

SORPTION BEHAVIOR OF Np(IV), Np(V) AND Am(III) IN THE
DISTURBED ZONE BETWEEN ENGINEERED AND NATURAL BARRIERS

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In order to be more confident of the performance assessment of high-level radioactive waste disposal, radionuclide transport must be investigated in more detail in the disturbed host rock region adjacent to the engineered barriers where disturbance has been introduced during the construction and waste-emplacement period. Geochemical, hydrological, and rock-mechanical properties should be quite different from those of undisturbed host rock. We have to elucidate the effect of bentonite intrusion into intersecting fractures from the standpoint of radionuclide confinement. In the present work, sorption distribution ratios (K_d 's) of Np and Am are measured experimentally for various values of redox potential (Eh) in a simulated rock fracture filled with bentonite. The K_d of Am is approximately 6.5×10^3 ml/g and found to be insensitive to the redox potential. Under anaerobic conditions, the K_d of Np is approximately 6×10^4 ml/g. Under aerobic conditions, K_d is as small as 30 to 100 ml/g. This is the first report to measure the sorption behavior of Np and Am in a simulated rock fracture filled with bentonite (namely, in a disturbed zone) under pH, Eh and ionic strength control. We can make use of these K_d data for numerically evaluating the mass transfer from bentonite filled fractures into the water-flowing fracture network¹.

INTRODUCTION

Results of recent Japanese performance assessment studies² for high-level radioactive waste (HLW) geological disposal show that multiple engineered barriers consisting of borosilicate waste glass, carbon steel overpack, and bentonite-filled buffer region can limit the release of most radionuclides toward the surrounding host rock far below their annual limits on intake, and that host rock of at most 100-meter thickness can achieve sufficient attenuation of radioactivity.

To be more confident with such results, radionuclide transport must be investigated in more detail in the disturbed host rock region adjacent to the engineered barriers (EBS) where disturbance has been introduced during the construction and waste-emplacement period. Geochemical, hydrological, and rock-mechanical properties should be quite different from those of undisturbed host rock. In the disturbed zone, some fractures intersecting the EBS are newly introduced and connect with a fracture network bearing groundwater flow. Through such fractures connecting with a water-bearing fracture network, water is supplied to the bentonite and radionuclides are released from EBS to groundwater.

It is well known that water is imbibed by capillary suction and bentonite swells. Excess volume of bentonite then extrudes into the fractures intersecting the EBS. Bentonite extrusion distance in fractures is greater for fractures of larger aperture³, which will have a greater probability of being connected with the water-flowing fracture network. Therefore, from the standpoint of radionuclide release to the natural barrier, fractures of large aperture which connects the EBS with the water-flowing fracture network are of major concern.

In the present study, we experimentally measured sorption distribution ratios (Kd's) of Np and Am for various values of redox potential (Eh) in a simulated rock fracture filled with bentonite, which is useful for the mathematical analysis of the effect of bentonite intrusion into intersecting fractures from the standpoint of radionuclide confinement. The analytical results obtained by using the Kd data in this work will be presented in elsewhere¹.

EXPERIMENTAL

Materials

Americium-241 in 0.5M HNO₃ was supplied from Amersham (Am source solution). By repeatedly mixing the Am source solution with CMPO (*n*-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide), we prepared an Am stock solution of 1×10^{-8} M. This procedure allows removal of daughter nuclides such as ²³⁷Np.

Neptunium-237 source solution in 1M HNO₃ was obtained from CEA. To prepare a Np(IV) stock solution, the Np source solution was evaporated and the Np residue was dissolved in 1M HCl. This procedure was repeated three times to ensure the absence of HNO₃. The Np(V) ion in 1M HCl was reduced by heating and adding NH₂NH₂.HCl. The oxidation state of Np was spectroscopically confirmed to be tetravalent. The concentration of the Np(IV) stock solution was 1×10^{-5} M. The Np(V) stock solution was prepared by repeatedly mixing the Np source solution with CMPO to remove impurities such as Np(IV), Np(VI), and ²³³Pa.

Kunigel V1, Na-bentonite produced by Kunimine Industries Co. Ltd, was used in the present study. All

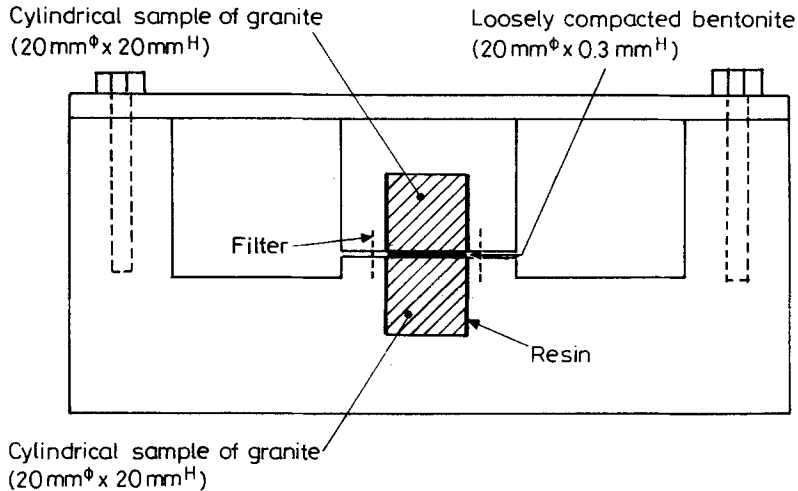


Fig. 1. Sorption experimental cell

other chemicals were of analytical grade (Wako Pure Chemical Industries Co. Ltd.). Water was doubly distilled and ultrafiltered by use of 2 nm ultrafilters (Molecut UFP1, Millipore) immediately before use.

A sorption cell was prepared by sandwiching loosely compacted bentonite (0.8 g/cm^3) with two cylindrical samples of granite (20 mm in diameter and 20 mm in height; Inada, Japan). Granite is one of the most likely host rocks in Japan. Thickness of the bentonite layer is 0.3 mm, which is the same order of fracture thickness⁴. The experimental cell is schematically shown in Fig. 1. By using this cell, we can simulate the disturbed zone where the fractures are filled with the intruding bentonite.

Procedure

A small amount of Am stock or Np stock was injected to the experimental cell immediately after ultrafiltering the stock solution (2 nm). pH was adjusted to 9 by ad-

dition of CO₂-free NaOH and HCl, and the ionic strength was adjusted to 0.1M by using NaClO₄. The concentrations of Am and Np were 1x10⁻⁹M and 1x10⁻⁸M, respectively. These concentrations were below the solubilities of Am, Np(IV) and Np(V), and were free from any error in determining sorption ratios due to precipitation.

In one series of measurements in which Am or Np(V) stock was used, Eh was changed from aerobic (+200 mV) to anaerobic (-100 mV) conditions by addition of hydrazine. In the other series, where Np(IV) stock solution was used, Eh was changed from anaerobic (-100 mV) to aerobic (0 mV) introducing oxygen. The pH and Eh were measured with a combination glass electrode (type ROSS, Orion Co.) calibrated against a pH buffer solution and with a platinum electrode (type 97-78, Orion Co.), respectively.

After Eh was adjusted to a certain value, we kept the Eh constant at that value and measured sorption distribution ratios of Am and Np. When the K_d value was constant for more than three days, we considered that sorption equilibrium was reached (one week for Am and two weeks for Np). In the measurement of K_d, the specimens were sampled and centrifuged (5000 rpm, 10 min), and pH was checked. An aliquot was taken from the supernatant and ultrafiltered by use of a 2 nm ultrafilter. Activities of Am and Np in the ultrafiltrates were measured by a 2π gas flow counter and a well-type Ge counter. From the initial activity of the spiked solution and the activity measured after equilibrium, K_d values of Am and Np were calculated. Sorption of Am and Np on the tube walls and on the ultrafilters were also investigated according to the experimental procedures of Lieser and Hill⁵ and Nitsche⁶, respectively, and were taken into account for calculating the sorption distribution ratios.

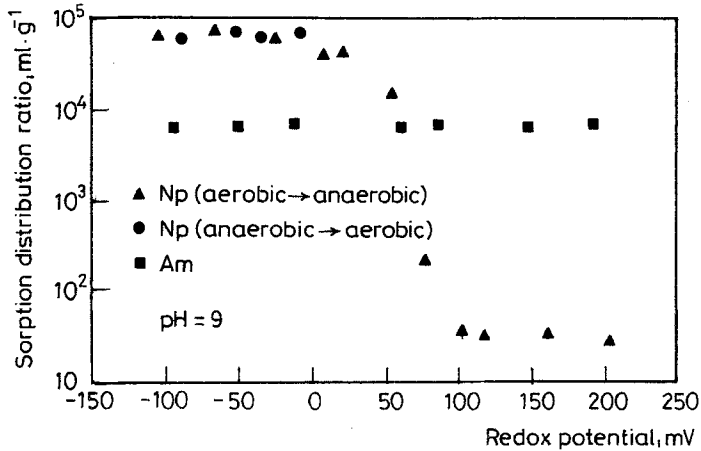


Fig. 2. Sorption distribution ratio of Np and Am as a function of Eh

Experiments were carried out in inert gas boxes filled with nitrogen. The temperature was 25 ± 0.5 °C. All samples were stored in a dark place.

RESULTS AND DISCUSSION

The results are illustrated in Fig. 2 as a function of the redox potential. The K_d of Am on Kunigel V1 is approximately 6.5×10^3 mg/g, which is within the range of those in the Sorption DataBase (SDB) of OECD/NEA⁷. This means that Am is sorbed on the intruding bentonite to the same extent as on the bentonite in EBS. The K_d for Am is insensitive to the redox potential. These results suggest that Am decays out to negligible levels, after transport through the disturbed zone.

With regard to Np, the K_d increases dramatically at the Eh corresponding to the reduction of Np(V) to Np(IV). While the K_d of Np(V) on Kunigel V1 is as small as 30

to 100 ml/g in aerobic conditions, the K_d of Np(IV) is approximately 6×10^4 ml/g in anaerobic conditions (between -100 mV to 0 mV). Since there is no difference in the K_d values between the two experiment series in the Eh range of -100 mV to 0 mV, K_d in this Eh range can be identical to that of Np(IV). We can normally expect the anaerobic conditions in EBS⁴, but cannot predict whether the fractures filled with intruding bentonite in the disturbed zone are under aerobic or anaerobic conditions. That depends on many factors, such as chemical conditions of groundwater and matrix rocks/minerals/sediments. Our results suggest that if the environment is anaerobic, Np decays out to negligible levels, after transport through the disturbed zone, but if not, the decay of Np in the disturbed zone is negligibly small.

This is the first report to measure the sorption behavior of Np and Am in a simulated rock fracture filled with bentonite under the pH, Eh and ionic strength control and to show the Eh dependence of Np and Am sorption on Kunigel V1. Based on the experimental results obtained in this work, we may consider that, if the environment in the disturbed zone keeps anaerobic conditions, the radionuclides will markedly decay out there. However, under aerobic conditions, there is a possibility that the disturbed zone does not play a role as a barrier for the Eh sensitive radionuclides.

Under our experimental conditions, the dominant species are $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3$, AmCO_3^+ and $\text{Am}(\text{CO}_3)_2^-$ for Am, $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$ for Np(V), and $\text{Np}(\text{OH})_4$ and/or Np^{4+} -carbonate complexes for Np(IV). Considering that the K_d of Am obtained in the present work is within the range of those in the Sorption DataBase (SDB) of OECD/NEA, there is a possibility that the host rock with large-aperture

fractures has little effect on the retardation of radionuclides. However, the host rock with smaller-aperture fractures may have an effect on retardation by sorption and matrix diffusion. Sorption behavior is strongly dependent on the speciation of radionuclides, properties of sorption sites, cation exchange capacity and chemical conditions of groundwater (pH, Eh, ionic strength, kinds and concentrations of ligands, temperature, coexisting cations). Our present work is really the first report of a measurement of K_d in a disturbed zone, but the K_d value shows the overall sorption behavior of all radionuclides in the given system. Hence, to understand the effect of disturbed zone in more detail and give full confidence to performance assessment for HLW disposal, we will elucidate the sorption mechanism for each species, model the sorption behavior in the disturbed zone and determine the maximum aperture width where the host rock has an effect on retardation.

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