

Evaluation of Adsorption Properties for Cs and Sr Selective Adsorbents-13171

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ABSTRACT

The development of effective treatment and disposal methods is very urgent and important subject. Tohoku University and UNION SHOWA have developed various selective adsorbents (zeolites, zeolite sheets and composites loaded with insoluble ferrocyanides) for the effective decontamination of radioactive Cs^+ and Sr^{2+} . As for Cs^+ adsorption, CST, chabazite and insoluble ferrocyanides composites had relatively large distribution coefficients (K_d) above $10^3 \text{ cm}^3/\text{g}$ and excellent adsorption kinetics in seawater. Even after high temperature calcination at $1,100^\circ\text{C}$, cesium was still immobilized in the calcined products of Cs^+ -zeolites, suggesting high immobilization ability of zeolites for Cs^+ . As for Sr^{2+} adsorption, A and X zeolites had relatively large K_d values around $10^2 \text{ cm}^3/\text{g}$, and zeolite sheet (A zeolite) exhibited excellent adsorption kinetics in seawater. Considering the decontamination of radioactive Sr^{2+} in groundwater, the effects of Ca^{2+} and Mg^{2+} ions on the K_d value of Sr^{2+} were further examined by batch method. The K_d value of Sr^{2+} was almost independent of Mg^{2+} concentration up to 2,500 ppm, while gradually lowered in the presence of Ca^{2+} above 200 ppm, due to the differences in the ionic radius of hydrated ion. The Cs^+ and Sr^{2+} adsorption ability for KNiFC-A (composite of A zeolite loaded with insoluble ferrocyanides) was examined by batch method. Here the matrix of composite (A zeolite) and loaded ferrocyanides (KNiFC) have high selectivity towards Sr^{2+} and Cs^+ , respectively. The K_d values of Sr^{2+} and Cs^+ in seawater were estimated to be above 10^2 and $10^3 \text{ cm}^3/\text{g}$, respectively, indicating the effectiveness for the decontamination of both Sr^{2+} and Cs^+ . The basic data on the Cs^+ and Sr^{2+} adsorption properties for selective adsorbents are effective for the practical decontamination processes of these metal ions in seawater and groundwater.

INTRODUCTION

Large amounts of high-activity-level water accumulated in the reactor, turbine building and the trench in the facility were generated from the nuclear accident of Fukushima NPP-1 caused by the Great East Japan Earthquake, which resulted in the operation obstacles and environmental contamination. As of October, 2011, the circulating injection cooling system (**Fig. 1**) is effectively operated and the cold shutdown is completed, while the amounts of high-activity-level water are estimated to be over $200,000 \text{ m}^3$ in future. There was no experience for the treatment and disposal of high-activity-level water containing seawater and groundwater. Further, at present, the treatment and disposal methods for the solid wastes (zeolites, insoluble ferrocyanides and crystalline silicotitanate) are not yet decided. Hence the development of effective treatment and disposal methods are very urgent and important subjects. Tohoku

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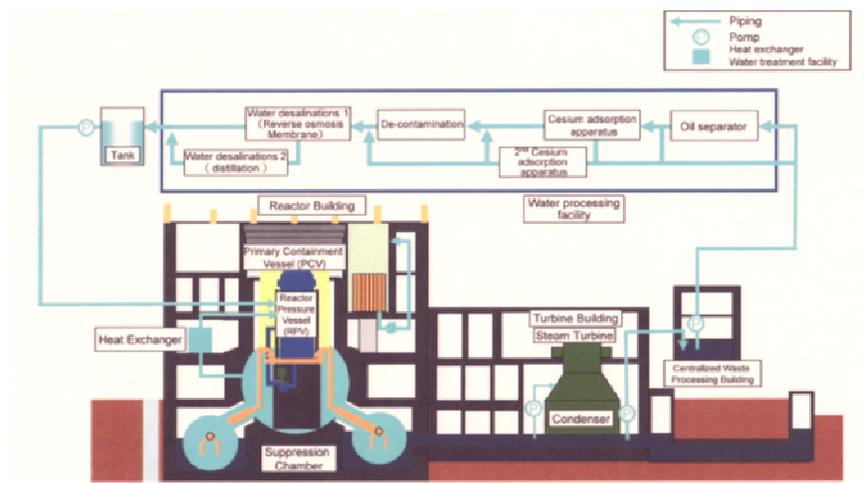


Fig. 1. Decontamination system for high-activity-level water[2]

The present study deals with the preparation and characterization of Cs^+ and Sr^{2+} selective adsorbents and their adsorption properties of radioactive Cs^+ and Sr^{2+} (^{137}Cs , ^{85}Sr) in seawater and groundwater by batch experiments.

EXPERIMENTAL

Materials

In this study, various kinds of zeolites and zeolite sheets produced by UNION SHOWA K.K. (Table I, Table II) and crystalline silico-titanates (CST) were used for the batch adsorption experiments. Fig. 2 illustrates the chemical structures of zeolites used in this study. The composites loaded with insoluble ferrocyanides (KCoFC, KNiFC) were prepared by Tohoku University and UNION SHOWA K.K. The composites of insoluble ferrocyanides and zeolite were prepared by successive impregnation/precipitation methods as follows (Fig. 3). For example, NiFC loaded composites were prepared by the repeated impregnation of $\text{Ni}(\text{NO}_3)_2$ and $\text{K}_4(\text{Fe}(\text{CN})_6)$ solutions into the macropores of zeolite matrices under the experimental conditions of zeolite: 3 g, 1 M $\text{Ni}(\text{NO}_3)_2$ solution: 20 cm^3 , 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$ solution: 20 cm^3 , impregnation time: 3 h and reaction temperature: 25°C.

TABLE I. Characteristics of zeolites.

	1	2	3	4	5	6	7	8
Sample Name	4A	13X	LSX	USY	ZMS-5	IE-96	IE-911	AZ-300
1) Structure	A	2.5X	2.0X	Y	MFI	Chabazite	CST	Alumina+2.5X
2) $\text{SiO}_2/\text{Al}_2\text{O}_3$	2	2.5	2	5	≥ 200	4~6		
3) Exchangeable Cation Group	Na	Na	Na	H	Na	Na,Ca	Na	
4) Specific Surface Area (m^2/g)	≥ 400	≥ 600	≥ 600	≥ 400	≥ 400	≥ 400		
5) Kinetic Diameter (\AA)	4 \AA	9 \AA	9 \AA	9 \AA	6 \AA	5 \AA	4 \AA	
6) Ion Exchange Capacity (meq/g)	5.0~5.5	4.5~5.0	5.0~5.5	≤ 2	≤ 0.5	2.0~2.5	4.0~4.6	2.0~2.5

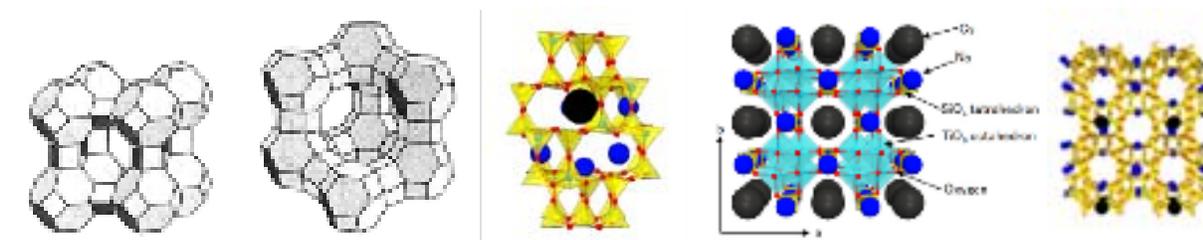


Fig. 2. Structure of zeolite (A, X, Chabazite, CST, Mordenite).

TABLE II. Zeolite sheets

	NA-1	NX-1	CA-1	CX-1
Thickness (mm)	0.26	0.23	0.45	0.45
Weight (m ² /g)	154	153	104	104
Density (m ² /g)	0.59	0.67	0.23	0.23
Attachment method of zeolite	Loading		Coating	
Paper type			PAT-042V(42g/m ²)	
Zeolite wight (m ² /g)	90~93		40~44	
Zeolite type	4A	2.0X	4A	2.0X

Characterization

Surface morphologies of zeolites, composites and calcined specimens were analysed by scanning electron microscopy (SEM, HITACHI, TM-1000) and digital microscope (DM, HiROX, KH-1300). The chemical composition and structure were examined by energy dispersive spectroscopy (EDS, SwiftED-TM, HITACHI, TM-1000) and IR (FT-IR, HORIBA, FT-200).

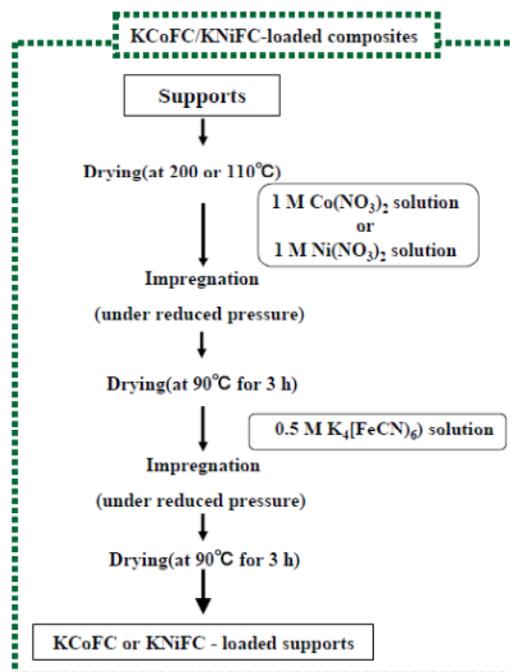


Fig. 3. Loading method for insoluble ferrocyanides.

Determination of Uptake (%) and Distribution Coefficient (K_d)

The distribution of Cs^+ and Sr^{2+} ions for zeolites and composites was estimated by batch method. An aqueous solution (5 cm³) containing 1 ppm Cs^+ or Sr^{2+} ions was contacted with 50 mg of zeolites and composites at $25 \pm 1^\circ\text{C}$ up to 1 d, which was found to be sufficient for attaining equilibrium. The concentrations of Cs^+ and Sr^{2+} ions were measured by NaI(Tl) scintillation counter (Chiyoda Technol, JDC715). The uptake percentage (R , %) of metal ions removed from the solution and the distribution coefficient (K_d , cm³/g) are defined as :

$$R = (C_0 - C_t) / C_0 \times 100, \quad (\%) \quad (\text{Eq. 1})$$

$$K_d = ((C_0 - C_f) / C_f) \times V / m, \quad (\text{cm}^3/\text{g}) \quad (\text{Eq. 2})$$

where C_0 , C_t and C_f (ppm) are the concentration of metal ions at initial, at time t , and at equilibrium, respectively; m (g) the weight of zeolites, zeolite sheets and composites loaded with insoluble ferrocyanides; V (cm³) the volume of aqueous phase.

RESULTS AND DISCUSSION

Uptake of Cs⁺

In order to check the equilibration time of Cs⁺ for zeolites and composites, the effect of shaking time on uptake(%) was examined using distilled water and actual seawater (collected from Matsushima Bay, Miyagi prefecture, filtered by 0.45 μ m Millipore filter) by batch method. Comparing the Cs⁺ uptake (%) among various zeolites, zeolites sheets and CST, CST and chabazite exhibited relatively large uptake (%), indicating the effectiveness of these ion exchangers for the decontamination of Cs⁺ (**Fig. 4**). As for the insoluble ferrocyanide loaded composites, in either case, relatively large uptake (%) above 90% was obtained.

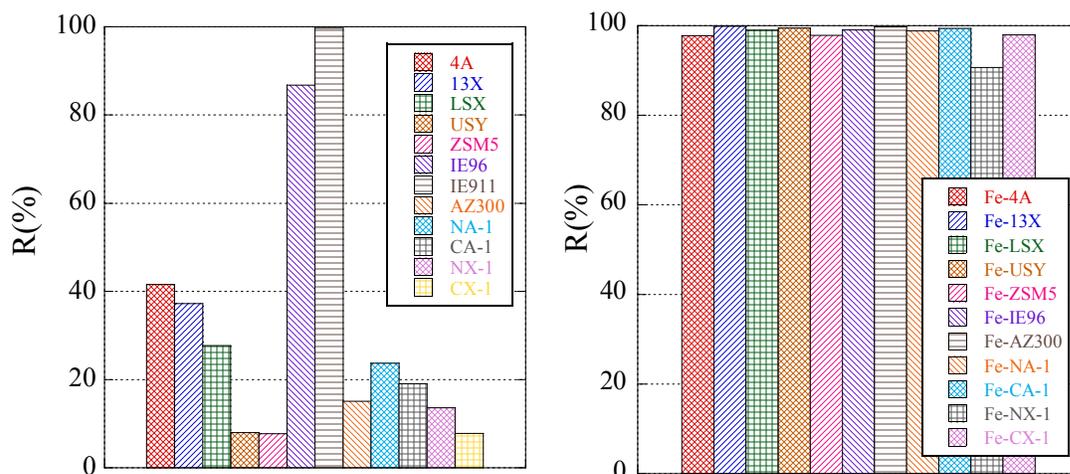


Fig. 4. Uptake(%) of Cs⁺. Zeolites, zeolite sheets and insoluble ferrocyanide loaded composites. 1 ppm Cs⁺ in seawater; 25°C.

Further, the comparison between K_d value of Cs⁺ and adsorption rate constant (relative value) in seawater is shown in **Fig. 5**. The adsorbents are roughly divided into two groups: insoluble ferrocyanide loaded composites and zeolites/CST. As clearly shown in **Fig. 5**, insoluble ferrocyanide loaded composites tend to have relatively large K_d value above 10³ cm³/g, and especially CST(IE911) has the largest K_d value and excellent adsorption kinetics.

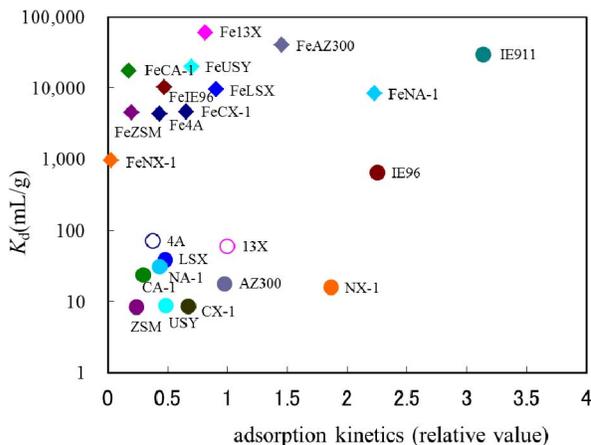


Fig. 5. Distribution property of Cs⁺ and adsorption kinetics. 1 ppm Cs⁺ in seawater ; 25°C.

Immobilization of Cs

The stable immobilization of cesium adsorbed on zeolites is important subject from the stand point of environmental remediation. The adsorbed cesium ions on zeolites were immobilized in the ceramic solid forms by the high temperature calcining treatment. For example, the Cs⁺ content (20.2 wt%) of calcined products is similar to that of Cs⁺ saturated natural zeolites (21.3 wt%), suggesting high immobilization ability of zeolites for Cs⁺ (**Fig. 6**).

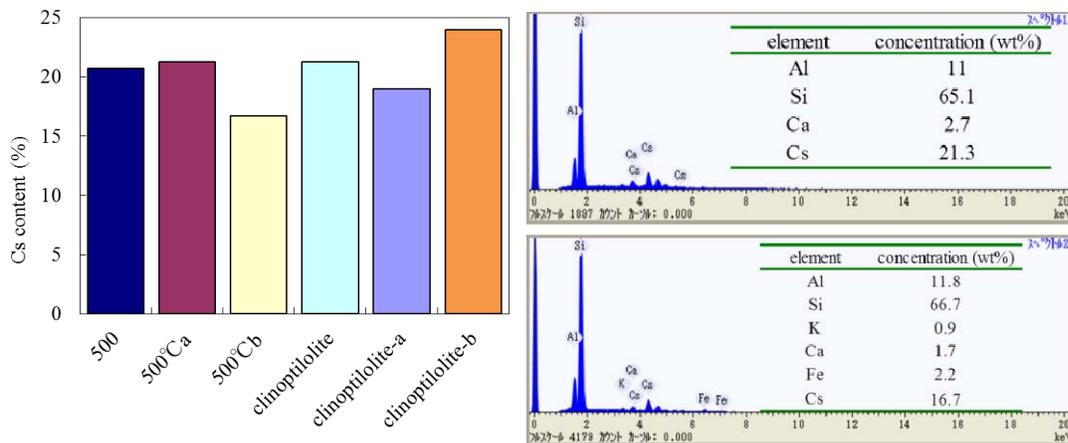


Fig. 6. Cs⁺ content of calcined products (a:1000°C, b:1100°C calcination treatment).

Uptake of Sr²⁺

Similarly to the case of Cs⁺, the equilibration time of Sr²⁺ for zeolites and composites, the effect of shaking time on uptake (%) was examined using distilled water and actual seawater by batch method. Comparing the Sr²⁺ uptake (%) among various zeolites and zeolites sheets, zeolite A and X and their sheets exhibited relatively large uptake (%), indicating the effectiveness of these zeolites for the decontamination of Sr²⁺ (Fig. 7). Especially, CA-1 has relatively large uptake (%) and excellent adsorption kinetics (Fig. 8). On the other hand, the contamination of seawater and groundwater in the high-activity-level water from Fukushima NPP-1 becomes severe problem; hence the effects of Ca²⁺ and Mg²⁺ ions on the uptake (%) of Sr²⁺ for zeolites A were examined by varying the concentration of Ca²⁺ and Mg²⁺ up to 2,500 ppm (Fig. 9).

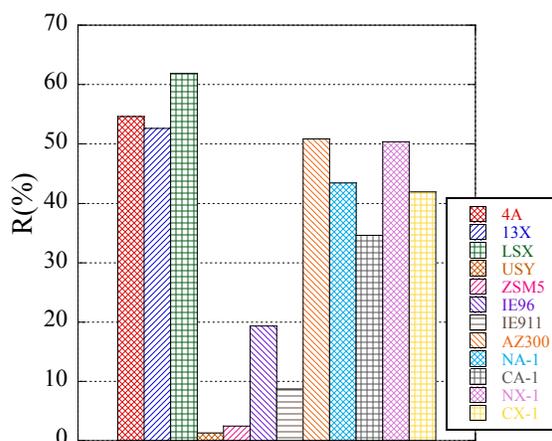


Fig. 7. Uptake(%) of Sr²⁺. Zeolites, zeolite sheets and insoluble ferrocyanid loaded composites. 1 ppm Sr²⁺ in seawater; 25°C.

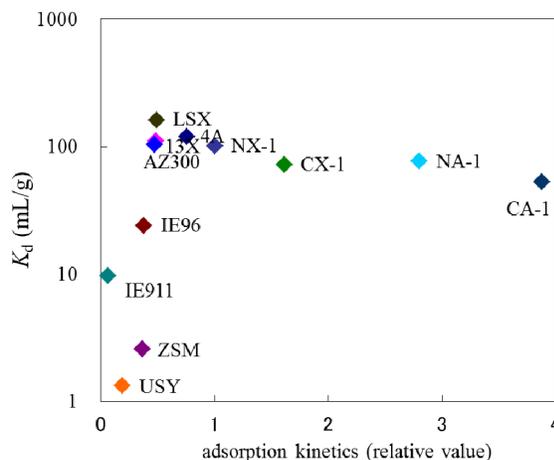


Fig. 8. Distribution property of Sr²⁺ and adsorption kinetics. 1 ppm Sr²⁺ in seawater; 25°C.

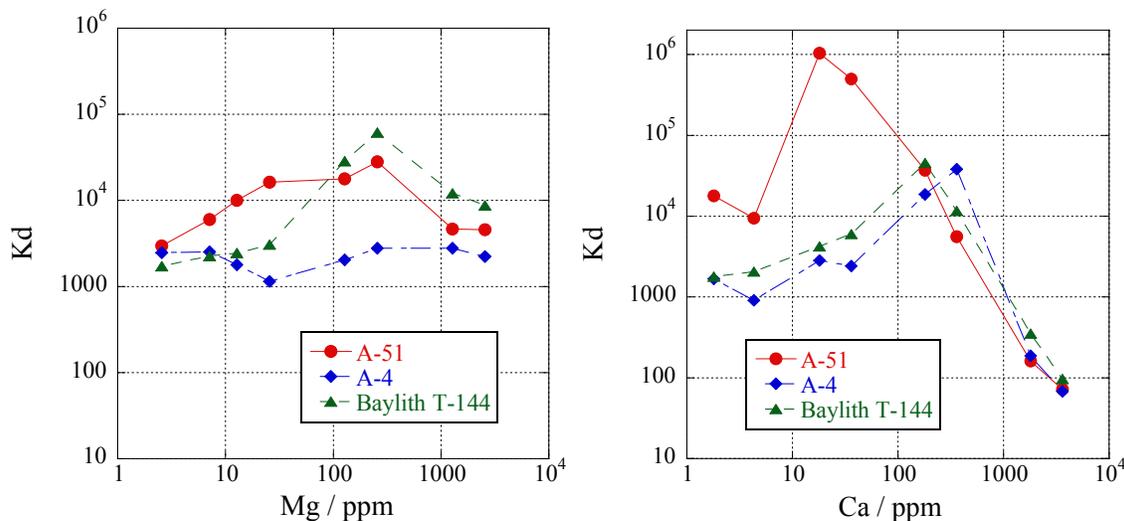


Fig. 9. Effects of Ca^{2+} and Mg^{2+} ions on distribution property. 1 ppm Sr^{2+} ; 25 °C.

In the presence of Mg^{2+} ions up to 2,500 ppm, the K_d value of Sr^{2+} was almost constant, indicating low selectivity; the concentration of Mg^{2+} in seawater has no effect on the uptake of Sr^{2+} for zeolite A. On the other hand, the K_d value of Sr^{2+} tended to decrease with Ca^{2+} concentration above 200 ppm. For example, the concentrations of Ca^{2+} and Mg^{2+} in seawater were estimated to be 400 and 1,400 ppm, respectively. These findings suggest the effect of Ca^{2+} concentration is more significant on the uptake of Sr^{2+} and the removal of Ca^{2+} is essential for the effective uptake of Sr^{2+} .

Uptake of Cs^+ and Sr^{2+} by Composites

Zeolites A is confirmed to have relatively high selectivity towards Sr^{2+} . Hence the insoluble ferrocyanide (KNiFC) with high Cs^+ selectivity was loaded into different zeolite matrices for the effective uptake of both Cs^+ and Sr^{2+} . The fine insoluble ferrocyanides are seen to be loaded on the surface of zeolite matrices and the components of K and Ni are contained in the EDS spectra of composites (**Fig. 10**). The uptake (%) of Cs^+ and Sr^{2+} for the composites in seawater is shown in **Figs. 11**. As clearly shown in **Fig. 11**, relatively large uptake (%) of Cs^+ above 90% was obtained for the composites within 3 h, while single zeolites A had low uptake (%) of Cs^+ . As for the uptake (%) of Sr^{2+} for the composites (Fe-Mordenite, Fe-A51J, Fe-LSX), the insoluble ferrocyanide loaded zeolite A (A51) had relatively large uptake (%) of Sr^{2+} , indicating the high selectivity of zeolite A towards Sr^{2+} is still maintained after loading of insoluble ferrocyanides. Thus the insoluble ferrocyanide loaded zeolite A is confirmed to have adsorbability for both Cs^+ and Sr^{2+} . In addition, the novel zeolite A granule (A-51J and A-51JCD) with small diameter of 0.5~1.0 mm had relatively large uptake (%) of Sr^{2+} . In particular, A-51JCD with no binder exhibited uptake (%) of Sr^{2+} above 80% which is the highest value in the conventional granular zeolites A. The basic data on the Cs^+ and Sr^{2+} adsorption properties of selective adsorbents are effective for the practical decontamination processes of these metal ions in seawater and groundwater.

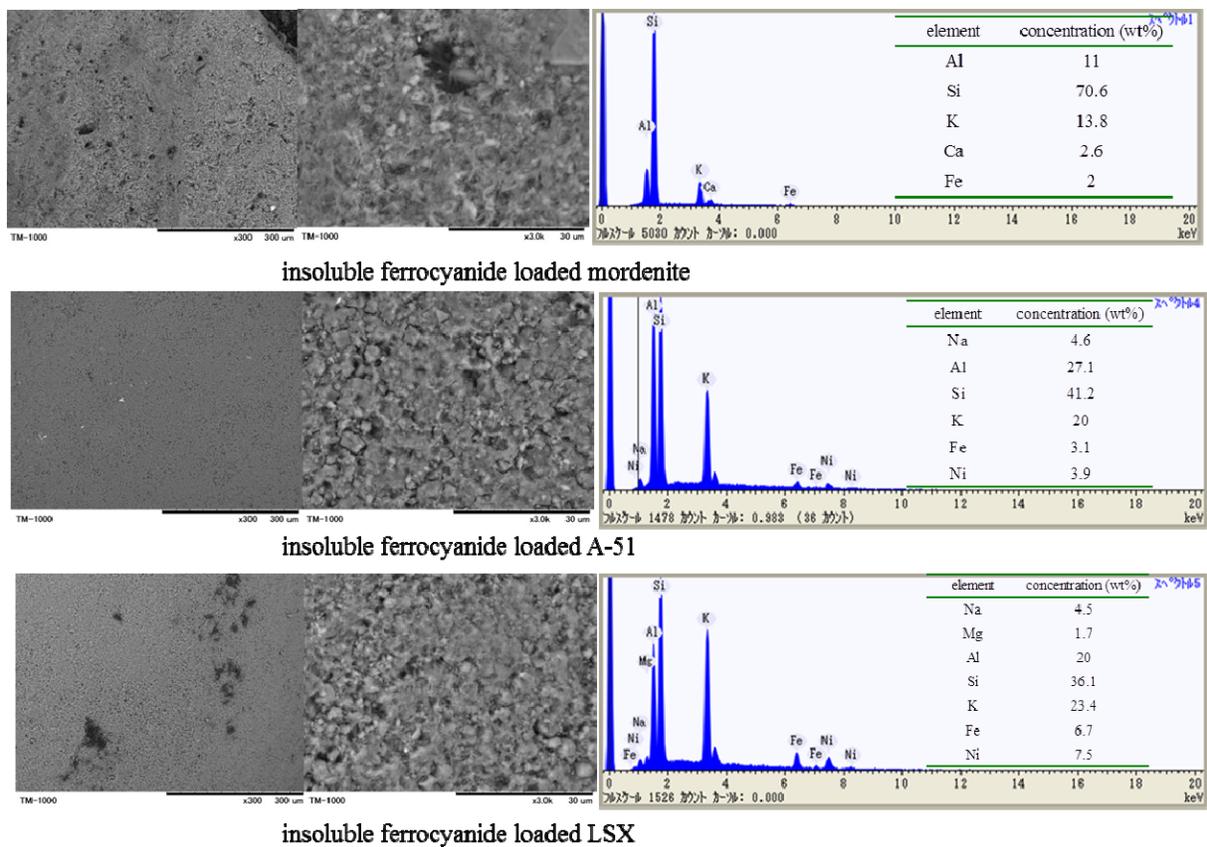


Fig. 10. SEM images and EDS spectra of insoluble ferrocyanide loaded zeolites.

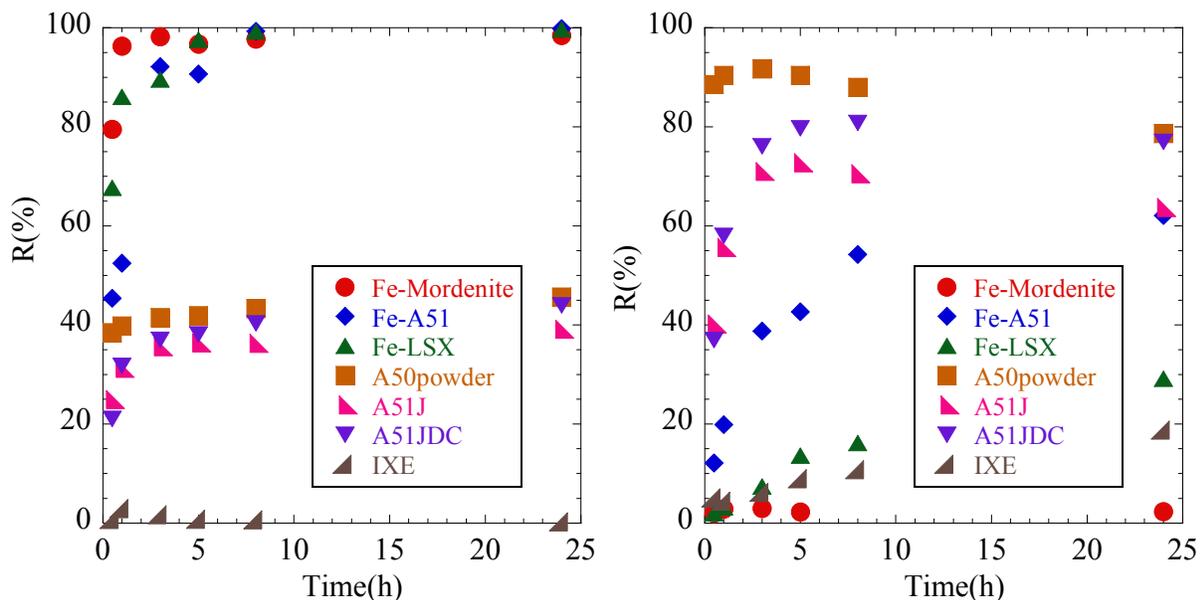


Fig. 11. Effects of shaking time on uptake(%) of Cs⁺(left) and Sr²⁺(right). Zeolite, composites of insoluble ferrocyanides. 1 ppm Cs⁺ and Sr²⁺ in seawater; 25°C.

CONCLUSIONS

The Cs^+ and Sr^{2+} adsorption ability of zeolites, zeolite sheets and composites loaded with insoluble ferrocyanides were examined by batch method. Comparing the Cs^+ uptake (%) among various zeolites, zeolites sheets and CST, CST and chabazite which used in the radioactive accumulated water treatment system exhibited relatively large uptake (%) in seawater. As for the insoluble ferrocyanide loaded composites, in either case, relatively large uptake (%) above 90% was obtained. The adsorbed cesium ions on zeolites were immobilized in the ceramic solid forms by the high temperature calcining treatment. Further, Cs^+ content (20.2 wt%) of calcined products is similar to natural zeolites (21.3 wt%), suggesting high immobilization ability of zeolites for Cs^+ . Similarly to the case of Cs^+ , Sr^{2+} uptake (%) for zeolites and zeolite sheets examined using actual seawater by batch method. Comparing the Sr^{2+} uptake (%) among various zeolites and zeolites sheets, zeolites A and X and their sheets exhibited relatively large uptake (%), indicating the effectiveness of these zeolites for the decontamination of Sr^{2+} . The effects of Ca^{2+} and Mg^{2+} ions on the uptake (%) of Sr^{2+} for zeolite A were examined by varying the concentration of Ca^{2+} and Mg^{2+} up to 2,500 ppm. In the presence of Mg^{2+} ions up to 2,500 ppm, the K_d value of Sr^{2+} was almost constant. The concentration of Mg^{2+} in seawater has no effect on the uptake of Sr^{2+} for zeolite A. On the other hand, the K_d value of Sr^{2+} tended to decrease with Ca^{2+} concentration above 200 ppm. The uptake rate of Cs^+ and Sr^{2+} ions for the insoluble ferrocyanide loaded A zeolite are examined by seawater. Large uptake (%) of Cs^+ above 90% was obtained for the composites within 3 h, while single zeolites A had low uptake (%) of Cs^+ . As for the uptake (%) of Sr^{2+} for the composites, the insoluble ferrocyanide loaded zeolite A had relatively large uptake (%) of Sr^{2+} , indicating the high selectivity of zeolite A towards Sr^{2+} is still maintained after loading of insoluble ferrocyanides. Thus the insoluble ferrocyanide loaded zeolite A is confirmed to have adsorbability for both Cs^+ and Sr^{2+} . The practical study of zeolites and insoluble ferrocyanide loaded composites is essential for the improvement of radioactive accumulated water treatment system.

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