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Sorption behavior of U and Np on zeolite

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At the Fukushima Daiichi nuclear power station, spent zeolite used to remove radionuclides from contaminated water will be disposed of as the secondary wastes of water treatment. To estimate radionuclides inventory in the spent zeolite, sorption ability of radionuclides needs to be investigated. In this study, distribution coefficients (K_d) of U and Np on chabazite, which is the zeolite used in the second cesium adsorption apparatus (SARRY), were obtained by batch sorption experiments. The obtained K_d of U was 0.0021 m³/kg in simulated seawater, while the K_d was 0.68 m³/kg in simulated seawater diluted ten times by deionized water. On the other hand, the K_d of Np was 0.0085-0.0087 m³/kg and independent of seawater concentration. From the experiments as functions of Na⁺, carbonate concentrations and pH, the K_d of U was found to be strongly affected by carbonate concentration in the pH range 8-9, while both Na⁺ and carbonate concentrations had little effect on the K_d of Np.

Keywords: Fukushima Daiichi nuclear power station; secondary waste; zeolite; radionuclides inventory; sorption; Uranium; Neptunium; carbonate

1. Introduction

At the Fukushima Daiichi nuclear power station, contaminated water retained in the reactor buildings has been circulated as reactor cooling water. Radionuclides has been continuously released from damaged fuel into the contaminated water. The contaminated water has been, therefore, processed by different types of water treatment apparatuses to decrease the concentration of radionuclides. In the operation of water treatment apparatuses, a certain amount of spent absorbing materials are generated and need to be disposed of as the secondary wastes of water treatment. Conventional radioactive waste disposal concepts such as trench disposal, concrete pit disposal, subsurface disposal and geological disposal are estimated to be modified and applied for the disposal of secondary wastes. In order to select the suitable disposal concept for each secondary waste, the inventory of radionuclides in the wastes need to be estimated.

Radionuclides inventory in the secondary wastes can be evaluated by analyzing the radionuclides concentration in the samples collected from the waste. Sampling the secondary waste is, however, sometimes difficult because of the high dose rate from the waste. Radionuclides inventory can be also evaluated from the radionuclides concentration in the contaminated water at the inlet and outlet of the water treatment apparatuses

[1]. Even using this method, it is unavoidable to overestimate the inventory for the radionuclides whose concentrations are lower than the detection limit, because the inventory need to be estimated conservatively under assumptions that the concentration of radionuclides are the same as the detection limit values and that entire amount of the radionuclides are removed by the water treatment apparatuses due to the difficulty to quantify the radionuclides concentration at the outlet. To avoid the overestimation of inventory, fundamental data such as distribution coefficient of each radionuclides on the absorbing materials should be employed to evaluate the validity of estimated inventory. Theoretically, the inventory does not exceed the value calculated by multiplying radionuclide concentration by distribution coefficient of the radionuclide and the weight of absorbing material.

Zeolite is used as the absorbing material for the water treatment apparatuses named KURION and SARRY. These apparatuses locate just after the contaminated water outlet of reactor buildings and remove cesium from the contaminated water. The dose rate from the spent zeolite are relatively high due to the radiation from the absorbed radioactive cesium. In addition, sampling of zeolite from the spent zeolite vessels is sometimes difficult due to the vessel structure. The zeolite used in KURION and SARRY are known to have high adsorption performance for cesium. However, the adsorption ability for the other radionuclides contained in the contaminated water is also important for inventory

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estimation. The fundamental information such as distribution coefficients of radionuclides on zeolite need to be sufficiently collected.

In this study, distribution coefficients of U and Np on zeolite were obtained by sorption experiments. The sorption experiments were conducted under two different solution conditions. At first, simulated seawater was used as the experimental solution considering the actual contaminated water composition, because seawater was injected into the reactor buildings as cooling water at the initial stage of accident recovery. Following this experiment, the effect of solution composition on distribution coefficient was investigated to clarify important factors which control the sorption behavior of U and Np on zeolite.

2. Experimental

2.1. Materials

The zeolite used in this study was chabazite (IONSIV^{TM} IE-96, UOP), which is the zeolite used in the water treatment apparatus SARRY. Chabazite was hydrated in a closed container under 80% of relative humidity for more than 1 week before measuring the weight to keep the amount of absorbed water constant. Relative humidity was controlled by placing a bottle containing saturated ammonium chloride solution in the container with the lid open at room temperature.

Uranium used for the tracer was prepared by dissolving uranyl nitrate into deionized water. The uranyl nitrate was processed from depleted uranium by a crystallization method. Neptunium-237 was used as Np tracer and purchased from Japan Radioisotope Association (Tokyo, Japan) as HNO_3 solution.

2.2. Sorption experiments

Batch-type sorption experiments were carried out under two different conditions. In a first experiment, the sorption of U and Np on chabazite was measured in simulated seawater (SW) and in simulated seawater diluted ten times by deionized water (SW10). The composition of SW is shown in **Table 1**. The pH of SW was adjusted to 8.0 ± 0.1. The pH was measured by a glass electrode (HORIBA, 9615-10D). The experiments of U were conducted using polystyrene bottles while PFA centrifuge tubes were used for Np. Chabazite was initially immersed in the experimental solution for 1 week. This process was repeated three times before adding tracers to establish sorption equilibrium between the ions in solution and the ions sorbed on chabazite. Solid/liquid ratios were 100 and 10 ml/g for the experiments of U and Np, respectively. The initial concentrations of U and Np were 1×10^{-6} and 1×10^{-7} mol/dm^3, respectively. After the addition of tracers, the solution was sampled after a certain reaction period. The concentration of U in the sampled solution was measured by ICP-MS (Perkinelmer, ELAN6100 DRC), while the radioactivity of Np-237 in the solution was measured by liquid scintillation counter (Perkinelmer,

Tri-Carb 2770TR/SL or Tri-Carb 4910TR). The sampled solution was not filtered before the measurement to avoid filtration of intrinsic colloid of U and Np, which results in the underestimation of tracer concentration in the solution.

In a second experiment, sorption experiments of U and Np on chabazite were carried out as functions of Na$^+$ concentration, carbonate concentration and solution pH to investigate in detail the effect of solution composition on the sorption behavior of U and Np. The experimental conditions are shown in **Table 2**. The Na$^+$ and carbonate concentrations were adjusted by mixing of NaCl and NaHCO$_3$ solutions. The solution pH was initially adjusted to the pH range from 5 to 9 for U while the experiments for Np was carried out at initial pH of 9.0. The solution pH was adjusted by NaOH or HCl. The other experimental conditions and procedure were the same as those in the experiment using simulated seawater.

Distribution ratio was calculated by the following equation:

$$\text{Distribution ratio (m}^3/\text{kg)} = \frac{C_0 - C}{C} \cdot \frac{V}{m} \qquad (1)$$

where C_0 is the initial concentration of tracer (mol/m^3), C is the concentration of tracer in the sampled solution (mol/m^3), m is the weight of chabazite (kg) and V is the volume of solution (m^3). Distribution coefficient (K_d) was determined from the distribution ratio at the sorption equilibrium, where the tracer concentration in the solution was constant with time.

Table 1.   Composition of SW (mol/dm^3)

Ions	Concentration	Ions	Concentration
Na$^+$	4.8×10^{-1}	Cl$^-$	5.6×10^{-1}
Mg^{2+}	5.5×10^{-2}	SO$_4^{2-}$	2.9×10^{-2}
Ca^{2+}	1.1×10^{-2}	HCO$_3^-$	2.8×10^{-3}
K$^+$	1.0×10^{-2}		

Table 2.   Conditions for the experiments as functions of Na$^+$, carbonate concentration and pH

Tracers	Na$^+$ (mol/dm^3)	HCO$_3^-$ (mol/dm^3)	Initial pH
U(VI)	0.05	5×10^{-4}	5-9
		5×10^{-3}	
	0.5	5×10^{-4}	
		5×10^{-3}	
Np(V)	0.05	-	9
		5×10^{-4}	
		5×10^{-3}	
	0.5	5×10^{-3}	

3. Results and discussion

3.1. Sorption of U and Np in simulated seawater

Figure 1 shows the changes of distribution ratios of U and Np to chabazite in SW and SW10 with time. The distribution ratios increased with increasing in the reaction time and the reactions approached sorption equilibrium within 24 days for U in SW10 and 49 days for Np. The distribution ratio of U in SW was almost

constant during the reaction period, suggesting that the sorption equilibrium was quickly established. The K_d determined from the distribution ratios at the sorption equilibrium are listed in **Table 3**. The K_d of U in SW was more than 2 orders of magnitude lower than that in SW10, while the K_d of Np was almost independent of the seawater concentration.
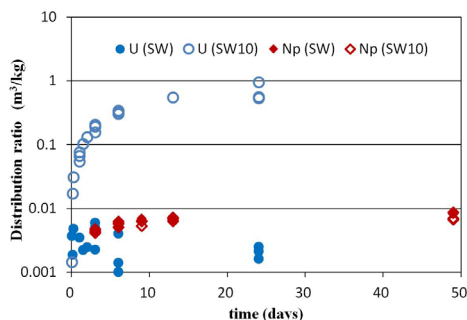

Figure 1.   Changes of distribution ratios of U and Np in SW and SW10 to chabazite with time.

Table 3.   Distribution coefficients of U and Np on chabazite in SW and SW10 (m^3/kg)

Solution	K_d of U	K_d of Np
SW	0.0021 ± 0.0004	0.0087 ± 0.0005
SW10	0.68 ± 0.23	0.0085 ± 0.0005

There was a large difference in the K_d of U between in SW and in SW10. The sorption of U on zeolite has been reported to be dependent on the solution pH in the neutral or weakly alkaline region[2-5]. However, in this study, the change of K_d cannot be interpreted by the pH dependence of sorption behavior of U, as the pH of SW10 was almost the same as that of SW. The measured pH values were 7.8-8.0 and 7.6-8.1 for SW and SW10 at the end of the experiments, respectively. The change of K_d might be, therefore, caused by the change of salinity in the solution. In addition, there is a possibility that the change of aqueous species of U affected the sorption behavior. To discuss this possibility, the aqueous speciation was calculated based on the thermodynamic database developed by Japan Atomic Energy Agency (JAEA-TDB)[6]. In SW, more than 98 % of U forms a carbonate complex of $UO_2(CO_3)_3^{4-}$, while the species of $(UO_2)_2CO_3(OH)_3^-$ is dominant in SW10. The total ratios of hydrolysis species such as $UO_2(OH)_3^-$, $(UO_2)_4(OH)_7^+$, UO_2OH^+ are calculated to be 0.003 % in SW and 1.9 % in SW10. These changes of aqueous species might affect the sorption behavior of U. As for Np, the sorption behavior on zeolite has been scarcely reported. In this study, almost no difference in the K_d values between in SW and in SW10 were observed, suggesting that the salinity was not the dominant factor which controlled the sorption behavior of Np. On the other hand, the speciation of Np changes depending on the seawater concentration. The ratio of carbonate complex of $NpO_2CO_3^-$ increases from 8 % in SW10 to 42 % in SW. Accordingly, the ratio of NpO_2^+ decreases with increasing in the seawater concentration. The change of the species of Np seems to have little effect on the sorption behavior.

3.2. Sorption behavior of U and Np as functions of Na^+, carbonate concentrations and pH

To clarify the dominant factor which controls the sorption behavior of U and Np, sorption experiments were carried out as functions of Na^+ concentration, carbonate concentration and solution pH. **Figure 2** shows the dependence of K_d of U on pH in the presence of 5×10^{-3} or 5×10^{-4} mol/dm^3 carbonate in the solutions with Na^+ concentrations of 0.5 and 0.05 mol/dm^3. The K_d values are plotted to the pH measured after the reaction period as the pH changed toward pH 7-8 from the initial pH values. In the pH range from 8 to 9, carbonate concentration strongly affected the K_d values. The K_d obtained in the solution at a carbonate concentration of 5×10^{-3} mol/dm^3 were obviously lower than those obtained at a 5×10^{-4} mol/dm^3. In contrast, the K_d values were independent of Na^+ concentration in this pH range. This result indicates that the sorption of U on chabazite was not caused by ion exchange reaction. The decrease in K_d observed in the experiments using simulated seawater is considered to be due to the increase of carbonate concentration in the solution. The sorption of U has been reported to decrease with increasing pH at the pH higher than around 7 on the other types of zeolites[2-5]. Also in these studies, the decrease of sorption has been presumed to be caused by the increase in the concentration of uranium-carbonate complexes at alkaline pH.

The ratios of aqueous species of U in the presence of 5×10^{-3} and 5×10^{-4} mol/dm^3 carbonate at pH 8.5 and 6.5 are shown in **Table 4**. At pH 8.5, the dominant species is $UO_2(CO_3)_3^{4-}$ at both carbonate concentrations. The ratios of hydrolysis species are 0.82 and 0.0009 at carbonate concentrations of 5×10^{-4} and 5×10^{-3} mol/dm^3, respectively. The ratio of hydrolysis species is decreased by 3 orders of magnitude due to the increase in carbonate concentration. Whereas, the K_d values obtained at a carbonate concentration of 5×10^{-3} mol/dm^3 were around 2 orders of magnitude lower than those obtained at a 5×10^{-4} mol/dm^3 carbonate concentration at around pH 8.5 as shown in Figure 2. Also at pH 6.5, the ratios of hydrolysis species are 3.3 and 0.12 at carbonate concentrations of 5×10^{-4} and 5×10^{-3} mol/dm^3, respectively. The difference of hydrolysis species ratio is more than 1 order of magnitude, while the difference of K_d values between these two carbonate concentrations at pH 6.5 seemed to be within 1 order of magnitude from the plots at around pH 6.5 shown in Figure 2. This difference suggests that the decrease in K_d cannot be interpreted only by the difference of hydrolysis species ratio. Carbonate complexes of U were likely to be sorbed on the surface of chabazite in addition to the sorption of hydrolysis species. Marques Fernandes et al. reported the possibility that uranyl carbonate surface complexes were forming on the montmorillonite surface from batch sorption experiments [7]. This data supports our conclusion that the carbonate complexes of U were
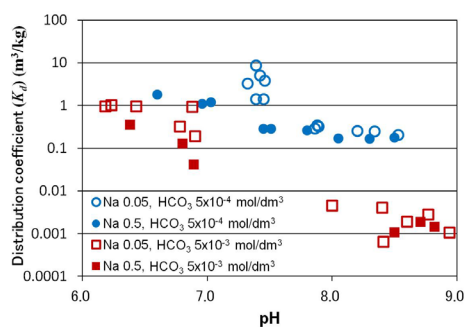
sorbed on chabazite surface.

Figure 2.　Dependence of Uranium K_d on pH under different Na^+ and carbonate concentrations.

Table 4.　Ratios of aqueous species of U and Np in the presence and absence of carbonate calculated based on JAEA-TDB (%) [6].

	Carbonate concentration (mol/dm^3)		
	0	5×10^{-4}	5×10^{-3}
U at pH 8.5			
$UO_2(CO_3)_2^{2-}$	-	8.3	0.9
$UO_2(CO_3)_3^{4-}$	-	85.7	99.1
$(UO_2)_2CO_3(OH)_3^-$	-	5.0	< 0.1
Hydrolysis species	-	0.82	0.0009
U at pH 6.5			
$UO_2(CO_3)_2^{2-}$	-	13.9	50.8
$UO_2(CO_3)_3^{4-}$	-	0.94	35.7
$(UO_2)_2CO_3(OH)_3^-$	-	23.4	0.31
Hydrolysis species	-	3.3	0.12
Np at pH 8.5			
$NpO_2CO_3^-$	0	34.4	83.2
NpO_2^+	99.9	65.5	15.9
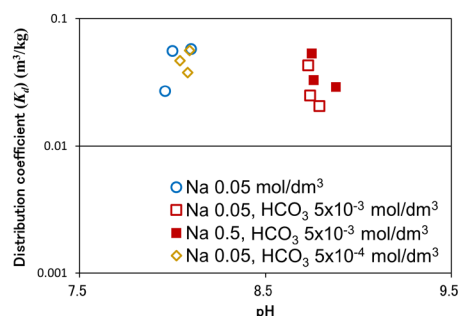
Figure 3.　The K_d of Np in the absence of carbonate and in the presence of 5×10^{-3} and 5×10^{-4} mol/dm^3 carbonate.

Figure 3 shows the K_d of Np obtained in the absence of carbonate and in the presence of 5×10^{-3} and 5×10^{-4} mol/dm^3 carbonate. The K_d values were independent of Na^+ and carbonate concentrations for Np. This result is consistent with the trend of K_d observed in the experiments using SW and SW10, where the K_d values were independent of seawater concentration. Meanwhile, the speciation of Np considerably changes as shown in Table 4. The carbonate complex of $NpO_2CO_3^-$ is dominant at a carbonate concentration of 5×10^{-3} mol/dm^3 while 99 % of Np forms NpO_2^+ in the solution without carbonate. This suggests that $NpO_2CO_3^-$ sorbed on chabazite to the same degree with NpO_2^+ in the pH range from 8 to 9 as shown in Figure 3. The K_d values

were considered to be independent of seawater concentration in the experiments using SW and SW10.

4. Conclusion

For the disposal of secondary waste generated in the treatment process of contaminated water at the Fukushima Daiichi nuclear power station, radionuclides inventory in the secondary wastes is the important information to select the suitable disposal concept. In this study, the sorption behavior of U and Np on chabazite, which is the zeolite used in the water treatment apparatus SARRY, was investigated by batch sorption experiments to obtain the fundamental data for inventory estimation. High K_d value of U was obtained in the experiment using ten times diluted simulated seawater, while the K_d value was low in the simulated seawater. The K_d values of Np were low and independent of seawater concentration. From the experiments as functions of Na^+, carbonate concentrations and pH, carbonate concentration was the dominant factor which controlled K_d values of U while the K_d of Np was not dependent on Na^+ and carbonate concentrations.

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