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Leaching and migration of neptunium in a simulated engineered barrier system consisting of HLW glass and compacted bentonite

Y. Inagaki [a,*], H. Furuya [a], K. Idemitsu [a], T. Arima [a], H. Osako [a],
T. Banba [b], T. Maeda [b], S. Matsumoto [b], I. Nomura [b], S. Kikkawa [b],
M. Saito [b], H. Okamoto [b]

[a] *Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581, Japan*
[b] *Japan Atomic Energy Research Institute, Tokai Research Establish., Ibaraki 319-1195, Japan*

Abstract

In a simulated engineered barrier system consisting of a simulated HLW glass doped with ^{237}Np, a compacted bentonite and water under reducing conditions, leaching of Np from the glass and diffusion of the leached Np through the bentonite were measured systematically. The following results were obtained: (1) The concentration of dissolved species of Np in the leachate is 10^{-7}–10^{-8} M, which indicates that Np(IV) is the dominant oxidation state in the system and the concentration may be controlled by solubility of $NpO_{2x}H_2O$ (am). (2) The presence of compacted bentonite facilitates reduction of Np(V) to Np(IV) in the system. (3) The apparent diffusion coefficient of the leached Np through the bentonite is evaluated to be lower than 1.5×10^{-13} m^2/s, showing that the diffusivity of Np(IV) is more than one order of magnitude lower than that of Np(V). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

For last few decades, a large number of studies have been done on migration of radionuclides in the engineered barrier system for HLW disposal. Although radionuclides can migrate in the engineered barrier system with three major physicochemical processes, i.e., (1) leaching from HLW glass, (2) sorption/incorporation in engineered barrier materials, (3) diffusion through buffer materials, the previous studies have focused on evaluation of the individual process. Glass corrosion models for predicting the long-term leaching of radionuclides have been developed in a large number of studies on the glass corrosion [1–3]. A large number of studies on the sorption and on the diffusion have evaluated the distribution coefficients and the diffusion coefficients for some radionuclides at various conditions [4,5]. However, there have been only a few studies on the coupling of the data of the individual process for evaluating the overall performance of the engineered barrier system [6–8]. It has been reported that interactions between the glass and buffer materials can enhance the glass corrosion, consequently increasing the release of radionuclides [8–12]. The mechanism of these interactions, however, have not been evaluated sufficiently, and the performance assessments of the engineered barrier system have not taken the interactions into account up to the present. Evaluation of the interfaces between the individual process is an important point affecting the validity of the performance assessment.

The purpose of this study is to investigate leaching and migration behavior of Np considering the interactions between the glass and the bentonite for evaluating the overall performance of the engineered barrier

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[*] Corresponding author. Tel.: +81-92 642 3779; fax: +81-92 642 3800.

E-mail address: inagytne@mbox.nc.kyushu-u.ac.jp (Y. Inagaki).

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system. In a simulated engineered barrier system consisting of a simulated HLW glass doped with ^{237}Np, a compacted bentonite and water under reducing conditions, leaching of Np from the glass and diffusion of the leached Np through the bentonite were measured systematically. On the basis of the results, mechanism of Np migration in the engineered barrier system is discussed.

2. Experimental

A powdered simulated waste glass (similar composition to R7T7 glass) doped with ^{237}Np (0.19 wt%, $^{237}NpO_2$) was used as a glass specimen. Grain sizes of the glass specimen ranged from 75 to 150 μm. Sodium bentonite of Kunipia F (Na-montmorillonite: 99%, Kunimine Industry, Japan) was used as a bentonite specimen. The chemical composition of Kunipia F is given elsewhere [13]. The bentonite powder was compacted into a cylinder of 10 mm in diameter and 20 mm in height with a dry density of 1.2 g/cm^3.

Static corrosion tests were performed in the presence of the compacted bentonite (leaching/migration tests) under reducing conditions. Fig. 1 shows schematics of the test apparatus. The compacted bentonite was packed in a Teflon column with one face contacting the solution through solution permeable filters of sintered stainless steel and membrane. The Teflon column was then placed in a Teflon container filled with deionized water in $(Ar + 4\%H_2)$ gas atmosphere at room temperature for one month in order to saturate the bentonite with water. The pH and Eh of the solution after the water saturation were measured to be 9.5 and −0.50 V versus SHE, respectively. After water saturation, the doped glass (3.2 g) was added into the solution, then the leaching/migration tests were performed at 90°C, a SA/V ratio of 2600 m^{-1} and a ratio of bentonite weight to glass surface area (bentonite/SA ratio) of 7.2 g/m^2. With the present system (glass/bentonite/water system), leaching of Np from the glass and diffusion of the leached Np through the bentonite can proceed simultaneously. Analogous corrosion tests without bentonite were performed on the undoped glass for comparison.

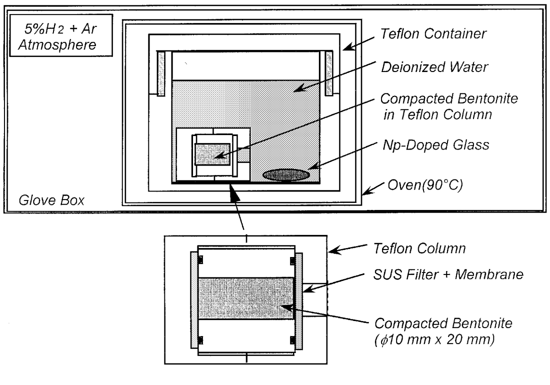

Fig. 1. Schematics of the leaching/migration test apparatus.

During the leaching/migration tests, the pH and Eh of the solution were measured every 20 days. An aliquot of the leachate was also passed through a Millipore filter with a pore size of 1.8 nm, and the solution concentrations of Np, Si and B were measured in the filtrates using α-spectrometry, α-liquid scintillation counter and ICP–AES. At the end of the tests, the bentonite was separated from the Teflon column and cut into 1 mm thick slices. Each slice was placed in 1 M HCl solution at 90°C for 2 days to extract Np. The concentrations of Np in the extracts were measured using an α-liquid scintillation counter to obtain the diffusion profile in the bentonite.

3. Results and discussion

3.1. Glass corrosion

The solution pH and Eh in the glass/bentonite/water system are shown in Fig. 2 as a function of corrosion time. The solution pH was stable at around 9.6, and the solution Eh was approximately −0.5 V versus SHE during the tests.

The concentrations of Si and B in the leachate after 1.8 nm filtration are shown in Fig. 3 as a function of corrosion time. The Si concentrations are saturated at 70 ppm while the B concentrations continue to increase with time after the Si saturation. Analogous corrosion tests without bentonite shows that the presence of bentonite causes a slight increase of the B concentrations, which indicates that the presence of bentonite enhances the glass corrosion. While the presence of bentonite has no remarkable influence on the Si concentrations.

Previous studies on HLW glass corrosion have reported that the presence of bentonite or clay minerals enhances the glass corrosion [8–12]. However, this enhancement is relatively complex depending on the test conditions, such as glass composition, SA/V, temperature, bentonite composition, bentonite state (compacted or uncompacted) and bentonite/glass ratio. The evaluation of the key parameters controlling the enhancement is impossible. Our previous corrosion tests performed on Pu-doped glass in the presence of compacted bentonite [8] showed that the presence of compacted bentonite enhances the glass corrosion by a factor of approximately two. Comparison of the present data with our previous data [8], listed in Table 1, indicates that magnitude of the enhancement in the present tests is much smaller. Between the present and the previous tests a difference can be found in the ratio of bentonite to glass, i.e., the bentonite/SA ratio was 7.2 g/m^2 in the present

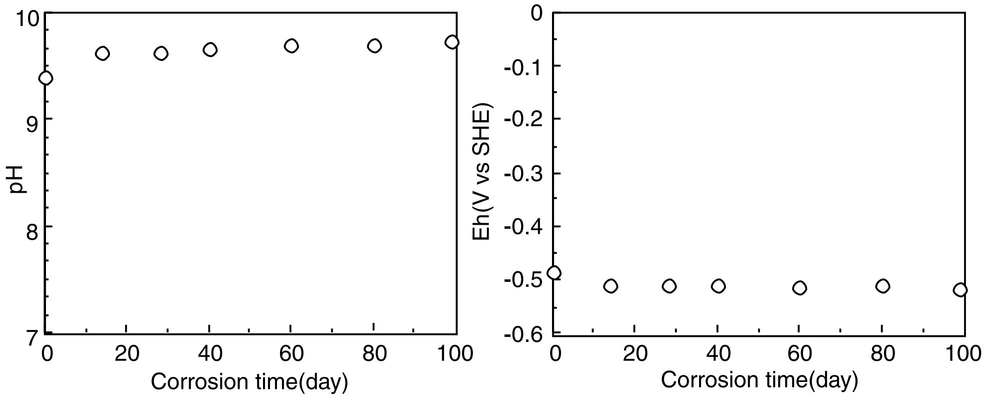

Fig. 2. Solution pH and Eh in the glass/bentonite/water system for the leaching/migration tests.

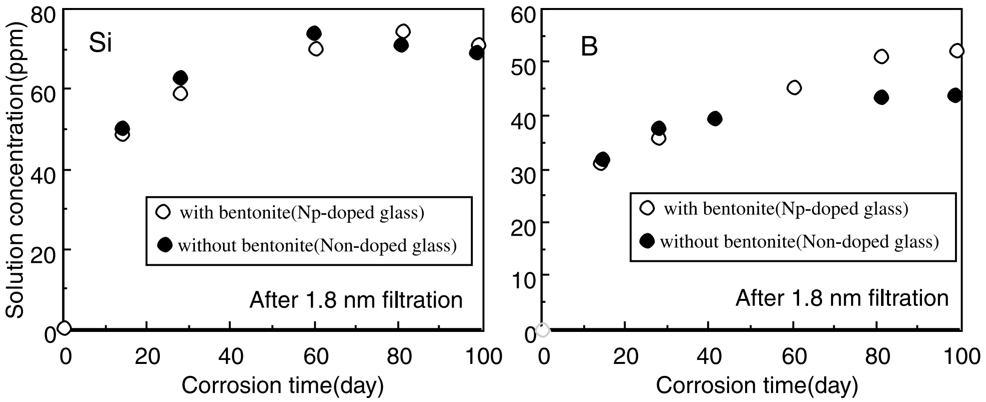

Fig. 3. Concentrations of Si and B in the leachate after 1.8 nm filtration for the leaching/migration tests.

Table 1
Previous data on enhancement of glass corrosion by the presence of bentonite, evaluated from Boron leaching data

Glass	Bentonite	SA/V (m^{-1})	Temp (°C)	Bentonite/ SA (g/m^2)	Magnitude of enhancement	Reference
R7T7	Kunipia F, compacted (dry density = 1.2 g/cm^3)	2600	90	7.2	1.2	Present study
R7T7	Kunipia F, compacted (dry density = 1.2 g/cm^3)	3000	90	36	2	[8]
P0798	Kunigel V1, uncompacted	2600	90	12	2	[8]
ABS-118	MX-80, uncompacted	1100	90	121	2	[10]
ABS-118	MX-80, uncompacted	10	90	13 000	3–6	[10]
SON68	Boom clay, uncompacted	10 000	40	50	3.6–12	[9]
	$+Fe_2O_3$		90		1.2–3.0	
SON68	Boom clay, uncompacted	2500	40	200	3.5–17	[9]
	$+Fe_2O_3$		90		3.0–6.9	
SON68	Boom clay, uncompacted	500	40	1000	4.6–12	[9]
	$+Fe_2O_3$		90		4.8–12	
SM539	Boom clay, uncompacted	10 000	40	50	1.7–4.8	[9]
	$+Fe_2O_3$		90		0.66–5.7	
SM539	Boom clay, uncompacted	2500	40	200	0.8–4.7	[9]
	$+Fe_2O_3$		90		1.0–19	
SM539	Boom clay, uncompacted	500	40	1000	8.6–13	[9]
	$+Fe_2O_3$		90		3.2–19	

study and 36 g/m^2 in the previous tests [8], which indicates that the enhancement of the glass corrosion increases with bentonite/SA ratio. Lemmens et al. [9] have performed the glass corrosion tests in the presence of Boom clay systematically to evaluate the effects of Boom clay on the glass corrosion. Some of the data are listed in Table 1. From comparison between the data listed in Table 1, however, it can be seen that the enhancement of glass corrosion is more complex depending on not only the the bentonite/SA ratio but other test conditions. In addition to the test conditions listed in Table 1, the reaction time can be an important parameter affecting the enhancement.

It has been suggested that the enhancement of the glass corrosion results from reactions at bentonite surface, such as Si sorption, growth of montmorillonite by consuming Si and other elements [9,10,12]. It has been also pointed out that formation of zeolite at the glass surface as the secondary phase can enhance the glass corrosion [14,15]. Therefore, reactive surface area of bentonite, that of the glass and the solution chemistry may be available parameters for evaluation of the enhancement. Since the glass corrosion in the presence of bentonite results from complicated processes, further works need systematic studies to understand geochemical mechanism of the glass corrosion in the presence of bentonite and to evaluate the key parameters controlling the glass corrosion in the system.

3.2. Leaching of Np

The concentration of Np in the leachate after 1.8 nm filtration is shown in Fig. 4 as open circles. It can be seen that the concentration of Np is almost stable in the range from 10^{-7} to 10^{-8} M during the tests. In our previous study [16], leaching of Np from the glass under reducing conditions has been measured in both the glass/water system and the glass/magnetite/water system. The data on the Np concentrations in the leachates after 1.8 nm filtration from the previous tests are shown in Fig. 4 as solid lines for comparison. It can be seen that the Np concentration in the glass/bentonite/water system is lower than those in the glass/water system and the glass/magnetite/water system. The same tendency of a decrease in the Np concentration by the presence of Boom clay has been reported by Lemmens et al. [9].

It is well known that the solubility of Np strongly depends on the oxidation state. Using redox potential data from the literature [17,18], it can be argued that the dominant oxidation state of Np in the leachates under the present reducing conditions ($\mathrm{pH} = 9.5$, $\mathrm{Eh} = -0.5\,\mathrm{V}$ versus SHE) is expected to be Np(IV), while Np(V) should dominate under oxidizing conditions. Table 2 lists the reactions most likely controlling the solubilities of Np(IV) and Np(V) in neutral aqueous solutions with the corresponding thermodynamic data [17,19,20] and the calculated solubilities of Np(IV) and Np(V) for comparison. From comparison of the measured concentrations of Np with the calculated concentrations, the previous study performed in the glass/magnetite/water system [16] concluded: (1) Np(V) is the dominant oxidation state in the glass/water system under reducing conditions due to an extremely slow rate of the reduction of Np(V) to Np(IV). (2) The reduction of Np(V) to Np(IV) occurs slowly at magnetite surface in the glass/magnetite/water system causing a decrease of the Np concentration. In the glass/bentonite/water system the Np concentration is in good agreement with the solubility of Np(IV), which suggests that the bentonite facilitates reduction of Np(V) to Np(IV) more than magnetite. Kunipia F includes some amount of pyrite (FeS_2) as impurity, and pyrite is a strong reductant. Therefore, dissolution of pyrite from the bentonite may facilitate the reduction of Np(V) to Np(IV) in the leachate. Corrosion of a sintered stainless steel filter, used in the present tests, is also likely to facilitate the reduction of Np(V) to Np(IV). Further works should investigate

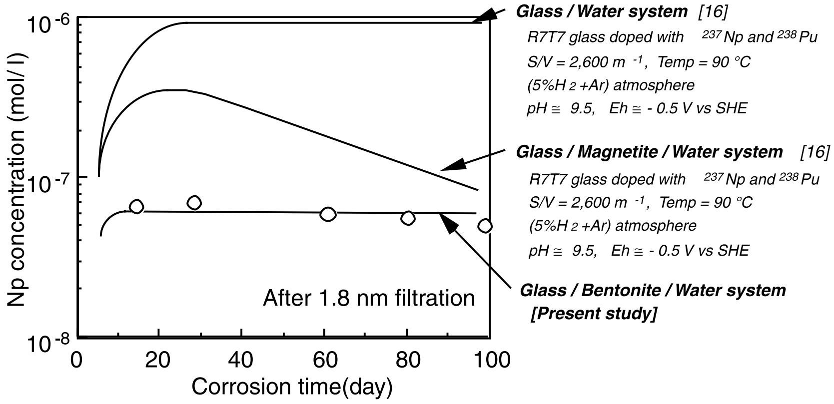

Fig. 4. Concentration of Np in the leachate after 1.8 nm filtration for the leaching/migration tests.

Table 2
Reactions and thermodynamic data used in calculations of Np solubility

Reaction	Calculated concentration
Np(V) NpO_2OH (am) = $NpO^{2+} + OH^-$, $\log K(25°C) = -10.2$ [20] $NpO^{2+} + OH^- = NpO_2OH^0$, $\log \beta(25°C) = 2.9$ [20] $NpO^{2+} + 2OH^- = NpO_2(OH)_{2-}$, $\log \beta(25°C) = 5.5$ [20]	(Dominant species at 25°C, pH = 9.5, Eh = +0.3 V versus SHE) $[NpO^{2+}] = 2 \times 10^{-6}$ mol/l
Np(IV) $NpO_2 \cdot xH_2O$ (am) = $Np^{4+} + 4OH^- + (x-2)H_2O$, $\log K(25°C) = -53.5$ [19] $Np^{4+} + OH^- = Np(OH)^{3+}$, $\log \beta(25°C) = 13.2$ [17] $Np^{4+} + 2OH^- = Np(OH)_2^{2+}$, $\log \beta(25°C) = 25.2$ [17] $Np^{4+} + 3OH^- = Np(OH)_3^+$, $\log \beta(25°C) = 36.4$ [17] $Np^{4+} + 4OH^- = Np(OH)_4^0$, $\log \beta(25°C) = 46.1$ [17] $Np^{4+} + 5OH^- = Np(OH)_5^-$, $\log \beta(25°C) = 50$ [17]	(Dominant species at 25°C, pH = 9.5, Eh = −0.5 V versus SHE) $[Np(OH)_4^0] = 4 \times 10^{-8}$ mol/l

mechanism and rate of the reduction of Np(V) to Np(IV) in the system.

3.3. Diffusion of Np through compacted bentonite

Fig. 5 shows the diffusion profiles of Np in the bentonite at 99 days, where the Np concentration (mol/g) represents the amount of Np in unit mass of dry bentonite. It can be seen that the diffusion of Np is extremely slow, and the Np concentrations are lower than the detection limit except in the bentonite of 2 mm depth from the contacting surface.

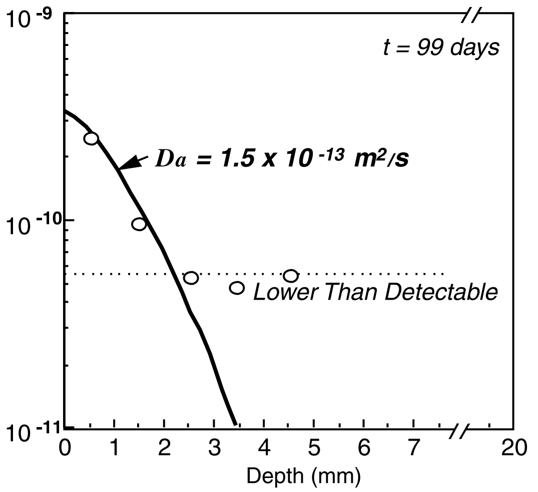

Fig. 5. Diffusion profile of Np in the bentonite in the glass/bentonite/water system for the leaching/migration tests at 99 days.

Although there were only a few data available, the apparent diffusion coefficient of Np through the bentonite, D_a, was estimated from the diffusion profiles by fitting of a diffusion equation as follows:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2},$$

$$\text{I.C.}: C = 0 \quad \text{at } t = 0,\ 0 < x < L,$$

$$\text{B.C.}: C = C_0 \quad \text{at } x = 0,\ t > 0,$$

where C is the Np concentration in bentonite, C_0 is the Np concentration at bentonite surface, x is the distance from bentonite surface and L is the length of bentonite.From the best fit of an error function, shown as a solid line in Fig. 5, the apparent diffusion coefficient was estimated to be less than 1.5×10^{-13} m²/s. The apparent diffusion coefficient of Np(V) for a bentonite of Kunigel V-1 was previously measured under aerobic condition by use of a conventional in-diffusion method [5]. The value is listed in Table 3 as well as the present data. It is noted that the values of D_a evaluated in the present study is more than one order of magnitude lower than that of Np(V). Therefore, we can suggest that Np(IV) is

Table 3
Apparent diffusion coefficient of Np in compacted bentonite

Bentonite/dry density (g/cm³)	Method	Temperature (°C)	Atmosphere/ oxidation state	D_a (m²/s)	Reference
Kunigel V-1/ 1.2(0.4–2.0)	Conventional in-diffusion	RT	Air Np(V)	$2–3 \times 10^{-12}$	[5]
Kunipia F/1.2	Glass/bentonite/ water coupled	90	Ar + 4%H_2 Np(IV)?	$< 1.5 \times 10^{-13}$	Present study

the dominant state in the diffusion process, and the diffusivity of Np(IV) is much slower than that of Np(V).

4. Conclusion

The present study on leaching and migration of Np in a simulated engineered barrier system consisting of HLW glass, compacted bentonite and water under reducing conditions gave the following results: (1) The concentration of dissolved species of Np in the leachate is 10^{-7}–10^{-8} M, which indicates that Np(IV) is the dominant oxidation state in the system and the concentration may be controlled by solubility of $NpO_{2x}H_2O$ (am). (2) The presence of compacted bentonite facilitates reduction of Np(V) to Np(IV). (3) The apparent diffusion coefficient of the leached Np through the bentonite is evaluated to be lower than 1.5×10^{-13} m^2/s, which indicates that Np(IV) is the dominant state in the diffusion process. Furthermore, the diffusivity of Np(IV) is more than one order of magnitude lower than that of Np(V). These results suggest that Np(IV) is the dominant oxidation state in the real engineered barrier system, and the migration of Np(IV) is evaluated to be extremely slow. However, further works should investigate mechanism of the reduction of Np(V) to Np(IV) and mechanism of Np(IV) diffusion through bentonite in order to confirm the slow rate of Np migration in the system for long-term.

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