

Uptake Selectivity for Different Types of Zeolites in the Presence of Boric Acid - 15244

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ABSTRACT

The development of selective adsorbents is very important subject for the effective multi-nuclide decontamination related to the severe accident of Fukushima NPP-1. Many removal methods have been developed to separate nuclide from decontaminated solutions containing multi-nuclide so far. From the standpoint of cost efficiency, stability for usage and safety handling, the decontamination methods using inorganic adsorbents are one of the most effective methods for the selective decontamination system. Thus, many researches related to inorganic adsorbents have been carried out after the accident; actually, in Fukushima NPP-1, zeolites are used to remove radioactive nuclides from decontaminated water as a main adsorbent in the circulating injection cooling system. However, the adsorption characteristics of zeolites in the presence of boric acid have not been clarified in detail. As for the decontamination in PWR[1], the adsorption properties should be examined in the presence of highly concentrated boric acid. Based on this background, the final objective of this study is to develop the decontamination methods in PWR-NPP by using various zeolites for multi-nuclide. In this study, the adsorption properties for eight kinds of zeolites (Zeolite A, Zeolite X, Zeolite Y, Zeolite L, Chabazite, Synthetic Mordenite, Natural Mordenite and Clinoptilolite) are evaluated in the presence of boric acid and seawater. The present study deals with (1) selective adsorption properties for single nuclide ion ($^{137}\text{Cs}^+$, $^{60}\text{Co}^{2+}$, $^{85}\text{Sr}^{2+}$ and $^{152}\text{Eu}^{3+}$), (2) preparation of Ag-loaded Natural Mordenite (Ag-NM) and uptake properties of I⁻ ions, and (3) multi-nuclide decontamination properties of 26 elements (typical elements in Advanced Liquid Processing System (ALPS) in Fukushima NPP-1) for the above zeolites.

INTRODUCTION

Large amounts of high-activity-level water (HALW) over 500,000 m³ accumulated in the reactor, turbine building and the trench in the facility were generated from the nuclear accident of Fukushima NPP-1 (BWR) caused by the Great East Japan Earthquake. At present, the cold shutdown is completed stably by the circulating injection cooling system (**Fig. 1**) for the decontamination of radioactive nuclides such as ^{134}Cs and ^{137}Cs ; Simplified Active Water Retrieve and Recovery System (SARRY) and KURION are operated very effectively for the separation of radioactive Cs by using zeolites, a kind of inorganic ion-exchanger. Further, the Advanced Liquid Processing System (ALPS) (**Fig. 2**) is under operation for the decontamination of 62 nuclides such as ^{90}Sr , ^{129}I and ^{152}Eu ; this multi-nuclide decontamination system consists of two coprecipitation processes and adsorption process using different adsorbents such as activated carbon, titanium hydroxides and chelating resins. In the case of PWR accident, the decontaminated water contains highly concentrated boric acid. Hence it becomes very important to evaluate the adsorption properties of radioactive nuclides in the presence of boric acid and seawater. In

this study, the adsorption properties of radioactive nuclides (single ion: $^{60}\text{Co}^{2+}$, $^{85}\text{Sr}^{2+}$, $^{137}\text{Cs}^{+}$ and $^{152}\text{Eu}^{3+}$; 26 elements-mixed solution referring to ALPS in Fukushima NPP-1) in the presence of highly concentrated boric acid (3,000 ppm) and seawater were examined by batch adsorption methods using various zeolites.

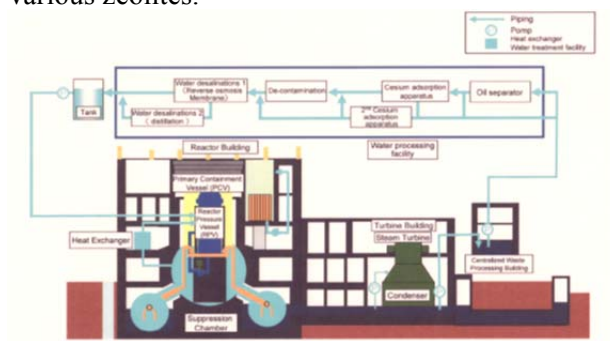


Fig. 1. Circulating injection cooling system for highly contaminated water in Fukushima NPP-1[3].

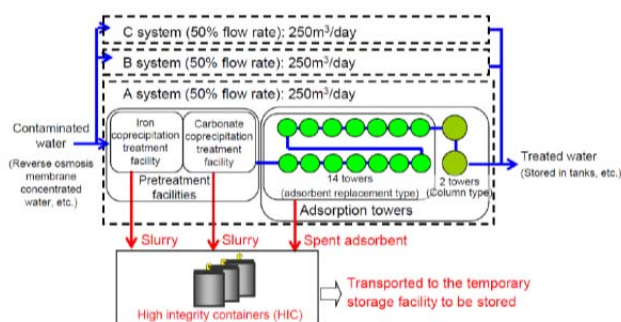


Fig. 2. Multi-nuclide decontamination system (ALPS) in Fukushima NPP-1[4].

EXPERIMENTAL

Materials

In this study, eight kinds of zeolites (Zeolite A, Zeolite X, Zeolite Y, Zeolite L, Chabazite, Synthetic Mordenite, Natural Mordenite and Clinoptilolite) were used as listed in **Table I**, and digital microscope images of these samples are listed in **Fig. 3**. Zeolite A (A-51JHP), Zeolite X (13X), Zeolite Y (USY), Zeolite L (UOP-L) and Chabazite (IE-96) were obtained from Union Showa K.K. Synthetic Mordenite (900Na, SM) and Natural Mordenite (2460#, NM, Ayashi) were obtained from Norton and Shin Tohoku Kagaku Kogyo and Clinoptilolite (Futatsui, CP) were obtained from San Zeolite.

TABLE I. Chemical compositions of zeolites

Zeolite	Typical Unit Cell Content	Si/Al
A	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)]27\text{H}_2\text{O}$	1.0
X	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]264\text{H}_2\text{O}$	1.23
Y	$\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]250\text{H}_2\text{O}$	2.43
L	$\text{K}_9[(\text{AlO}_2)_9(\text{SiO}_2)_{27}]22\text{H}_2\text{O}$	3.0
Chabazite	$\text{Na}_4[(\text{AlO}_2)_4(\text{SiO}_2)_8]13\text{H}_2\text{O}$	2.0
SM	$\text{Na}_{8.7}[(\text{AlO}_2)_{8.7}(\text{SiO}_2)_{39.3}]24\text{H}_2\text{O}$	4.52
NM	$\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{40}]24\text{H}_2\text{O}$	5.0
CP	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]24\text{H}_2\text{O}$	5.0

Zeolite	A-51JHP	13X	USY	UOP-L
DM				
Diameter	0.5mm	20-32 mesh	20-32mesh	20-32mesh
Zeolite	IE-96	900Na	2460#	CP(Futatsui)
DM				
Diameter	0.2-0.5mm	20-32 mesh	0.4-1mm	20-30mesh

Fig. 3. Digital microscope images and diameter of zeolites.

Preparation of Ag-NM

In order to remove I^- ions, the novel selective inorganic adsorbent of Ag-natural mordenite (Ag-NM) was prepared by ion-exchange methods. The conditions for the ion-exchange methods are as follows; amount

of NM: 0.05-50 g; concentration and volume of Ag⁺ solution: 1,000 ppm, 100 cm³; contacting and degassing time: 24 h.

Instrumental Analyses

The surface morphologies of zeolites were examined by scanning electron microscopy (SEM, Hitachi, TM-3030) and digital microscope (DM, HiROX, KH-1300). The chemical composition and the structure of zeolites were determined by energy dispersive spectrometry (EDS: Swift ED-TM, HITACHI, TM-3030) and powder X-ray diffractometry (XRD, Rigaku RINT2000) using monochromatized Cu-K_α radiation, respectively. The Ag content loaded in the natural mordenite was estimated by EDS.

Batch Adsorption Experiments

Table II summarized the target ions, experimental conditions and components of test solutions for the batch adsorption experiments. As for single nuclide ions (Co²⁺, Sr²⁺, Cs⁺ and Eu³⁺), three kinds of test solutions containing 3,000 ppm of boric acid and seawater (collected from Matsushima Bay, Miyagi prefecture, filtered by 0.45μm Millipore filter) were prepared. As for the uptake of iodide ions (I⁻), Ag-NM (Ag-loaded Natural Mordenite) was used. The adsorption experiments for multi-nuclide ions were carried out using the test solutions containing 26 elemental ions (**Table III**) referred to ALPS.

Table II Target ions, experimental conditions and components of test solutions for the batch adsorption experiments

Target ions	Experimental conditions	Test solutions
Single nuclide ions (Co ²⁺ , Sr ²⁺ , Cs ⁺ and Eu ³⁺)	Volume: 5 cm ³ Zeolite: 50 mg Carrier concentration: 1 ppm Temp.: 25±1°C Shaking time: 24h	(1)H ₃ BO ₄ : 3,000 ppm + LiOH: 10 ppb + DW (deionized water) (2)H ₃ BO ₄ : 3,000 ppm + seawater (30% diluted) + DW (3)H ₃ BO ₄ : 3,000 ppm + seawater
Single nuclide ion (I ⁻)	Volume: 5 cm ³ Zeolite (Ag-NM): 50 mg Carrier concentration: 10 ppm Temp.: 25±1°C Shaking time: 24h	(1)H ₃ BO ₄ : 3,000 ppm + LiOH: 10 ppb + DW (deionized water) (2)H ₃ BO ₄ : 3,000 ppm + seawater (30% diluted) + DW
Multi-nuclide ions (26 elements, Table III)	Volume: 20 cm ³ Zeolite: 200 mg Carrier concentration: 10 ppm Temp.: 25±1°C Shaking time: 24h	(1)H ₃ BO ₄ : 3,000 ppm + LiOH: 10 ppb + DW (deionized water)

TABLE III. Twenty six elements in mixed solution referring to ALPS

Valence	Ions
I	Cs, Rb, Ag, I
II	Sr, Cd, Ba, Co, Ni, Zn, Mn
III	Fe, Ru, Rh, Y, Ce, Pr, Sm, Eu, Gd, Tb
IV	Te, Sn
V	Sb, Nb
VI	Re

Determination of Uptake (%)

The distribution of Co^{2+} , Sr^{2+} , Cs^+ , Eu^{3+} and other ions for zeolites was examined by batch method. In the case of radioactive nuclides (^{60}Co , ^{85}Sr , ^{137}Cs and ^{152}Eu) experiments, NaI (TI) scintillation counter (Chiyoda Technol, JDC-715) was applied to determine the radioactivity concentration and in the case of non-radioactive nuclides experiments, ICP-AES (SII, SPS 7800) and AAS (Thermo Scientific, iCE 3000 SERIES AA Spectrometer) were used to determine the concentration of each elemental ions. The uptake percentage (R , %) of metal ions removed from the test solution was defined as :

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

where C_i and C_f (ppm or cpm) are the concentration of metal ions at initial, and at equilibrium, respectively.

RESULTS AND DISCUSSION

Characterization of Ag-NM and Uptake of I

As for the loading of Ag^+ ions into Natural Mordenite (NM), the Ag content in NM was determined by EDS. **Figure 4** shows EDS spectra of Ag-NM and mapping of Ag^+ ions on the surface of Ag-NM. In EDS and mapping, Ag^+ ions were detected and incorporated uniformly in mordenite structure. **Figure 5** shows the variation of Ag content with added amount of NM. Ag content markedly increased with decreasing with the amount of NM added; maximum content of Ag was estimated to be 7.0 wt%.

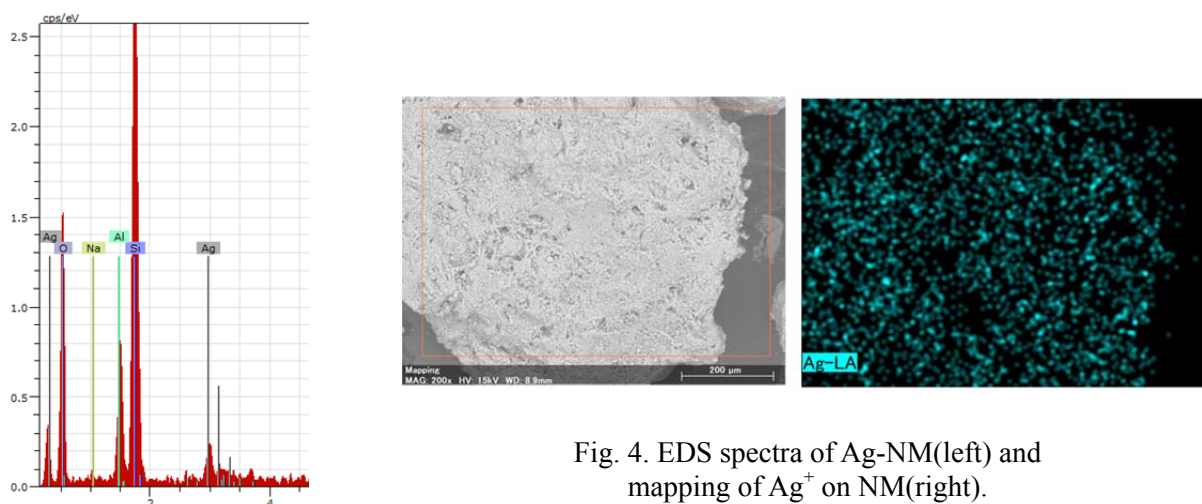


Fig. 4. EDS spectra of Ag-NM(left) and mapping of Ag^+ on NM(right).

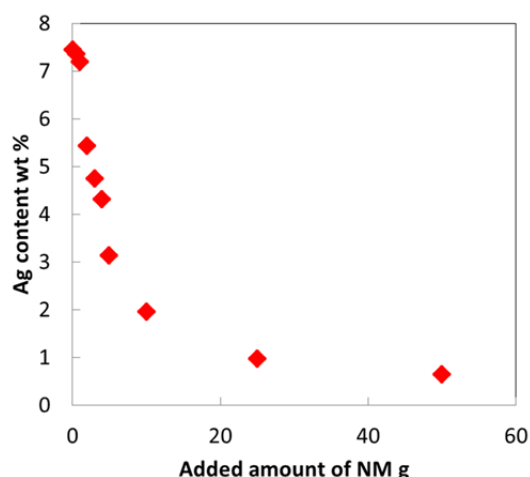


Fig. 5. Variation of Ag content with added amount of NM

Comparison of Uptake(%) of Co^{2+} , Sr^{2+} , Cs^+ and Eu^{3+} ions for Different Zeolites

In order to check the adsorption nuclide selectivity of nuclide ions ($^{60}\text{Co}^{2+}$, $^{85}\text{Sr}^{2+}$, $^{137}\text{Cs}^+$ and $^{152}\text{Eu}^{3+}$) for different types of zeolites, the uptake behaviors were examined by using three kinds of test solutions containing 3,000 ppm of boric acid and seawater (**Figs. 6(a)-(d)**). Most of zeolites had relatively large uptake (%) above 90% for these radioactive nuclides in deionized water (DW). On the other hand, the uptake (%) in the test solutions of seawater (30% diluted) and real seawater was markedly lowered and the difference of adsorption selectivity was clearly observed among zeolites.

(1) Co^{2+} and Sr^{2+} adsorption

In the case of Co^{2+} and Sr^{2+} adsorption, Zeolite A and Zeolite X with three-dimensional cage structure had relatively large uptake (%) even in the presence of seawater; around 90% in 30% diluted seawater.

(2) Cs^+ adsorption

Zeolites with lantern or tunnel structure such as Chabazite, SM and NM had relatively large uptake (%) of Cs^+ around 90% in real seawater; in these zeolites, ion-sieving effect for the metal ions except for Cs^+ ions is observed clearly.

(3) Eu^{3+} adsorption

In the case of Eu^{3+} adsorption, Zeolite A, Zeolite X and Zeolite L had relatively large uptake (%) in the presence of seawater. According to the previous study [5], Zeolite L had the highest K_d value of Eu^{3+} ions above $10^3 \text{ cm}^3/\text{g}$ in the presence of 0.1 M Na^+ (initial pH 3) among various zeolites. In order to compare the adsorption selectivity of Eu^{3+} ions for the above zeolites, the uptake (%) of Eu^{3+} ions is determined in a wide pH range (pH 2-8) using three kind of solutions (DW, seawater (30% diluted) and real seawater) as shown in **Fig. 7**. The uptake (%) of Eu^{3+} ions for zeolite A, X and L tended to increase with equilibrium pH. Especially, in the acidic region up to pH 5, zeolite L with main c-channels 7.1-7.8 Å in free diameter had relatively large uptake (%) for Eu^{3+} ions. On the other hand, above pH 5, zeolite X and A had larger uptake (%); above pH 5, the adsorption of hydrolysis species such as $\text{Eu}(\text{OH})_2^+$ and $\text{Eu}(\text{OH})_3$ is probably dominant.

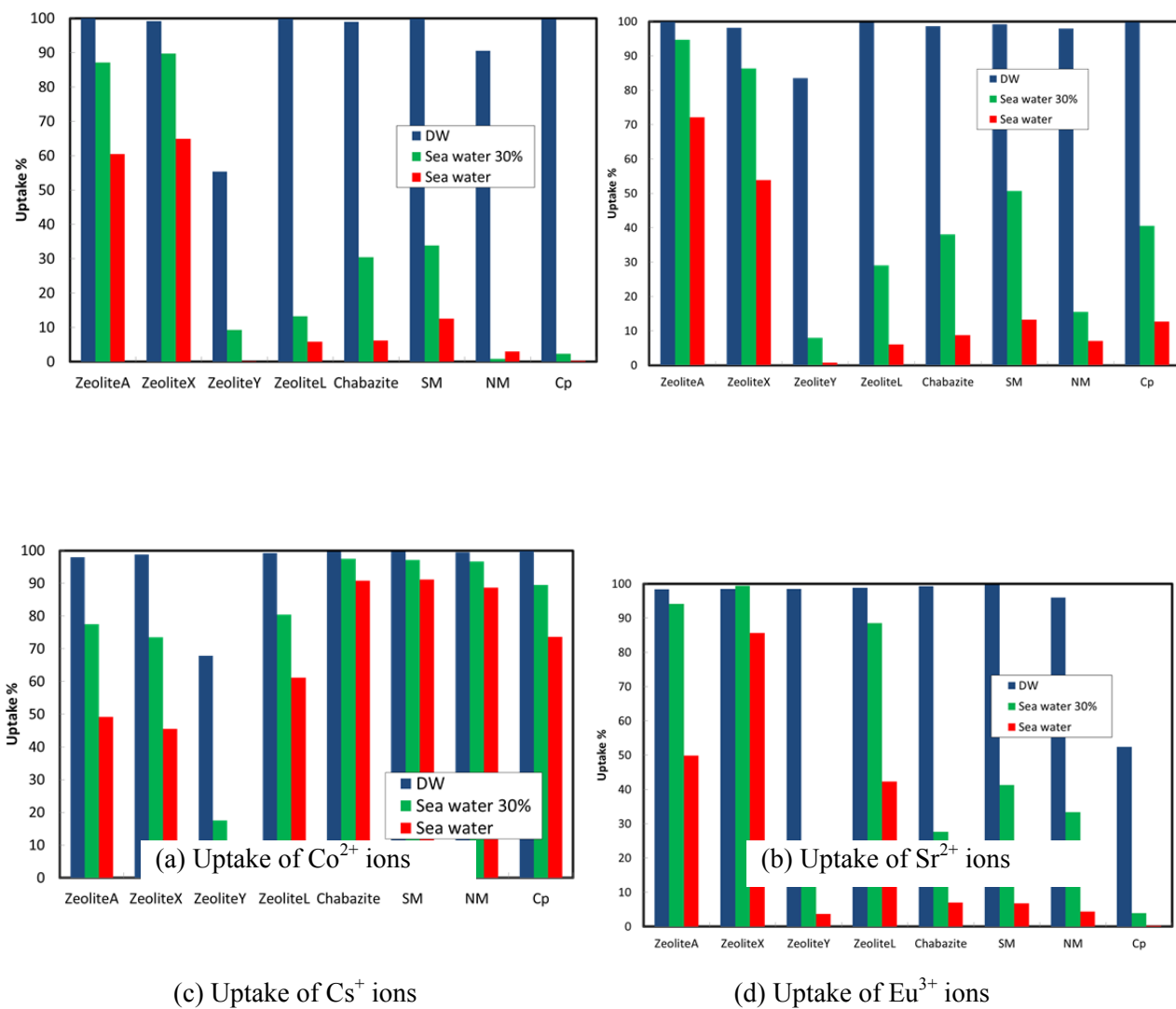


Fig. 6. Uptake (%) of Co^{2+} , Sr^{2+} , Cs^+ and Eu^{3+} for different types of zeolites.

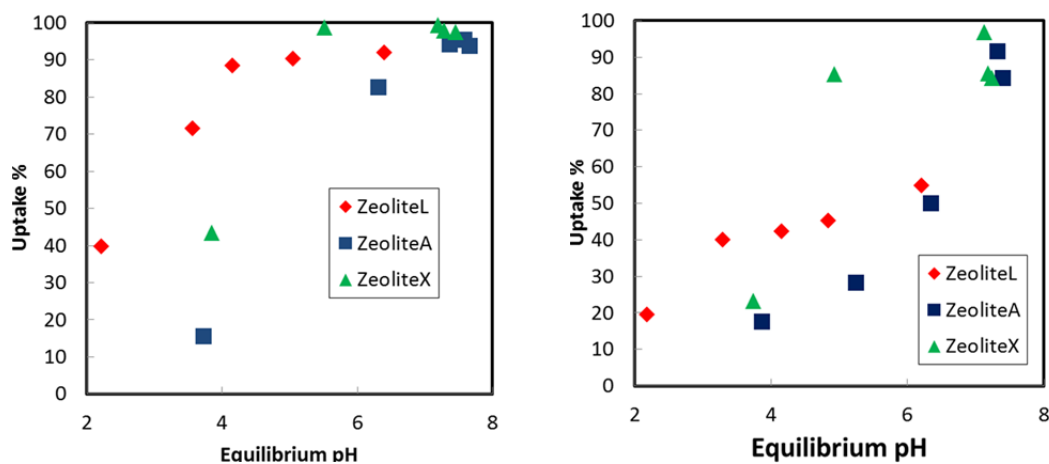


Fig. 7. Effect of equilibrium pH on uptake (%) of Eu^{3+} ions for zeolite A, X and L in 30% diluted seawater (left) and real seawater. (right).

Uptake of I⁻ ions

Corresponding to the results in Fig. 5, the effect of added amount of NM on the uptake (%) of I⁻ ions in deionized water (DW) and seawater (30% diluted) is shown in **Fig. 8**. The uptake (%) of I⁻ ions in DW was more than 95% below 10 g of added amount of Ag-NM with the content of Ag above 2 wt%. The uptake of I⁻ ions for Ag-NM is probably due to the precipitation of insoluble AgI in the macropores of NM; the solubility product of AgI is very low (solubility product: $[Ag^+][I^-]=1.5\times 10^{-16}$ [mol/l]²). On the other hand, the uptake (%) of I⁻ ions in seawater was estimated to be around 40% which was lower than that in DW. This is due to the existence of competitive Cl⁻ ions in seawater. As for Ag-NM, the mordenite matrix (NM) also has Cs selectivity as already shown in Fig. 6(c)), and hence the Ag-NM is effective for the selective adsorption of both Cs⁺ and I⁻ ions in contaminated water. The EDS shows the incorporation of I⁻ ions in Ag-NM (**Fig. 9**), and the incorporation of I⁻ ions inside the Ag-NM particle was uniform as shown in **Fig. 10**.

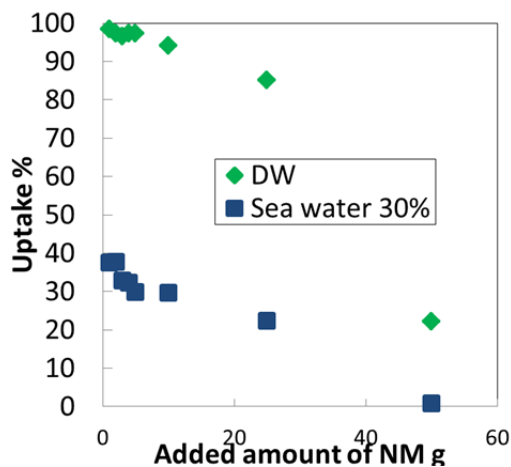


Fig. 8. Uptake (%) of I⁻ ions by Ag-NM.

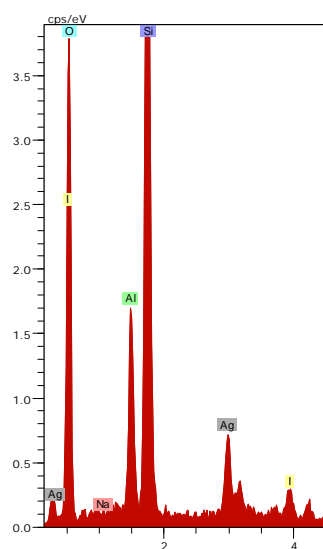


Fig. 9. EDS spectra of Ag-NM after adsorption for I⁻ ions.

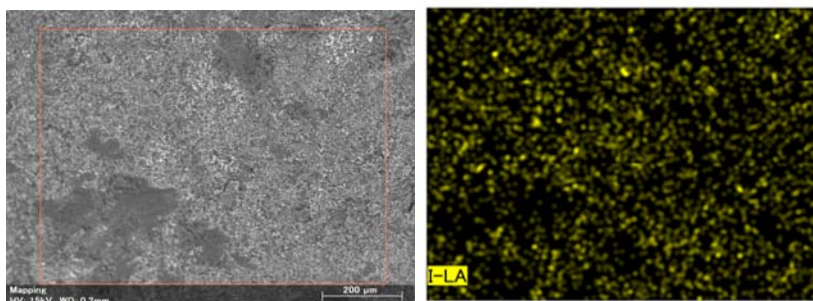


Fig. 10. EDS mapping of I⁻ ions in Ag-NM. SEM image (left) and mapping of I (right).

Uptake Tendencies for 26 Elements on Zeolites

Adsorption behavior of twenty six elements (Table II) referred to the ALPS in Fukushima NPP-1 for various zeolites (Zeolite A, Zeolite X, Zeolite Y, Zeolite L and Natural Mordenite) were examined from the standpoint of multi-nuclides decontamination. **Figure 11 (a)-(d)** show the uptake of twenty six elements in DW with boric acid (Table III). The uptake behavior was roughly divided into 4 groups. Most of the elements are adsorbed more or less by Zeolite A and Zeolite X. Compared with other zeolites, these zeolites tend to have relatively high adsorbability for divalent metal ions like Sr^{2+} , Cd^{2+} , Ba^{2+} , and Co^{2+} , etc.(Fig. 11(a)). In contrast, Zeolite Y and mordenite tend to have limited adsorbability only for a few elements; zeolite Y has adsorbability for multivalent metal ions like Sn(IV) and Nb(V), etc.(Fig. 11(b)), and mordenite for monovalent alkali metal ions like Rb^+ and Cs^+ . As for Zeolite L, relatively large uptake (%) above 90% was obtained for trivalent ions such as lanthanide ions (Ce^{3+} and Eu^{3+}). Even though hydrolysis of some metal ions should be considered, these findings indicate that high concentrated boric acid up to 3,000 ppm has no influence on the adsorption of these zeolites. The combination of these zeolites is thus effective for the multi-nuclide decontamination.

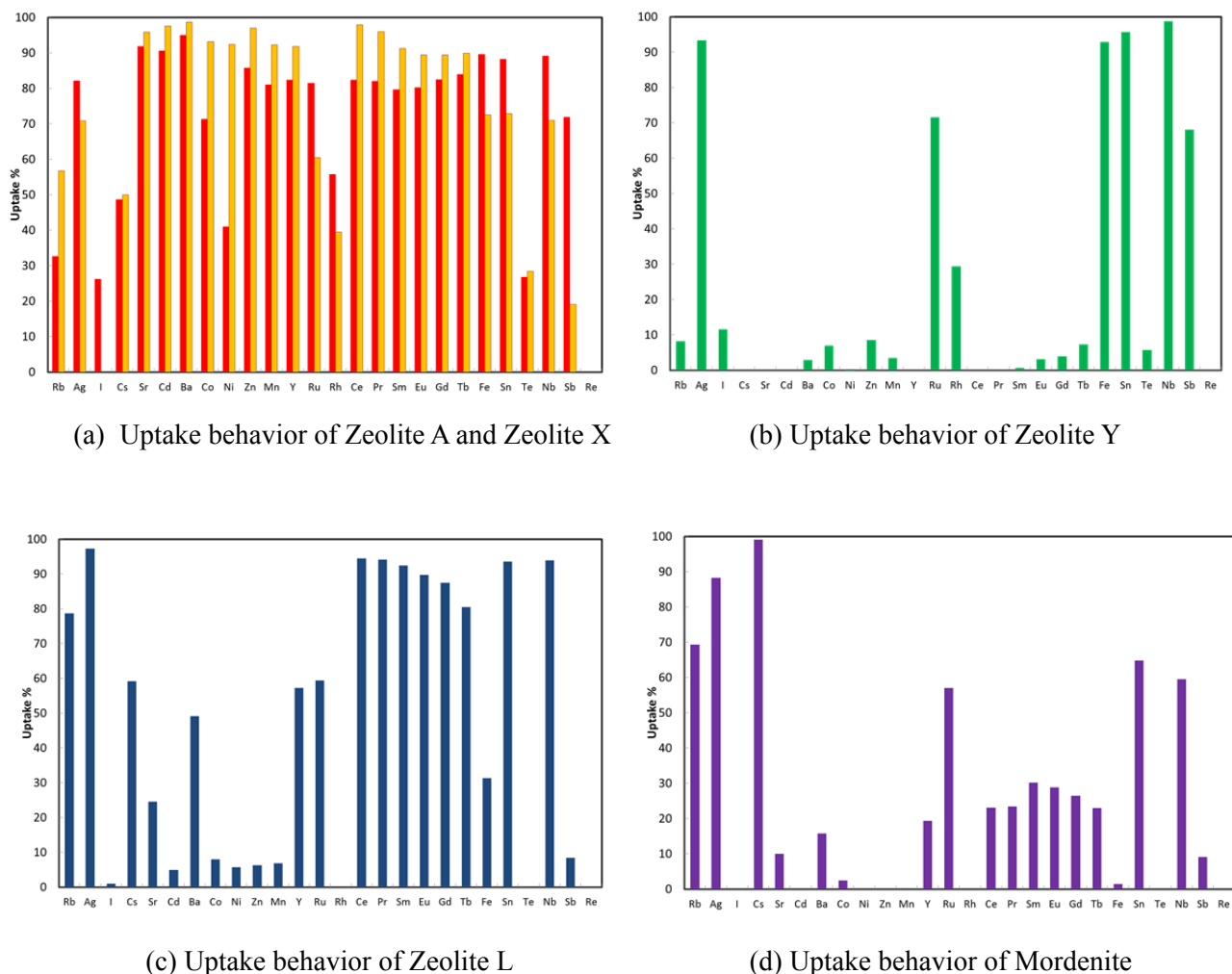


Fig. 13. Uptake (%) of twenty six elements in DW with boric acid.

CONCLUSIONS

As for the single nuclide experiment, the adsorption properties were evaluated in DW and seawater containing 3,000 ppm of boric acid. Most of the zeolites showed high adsorption performance for ^{85}Sr , ^{60}Co , ^{137}Cs and ^{152}Eu . As the concentration of seawater increased, the uptake (%) in some zeolites tended to decrease due to the difference of selectivity. It became apparent that zeolites A and X were effective for the adsorption of Sr^{2+} and Co^{2+} ions under the practical condition (30% diluted seawater). Chabazite, mordenite and clinoptilolite are very effective for the adsorption of Cs^+ ions even in real seawater, and zeolite L is effective for the adsorption of Eu^{3+} ions under practical condition, respectively.

As for the Ag-NM, Ag-NM are expected to have high adsorption performance for I^- ions. The content of Ag increased up to 7 wt% with decreasing the added amounts of NM. Relatively large uptake (%) of I^- ions above 90% was obtained for Ag-NM in the presence of boric acid, while the uptake of I^- ions was markedly lowered in 30% diluted seawater.

Selective adsorption tendencies for different zeolites were evaluated for 26 elements referred to ALPS. Comparing the uptake results for different zeolites, it became apparent that zeolites A and X exhibited relatively high adsorption selectivity for divalent ions of Sr^{2+} and Co^{2+} ions. Zeolite L had adsorption selectivity for trivalent lanthanide ions such as Ce^{3+} and Eu^{3+} . Mordenite had adsorption selectivity for monovalent alkali metal ions of Rb^+ and Cs^+ . These tendencies are the same as those without boric acid. From these results, it became clear that these zeolites show the similar tendencies even in the presence of boric acid. These findings suggest that zeolites are effective for the selective decontamination system for PWR-NPP considering the difference in their adsorption properties.

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