite	Si	Al	Cs	Na	K	Si/Al [-]		M/Al
	[mol%]					XRF	ICP	[-]
Na,Cs-RHO	64	20	2.7	14	-	3.2	3.5	0.84
K-RHO	60	19	0.2	0	18	3.2	3.4	1.0

M = Cs + Na + K

3.2 Removal of Cs^+

Results of Cs removal at an initial Cs^+ concentration of 100 ppm (0.75 meq/L) are shown in Fig. 3. The ion-exchange equilibrium was attained in only 30 sec. If all the K^+ cations at the exchange site could be exchanged with Cs^+, 0.17 mmol of Cs^+ could be removed, based on the amount of RHO that was used. The initial and final amounts of Cs^+ in water were 0.038 mmol

and 0.008 mmol, respectively. Thus, about 80% of Cs was removed quickly. This suggests that hydrated Cs^+ was small enough to pass through the zeolite pore, which was composed of the 3.6 Å-eight-membered oxygen ring[13,14].
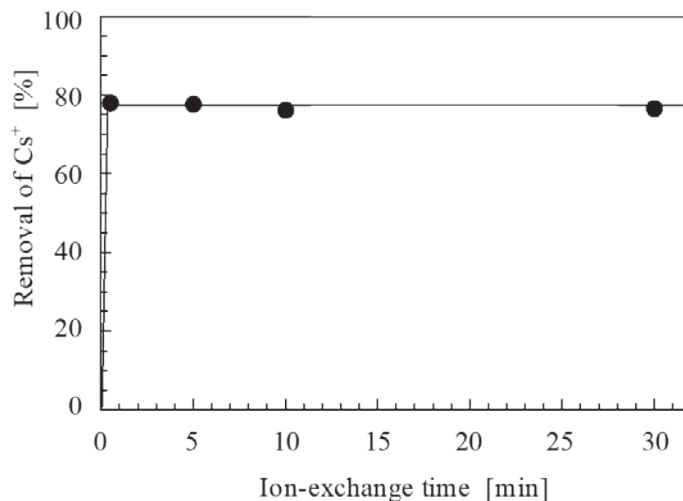

Fig. 3. Cs removal using K-RHO
Conditions: Initial Cs^+ concentration 100 ppm (0.75 meq/L), room temperature

By changing the equilibrium Cs concentration, the adsorption isotherm was obtained (Fig. 4). Based on these data, a single-site Langmuir model and a dual-site Langmuir model were applied[15,16]. The dotted line in Fig. 4 shows the results obtained by the single-site model. As shown in Fig. 4, the single-site model matched well with the data. The maximum exchange capacity was calculated to be 1.7 mmol/g. From the RHO formula where Si/Al = 3.3, if all the alkali cations could be exchanged, then the exchange capacity should be 3.3 mmol/g. However, only about 50% of the nominal capacity was experimentally shown and this means that a large portion of K^+ remained un-exchanged in RHO. Considering the framework structure of RHO[10], K^+ in the double eight-membered oxygen rings might be difficult to exchange because of its electrostatic stability.
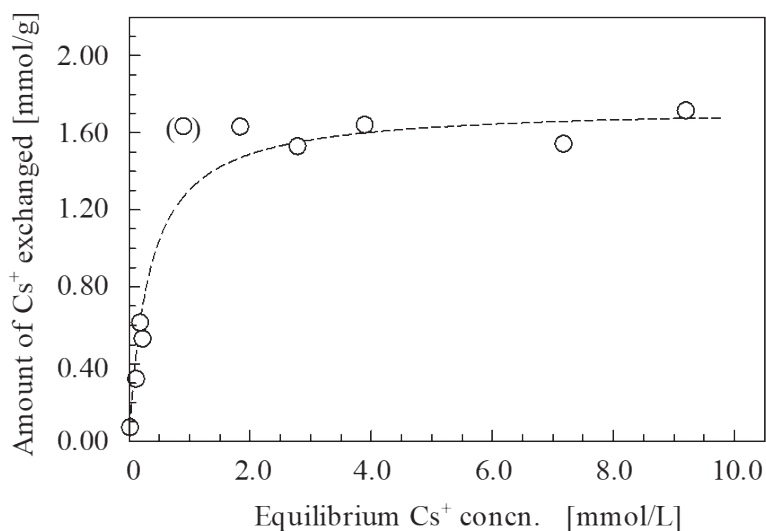
Fig. 4. Adsorption isotherm for Cs^+ with K-RHO

Cs^+ is not the only cation in water but the usual co-existence of other cations is estimated. Therefore, Cs removal from artificial seawater was studied[17,18]. Based on the seawater composition, the types and amounts of co-existing cations were fixed, as shown in Table 2. Cs removal decreased to about 60% in the artificial seawater compared to that in water (Fig. 5), suggesting that the co-existing cation(s) prevented its removal. To understand which element was the most influential, the influence of each element in Table 2 was investigated. As is shown in Fig. 6, K^+ was the most influential element. Because the size of hydrated Cs^+ and K^+ is similar (Cs^+, 3.29 Å; K^+, 3.31 Å)[19], K^+ showed significant influence on Cs removal. Because the radii of hydrated Na^+ (3.58 Å) and divalent cations (approximately 4.1 Å) are large compared to that of Cs^+, diffusion of these hydrated cations through the micro-pore in RHO was slow or inhibited, and less influence was observed.
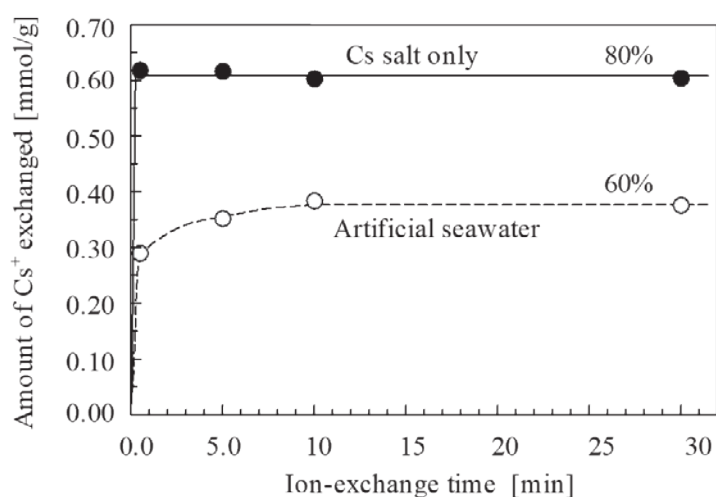

Fig. 5. Cs removal with K-RHO from pure water and artificial seawater

Table 2. Composition of artificial seawater

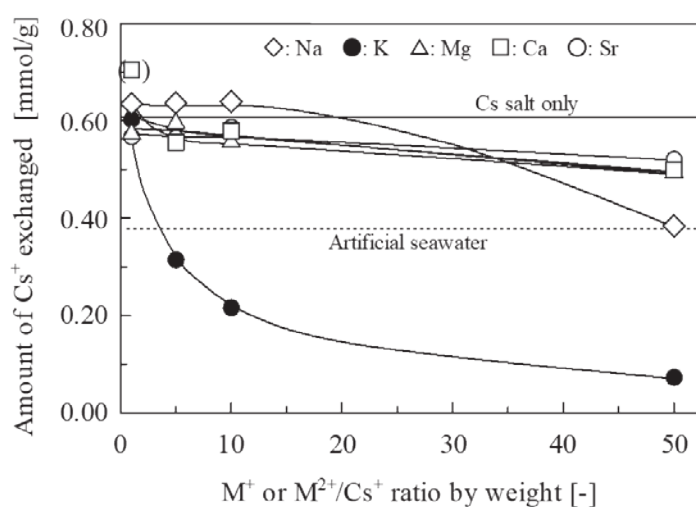|			[mg/L]
NaCl	20747	KBr	85
$MgCl_2 \cdot 6H_2O$	9474	$Na_2B_4O_7 \cdot 10H_2O$	34
Na_2SO_4	3505	$SrCl_2$	12
$CaCl_2 \cdot 6H_2O$	1326	NaF	3
KCl	597	LiCl	1
$NaHCO_3$	171	Other minerals	$\ll 1$
$CsNO_3$	147		

$Cs^+ = 100$ ppm

Fig. 6. Influence of co-existing cation on removal of Cs^+
Conditions: Initial Cs^+ concentration 100 ppm (0.75 meq/L)

4. Conclusions

Zeolite RHO was hydrothermally prepared at 110 °C for 3 days. Analysis by XRD showed formation of crystalline RHO having a BET surface area of approximately 95 m²/g. RHO was used as an ion-exchange material and it showed a high ion-exchange capacity for Cs^+ of 1.7 mmol/g, which was explained by the single-site Langmuir model. The exchange capacity was about 55% of the nominal capacity, and K^+ in the double eight-membered oxygen ring was thought to be stable and difficult to be exchanged. In an artificial seawater, Cs^+ removal decreased to 80% of that in water, and monovalent cations, especially K^+, reduced the removal ability because of its similar hydrated ionic radius to that of Cs^+.

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