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TRANSPORT OF NEPTUNIUM THROUGH YUCCA MOUNTAIN TUFFS

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Introduction

Neptunium has a high solubility in groundwaters from Yucca Mountain [1]. Uranium in nuclear reactors produces ^{237}Np which has a half-life of 2.14 x 10^6 years. Consequently, the transport of ^{237}Np through tuffs is of major importance in assessing the performance of a high-level nuclear waste repository at Yucca Mountain. The objective of this work is to determine the amount of Np retardation that is provided by the minerals in Yucca Mountain tuffs as a function of groundwater chemistry.

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 1g 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 the 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-25 p#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 is given in Table 1. Both of these waters are oxidizing with an Eh larger than 200 mV. The Np solutions are approximately 10^{-6} M.

Table1: Groundwaters Chemical Composition - Concentrations in mg/L

	J-13	UE25p#1		J-13	UE25p#1
Si	20.	14.	CO_3^{-2}	1.5	31.
Mg	1.6	32.	HCO_3^-	120	300
Ca	13.	8.0	F^-	2.2	4.0
Na	47.	150	Cl^-	7.2	25.
K	5.4	11.	SO_4^{-2}	27.	160
Li	0.04	0.5	NO_3^-	8.6	0.5
TOC	0.6	2.	pH	8.4	9.0

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. 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 size range of the tuff particles utilized is from 75 to 500 μm. The surface area of both of these tuffs is 4.5 m^2/g. The properties of the minerals utilized are given in Tables 2a and 2b.

Table 2a: Properties of Minerals for Batch Sorption Experiments

Mineral	XRD Results	Surface Area m^2/g	Size, μm	Zeta Potential in J-13, mV
quartz	No impurities	0.18	200	-40
clinoptilolite	No impurities	16.	6.8	-70
montmorillonite	+99% pure, trace of quartz	78.	16.	-22
hematite	No impurities	9.1	1.2	-33

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

Solid	% Fe_2O_3	%FeO
clinoptilolite		0.1
montmorillonite	1.4	
hematite	99.4	
G4-275	1.25	
G4-1530	0.66	0.02

Results

The ^{237}Np sorption coefficients obtained by batch sorption experiments are given in Table 3. Inspection of Table 3 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 experiments [2] indicating that Np sorption onto goethite has an adsorption edge in the pH range from 6-8. Oxide minerals (such as hematite) even at trace levels can effect a significant amount of Np retardation in tuff 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 speciation of Np in this pH range in J-13 water at 25 °C has been reported by Nitsche [3]. Nitsche's results indicate that 38% of the Np in solution exists as NpO_2^+ and 62% and $NpO_2CO_3^-$. The neptunyl cation is probably excluded from the exchange sites of the cation excanhgers due to its size.

Table 3: Np Batch Sorption Results

	Kd (ml/g)		pH after Sorption	
	J-13	UE25p#1	J-13	UE25p#1
quartz	2.7	43.	8.5	8.9
clinoptilolite	1.8	1.7	8.6	9.0
montmorillonite	20.	24.	8.5	8.7
hematite	250	860	8.5	8.7
G4-275	1.4	53.	8.5	8.9
G4-1530	2.4		8.4	

One aspect that makes these experiments difficult to interpret is the large sorption distribution coefficients for iron oxide minerals. As shown in Table 2a, 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 oxide mineral only.

The elution of Np through three columns packed with crushed tuff from Calico Hills G4-1530 was fitted using the code SORBEQ [4]. The overall model incorporated in the SORBEQ application is a mathematical represenation of one-dimensional solute transport incorporating advection, dispersion, and equilibrium sorption in porous medium. In the generai case, the transport equation [5] describing the migration of a solute in a saturated porous medium is given by equation 1.

$$\nabla \bullet (D\nabla C - CU) = \varepsilon\frac{\partial C}{\partial t} + Q, \qquad (1)$$

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,
$Q = \rho_b \frac{\partial F}{\partial t}$ for a sorbing solute,
ρ_b = bulk rock density , and
F = amount of solute sorbed per unit mass of solid.

Dispersion has tree 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.

$$D_L = \varepsilon d + \alpha_L |U|, \tag{2}$$

$$D_T = \varepsilon d + \alpha_T |U|, \tag{3}$$

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.

$$\frac{F}{C} = K_d \tag{4}$$

Substitution of equation 4 into equation 1 yields equation 5. The expression in brackets in equation 6 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 obatined using the linear relationship, given in equiation 4.

$$\nabla \bullet (D\, \nabla C - CU) = \varepsilon \left[1 + \frac{\rho b}{\varepsilon} K_d\right] \frac{\partial C}{\partial t} \tag{5}$$

$$R_f = 1 + \frac{\rho b}{\varepsilon} \rho b\, K_d \tag{6}$$

The hydrologic parameters: mean residence time and the Peclet number, Pe 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 analytic solution to the one-dimesional version of equation 1 was used to predict the elution data using the parameters listed in Table 4. As shown in Table 4, there is good agreement between the batch sorption Kd and the Kd obatined by fitting the Np elution data.

The fact that only a portion of the Np (~30%) elutes through the columns is puzzling. One reason could simply be an experimental artifact since the Np concentrations in the column experiments was determined using liquid scintillation counting (in a counter which is not capable to discriminate beta activity emmitted by the Pa daughter of Np). This problem would not invalidate the Kd observed but it would make it difficult to keep mass balance. If the reason for the elution behavior observed is not an experimental artifact various possibilities exist that could explain the observed behavior: slow kinetics of speciation or sorption, or irreversibility in the sorption process. There is insufficient data to determine the actual process that has led to the observed behavior.

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 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. Slow kinetics of Np sorption and speciation or irreversible Np sorption appears to occur during the column experiments.

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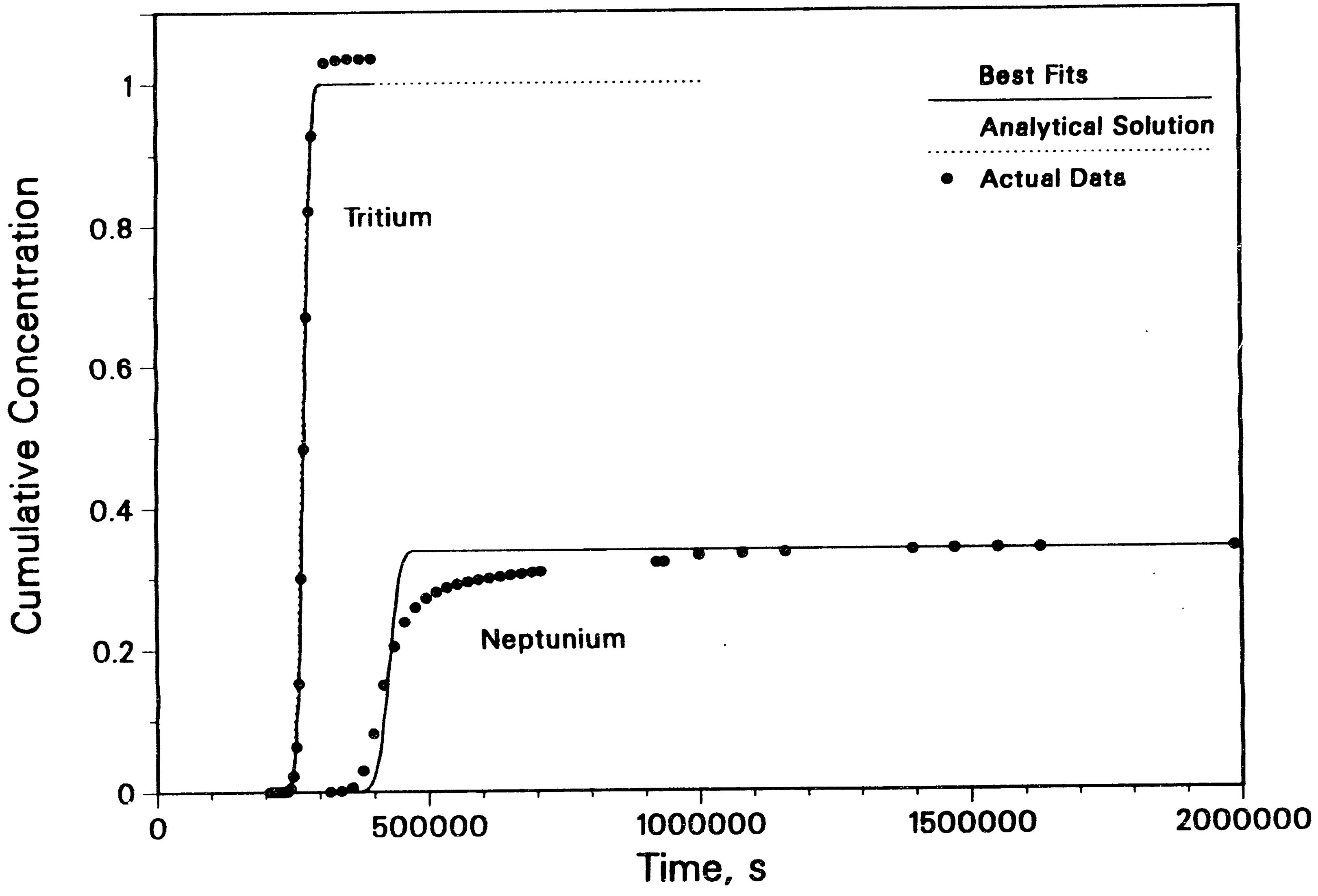
Table 4: Column Experiments for Np Elution

Solid: Tuff G4-1530
Particle Size: 75-500 μm
Water: J-13
pH range: 8.1 - 8.4
Np Batch Kd = 2.4 ml/g

Column Parameters	Column #1	Column #2	Column #3
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
P_e	1300	970	1500
Dispersivity, cm	0.14	0.19	0.12
% Np Eluted	34	31	27
Np Kd from fit	1.6	1.7	1.9

Breakthrough Curves Through G4-1530

Run 1



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