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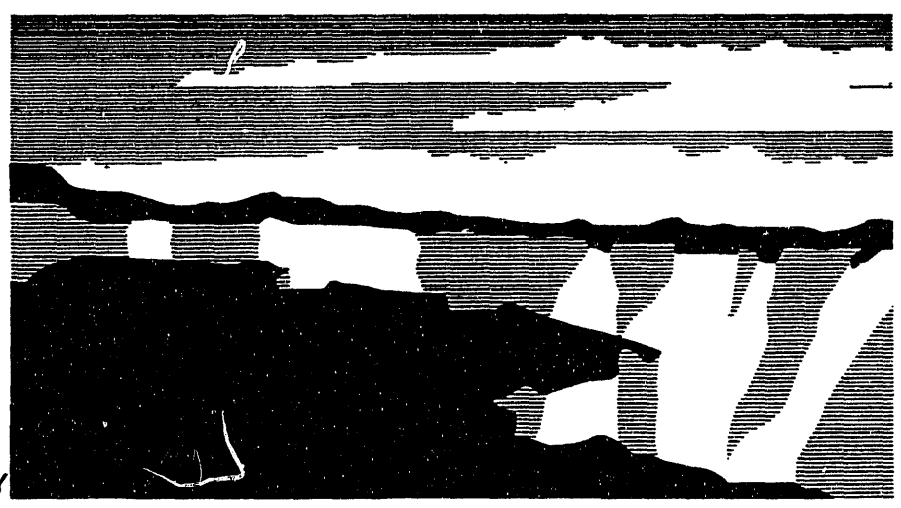
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NEPTUNIUM RETARDATION WITH TUFFS AND GROUNDWATERS FROM YUCCA MOUNTAIN

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ABSTRACT

The retardation of neptunium was studied using batch sorption and column techniques. Pure mineral separates, tuffs and groundwaters from Yucca Mountain were used for these experiments. Our results indicate that Np sorption increases rapidly as the pH of the water increases in cases where surface complexation is thought to be the dominant sorption mechanism. Oxide minerals (such as hematite) sorb Np strongly; therefore, these minerals even at trace levels in Yucca Mountain tuffs can result in significant Np retardation. Neptunium in groundwaters from Yucca Mountain exhibited a significant amount of sorption onto quartz. Neptunium sorption onto quartz is important because of the large quantity of silica in the tuffs. Elution of neptunium solutions in groundwater through columns made of crushed tuff yielded sorption coefficients that agree with the sorption results obtained using batch sorption techniques. Agreement between batch and column experiments indicates a neptunium sorption mechanism that is linear, reversible, and instantaneous.

INTRODUCTION

Neptunium is highly soluble in groundwaters from Yucca Mountain.¹ The speciation of Np in J-13 water at pH of 8.5 and 25°C has been reported by Nitsche.² Nitsche's results indicate that 38% of the Np in solution exists as NpO_2^+ and 62% as $\text{NpO}_2\text{CO}_3^-$. The sorption of Np onto Yucca Mountain tuffs in water from the wells J-13 and UE25p #1 has been reviewed by Meijer³. This review identified the study of Np sorption as a priority for the radionuclide migration investigations of the Yucca Mountain Site Characterization Project. Neptunium is highly soluble, has a low sorption potential, and composes a significant part of the waste inventory.³ The objective of this work was to determine the amount of Np retardation that is provided by tuffs using groundwaters from Yucca Mountain.

EXPERIMENTAL

The experiments conducted consist of batch sorption measurements and column experiments with crushed tuff and pure mineral separates. Batch sorption experiments consisted of pre-conditioning solid phases with groundwater (in the ratio 1 g to 20 ml) for two weeks. Solutions of ^{237}Np in groundwater were added to the pre-conditioned solid phases (in the ratio 1 g of solid to 20 ml of solution) and equilibrated for three weeks. After sorption, the two phases were separated by centrifugation and the amount of Np in each phase was determined by gamma spectrometry. The column experiments consisted of eluting tritiated water through columns of crushed tuff to determine each column's hydrologic parameters. This step was followed by eluting ^{237}Np solutions in groundwater through the columns and determining Np retardation by the tuff.

Neptunium solutions were prepared with two different groundwaters from Yucca Mountain: water from the wells J-13 and UE-25p #1. The Np solutions were prepared by adding an aliquot of a well-characterized Np(V) acidic stock to groundwater filtered through a 0.05 μm filter. The chemical composition of the filtered groundwaters at Los Alamos, NM is given in Table 1. Both of these waters are oxidizing with an Eh larger than 200 mV. The Np solutions were approximately 10^{-6} M.

The solid phases used for the batch and column experiments were tuffs from the Topopah Spring Member (G4-275) and Calico Hills (G4-1530) and the minerals quartz, clinoptilolite, montmorillonite and hematite. X-ray diffraction powder patterns showed no impurities for quartz, clinoptilolite, and hematite. The montmorillonite sample was found to be over 99% pure with traces of quartz. Tuff G4-275 consists of 61% feldspar, 24% tridymite, 11% cristobalite, 1% hematite, 1% quartz, and traces of smectite and mica. Tuff G4-1530 consists of 55% clinoptilolite, 16% opal-CT, 12% mordenite, 7% quartz,

7% feldspar, and 2% smectite. The tuff particles ranged in size from 75 to 500 μm . The surface area of both of these tuffs is 4.3 m^2/g . The properties of the minerals and tuffs used are given in Tables 2a and 2b.

Table 1. Groundwaters Chemical Composition Concentrations in mg/L

	J-13	UE-25p #1
Si	20.	14.
Mg	1.6	32.
Ca	13.	8.0
Na	47.	150
K	5.4	11.
Li	0.04	0.5
CO_3^{-2}	1.5	31.
HCO_3^-	120	300
Cl^-	7.2	25.
F^-	2.2	4.0
SO_4^{-2}	27.	160
NO_3^-	8.6	0.5
pH	8.4	9.0

Table 2a. Properties of Minerals for Sorption Experiments

Mineral	Surface Area m^2/g	Size, μm
quartz	0.18	200
clinoptilolite	16.	6.8
montmorillonite	78.	16.
hematite	9.1	1.2

Table 2b. Percent Iron Oxides in the Minerals and Tuffs

Solid	% Fe_2O_3	%FeO
quartz	< 0.01	0.02
clinoptilolite	0.14	0.16
montmorillonite	1.4	< 0.01
hematite	99.6	< 0.01
G4-275	1.2	0.02
G4-1530	0.53	< 0.01

RESULTS AND DISCUSSION

The ^{237}Np sorption results obtained by batch sorption experiments are given in Tables 3a and 3b. The amount of Np sorbed per gram of solid divided by the amount of Np per cubic centimeter of solution (in equilibrium with the sorbed Np) is defined as K_d (with units of cm^3/g). The sorption values presented in Table 3a are

given in terms of K_a . The value of K_a is given by the K_d divided by the surface area of the solid phase used. Reporting sorption results in terms of K_a allows normalization of surface effects resulting from differences in surface areas among different solids. Control sorption samples where the Np solutions were exposed to the walls of the container (used for batch sorption experiments) in the absence of any other solid phase indicated no precipitation or loss of Np to the container's walls.

Table 3a. Np Batch Sorption Results

	K_a (m)	
	J-13	UE-25p #1
quartz	$2. \times 10^{-5}$	$2. \times 10^{-4}$
clinoptilolite	$1. \times 10^{-7}$	$1. \times 10^{-7}$
montmorillonite	$3. \times 10^{-7}$	$3. \times 10^{-7}$
hematite	$3. \times 10^{-5}$	$1. \times 10^{-4}$
G4-275	$3. \times 10^{-7}$	$1. \times 10^{-5}$
G4-1530	$5. \times 10^{-7}$	

Table 3b. pH of Np Solutions after Sorption

	pH	
	J-13	UE-25p #1
quartz	8.5	8.9
clinoptilolite	8.6	9.0
montmorillonite	8.5	8.7
hematite	8.5	8.7
G4-275	8.5	8.9
G4-1530	8.4	

Inspection of Tables 3a and 3b indicates that Np sorption increases as the pH of the water increases in cases where surface complexation is thought to be the dominant sorption mechanism (such as in the case of quartz and hematite). This observation is in agreement with previous experiments⁴ indicating that Np sorption onto goethite increases rapidly in the pH range from 6-8. Oxide minerals (such as hematite) even at trace levels in Yucca Mountain tuffs can result in a significant amount of Np retardation provided the oxide minerals are accessible to the Np in solution. The fact that quartz is capable of retarding Np is significant because of the large amount of silica in the tuffs. The sorption of Np onto minerals that are capable of ion exchange (such as clinoptilolite and montmorillonite) seems to be insensitive to changes in the ionic strength of the groundwaters and pH changes. Ion exchange does not seem to be an important mechanism for Np sorption. The neptunyl cation is probably excluded from the exchange sites of the cation exchangers due to its size.

One aspect that makes these experiments difficult to interpret is the large sorption distribution coefficients for iron oxide minerals. As shown in Table 2b, all the minerals have some amount of iron oxide associated with them. Consequently it is difficult to deconvolve the sorption of the bulk rock from the sorption that is associated with the iron oxide mineral only. We attempted to address this problem by using a magnetic separator to enrich a fraction of the crushed tuff G4-1530 with respect to its iron oxide content. The composition of crushed tuff G4-1530 and the two fractions obtained by magnetic separation is given in Table 4.

Table 4. Composition of G4-1530 Fractions (obtained by Magnetic Separation)

	G4-1530	Fraction #1	Fraction #2
% SiO ₂	70	69	71
%TiO ₂	0.08	0.1	0.2
%Al ₂ O ₃	11	12	12
%Fe ₂ O ₃	0.5	0.5	1.5
%MnO	0.06	0.02	0.3
%MgO	0.04	0.03	0.09
%CaO	0.8	0.8	0.6
%Na ₂ O	2.8	2.7	3.2
%K ₂ O	4.1	4.1	4.4
%H ₂ O (-)	1.3	1.5	0.8
%H ₂ O (+)	8.6	9.2	5.2
+CO ₂			
%P ₂ O ₅	0.005	0.001	0.03
%BaO	0.02	0.01	0.04
%SrO	0.003	0.003	0.003

Batch sorption experiments were conducted with these two magnetically separated fractions of crushed tuff G4-1530. The batch sorption coefficient for tuff G4-1530 was 2 ml/g. The batch sorption coefficients for fractions #1 and #2 were 1 and 2 ml/g, respectively. It is not clear from these preliminary results whether there is a strong correlation between the quantity of trace metal oxides in the tuff and the magnitude of the sorption coefficient.

The elution of Np through three columns packed with crushed tuff from Calico Hills G4-1530 was fitted using the code SORBEQ.⁵ The overall model incorporated in the SORBEQ application is a mathematical representation of one-dimensional solute transport incorporating advection, dispersion, and equilibrium sorption in porous medium. In the general case, the transport equation⁶ describing the migration of a solute in a saturated porous medium is given by equation 1.

$$\nabla \cdot (D \nabla C - CU) = \epsilon \frac{\partial C}{\partial t} + Q, \quad (1)$$

where

D = dispersion tensor,
 C = concentration of solute in solution phase,
 U = Darcy's velocity,
 ε = porosity of medium,
 t = time,
 Q = 0 for a non-reactive solute,
 Q = ρ_b $\frac{\partial F}{\partial t}$ for a sorbing solute,
 ρ_b = density of rock in the column, and
 F = amount of solute sorbed per unit mass of solid.

Dispersion has three components: D_L, the longitudinal dispersion coefficient in the direction of the flow and D_T, the transverse dispersion coefficient in the two directions at right angles to the velocity of the flow. The longitudinal and transverse dispersion coefficients are given by equations 2 and 3, respectively.

$$D_L = \epsilon d + \alpha_L |U| \quad (2)$$

$$D_T = \epsilon d + \alpha_T |U| \quad (3)$$

where

d = effective diffusion coefficient in medium, and
 α = dispersivity.

The mechanism of sorption determines the relationship between F and C. When sorption is linear, reversible, and instantaneous, the relationship between F and C is given by equation 4, where K_d is the sorption coefficient.

$$\frac{F}{C} = K_d \quad (4)$$

Substitution of equation 4 into equation 1 yields equation 5. The expression in brackets in equation 5 is the retardation factor, R_f. Equation 6 provides a means of comparing results for sorption coefficients obtained under advective and diffusive conditions with the sorption coefficients obtained utilizing batch sorption experiments. The expression for R_f (given in equation 6) is only valid if sorption is linear, reversible and instantaneous. The Langmuir and the Freundlich isotherms are examples of non-linear relationships between F and C. The code SORBEQ is capable of fitting elution data using these isotherms. In the case of Np, reasonable fits were obtained using the linear relationship given in equation 4.

$$\nabla \cdot (D \nabla C - CU) = \epsilon \left[1 + \frac{\rho_b}{\epsilon} K_d \right] \frac{\partial C}{\partial t} \quad (5)$$

$$R_f = 1 + \frac{\rho_b}{\epsilon} K_d \quad (6)$$

The hydrologic parameters: mean residence time and the Peclet number (Pe), which is given by the column

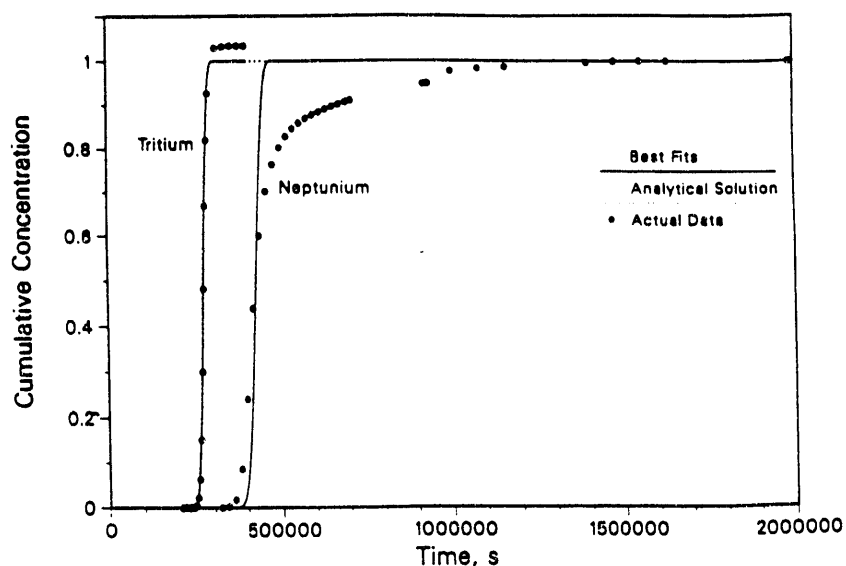


Figure 1. Breakthrough Curves through Column #1 of G4-1530

Table 5. Column Experiments for Np Elution

Solid: Tuff G4-1530
 Particle Size: 75-500 μm
 Water: J-13
 pH range: 8.1 - 8.4
 Np Batch $K_d = 2.2 \text{ ml/g}$

<u>Column Parameters</u>	<u>Column #1</u>	<u>Column #2</u>	<u>Column #3</u>
Length, cm	182	182	183
Diameter, cm	0.5	0.5	0.6
Volume, cm^3	32	32	58
Grams of Tuff	32	33	56
Density, g/ml	1.0	1.0	1.0
Porosity	0.4	0.4	0.4
Volumetric Flow Rate, ml/hr	0.3 for tritiated water 1 for Np	1	1
Interstitial Velocity, m/y	400 for tritiated water 1000 for Np	1000	700
Mean Residence Time, hr	75 for tritiated water 23 for Np	22	36
Pe	1300	970	1500
Dispersivity, cm	0.14	0.19	0.12
Np K_d from fit, ml/g	1.6	1.7	1.9

length divided by dispersivity, were determined for each column using the tritiated water elution data. These parameters were then used to fit the elution of Np through the columns to obtain a value for the sorption coefficient. The same fit was obtained (as shown in Figure 1) when the analytical solution to the one-dimensional version of equation 1 was used to predict the elution data using the parameters listed in Table 5. As shown in Table 5, there is good agreement between the batch sorption K_d and the K_d obtained by fitting the Np elution data.

The Np solution utilized for these experiment also contained ^{238}Pu and ^{239}Pu . The batch sorption coefficients were determined by gamma spectrometry (which is capable of determining the amount of ^{237}Np in each phase). The Np elution data in the column experiments was obtained by liquid scintillation counting. Approximately 30% of the total alpha activity injected into the columns was recovered. The amount of alpha activity due to ^{237}Np in the solution utilized for column injection was 30% of the total activity (as determined by alpha spectrometry). Consequently it appears that all the ^{237}Np injected into the column was recovered with a retardation corresponding to a sorption coefficient of approximately 2 ml/g (see Table 5).

CONCLUSIONS

Neptunium sorption is measurable in tuffs and pure minerals and increases rapidly with increasing pH for minerals that sorb actinides by surface complexation. Oxide minerals (such as hematite) that exist as trace minerals in Yucca Mountain tuffs may provide a significant amount of Np retardation due to their high Np sorption coefficients in groundwaters from Yucca Mountain. The vast amount of silicates in Yucca Mountain tuffs may also provide significant Np retardation due their sorption properties. The dependence of Np sorption on pH can be observed in the sorption behavior of tuff G4-275 and minerals such as quartz and hematite that sorb by surface complexation. Batch sorption coefficients agree with the distribution coefficients obtained under flowing conditions. Consequently, Np sorption appears to be linear, reversible, and instantaneous.

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The XRD data presented in this work was obtained by David Bish and Steve Chipera. The Np(V) stock solution was prepared by Phil Palmer.

The data utilized to compile this document is referenced in Notebook TWS-INC11-9/88-6.

The code SORBEQ used for data analysis has not been fully qualified per the Yucca Mountain Site Characterization Project Software Quality Assurance Plan.

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