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Uranium and Neptunium Desorption from Yucca Mountain Alluvium

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Abstract – Uranium and neptunium were used as reactive tracers in long-term laboratory desorption studies using saturated alluvium collected from south of Yucca Mountain, Nevada. The objective of these long-term experiments is to make detailed observations of the desorption behavior of uranium and neptunium to provide Yucca Mountain with technical bases for a more realistic and potentially less conservative approach to predicting the transport of adsorbing radionuclides in the saturated alluvium. This paper describes several long-term desorption experiments using a flow-through experimental method and groundwater and alluvium obtained from boreholes along a potential groundwater flow path from the proposed repository site. In the long term desorption experiments, the percentages of uranium and neptunium sorbed as a function of time after different durations of sorption was determined. In addition, the desorbed activity as a function of time was fit using a multi-site, multi-rate model to demonstrate that different desorption rate constants ranging over several orders of magnitude exist for the desorption of uranium from Yucca Mountain saturated alluvium. This information will be used to support the development of a conceptual model that ultimately results in effective K_d values much larger than those currently in use for predicting radionuclide transport at Yucca Mountain.

I. INTRODUCTION

The saturated alluvium south of the proposed high-level nuclear waste repository at Yucca Mountain, Nevada represents the final feature of the Lower Natural Barrier with characteristics and processes that can substantially reduce radionuclide migration before reaching the regulatory compliance boundary. The objective of this work is to demonstrate that radionuclide retardation in the saturated alluvium is likely to be significantly higher than is currently assumed in Yucca Mountain Project (YMP) models. [1] This work also involves the development of an improved reactive transport modeling approach that is compatible with YMP saturated zone transport process models. [1]

Our experimental efforts have focused on the radionuclides of uranium and neptunium because of their high solubility, relatively weak sorption, and their high potential contributions to offsite dose in the Yucca Mountain models. The focus has also been on *desorption* measurements rather than sorption measurements, as we hypothesize that desorption rates likely control radionuclide fate and transport to a much greater degree than sorption rates.

We have developed a flow-through experimental desorption method that provides a nearly continuous measure of desorption rates over a long period of time. [2] Almost all previous experiments conducted by the Yucca Mountain Project [3,4] have focused on batch sorption measurements or very short-duration desorption measurements, which tend to significantly underestimate radionuclide sorption parameters because they do not

interrogate the fraction of radionuclide mass that desorbs very slowly. Quantitative X-ray diffraction and other methods are being used to characterize the alluvium used in the experiments.

To support the interpretation of the experiments and to put the experimental results into a predictive context, we have developed a generalized sorption residence time distribution modeling approach to account for the drastically different desorption rates that have been experimentally observed. [5] This approach is consistent with a conceptual model that involves multiple sorption sites where rates of sorption onto the sites are similar but rates of desorption differ dramatically. The model so far has been able to account qualitatively for desorption behavior observed in the flow-through desorption experiments as well as some anomalous radionuclide transport results in column transport experiments that did not exhibit standard equilibrium or first-order reaction rate behavior. Through continued experimentation, we are developing a mechanistic basis for the model and validating the approach.

II. MATERIALS AND METHODS

II.A. Water and Alluvium

The alluvium used in the experiments is from drill cuttings obtained from NC-EWDP-19IM1A, NC-EWDP-22SA and NC-EWDP-10SA (Figure 1) at depth intervals of 225.6-227.0 meters (740.0-745.0 feet), 169.93-170.69 meters (557.5-560 feet) and 207.26-208.79 meters (680-685 feet) below ground surface, respectively. Alluvium

samples were sieved, and the size range between 75-2000 μm was proportionally recombined. The bulk mineralogies of the three recombined alluvium samples, as determined by quantitative X-ray diffraction, are listed in Table I.

Experiments with the 19IM1A and 22SA alluvium were conducted using a low carbonate (shallow zone from NC-EWDP-19D (Figure 1), referred to as Zone 1) and a high carbonate (deep zone from NC-EWDP-19D, referred to as Zone 4) groundwater. Experiments using 10SA alluvium were conducted with water from the same borehole as the alluvium. The groundwater was filtered using a 0.2 μm filter before use. The total inorganic carbon (carbonate plus bicarbonate) concentrations of the 19D Zone 1, 19D Zone 4 and 10S groundwaters, as measured in the laboratory, are 189, 212, and 100 mg/L, respectively. The pHs of the 19D Zone 1, 19D Zone 4 and 10S groundwaters, as measured in the laboratory, are 8.60, 8.85 and 7.78, respectively. Ionic strengths of the 19D Zone 1, 19D Zone 4 and 10S groundwaters are 0.0044, 0.0047 and 0.0030 $\text{mol}\times\text{L}^{-1}$, respectively.

The objective of the paired experiments using groundwater from Zone 1 and Zone 4 of 19D is to investigate the effect of uranyl and neptunyl carbonate

complex formation on sorption and long-term desorption. The $^{233}\text{U}(\text{VI})$ tracer solutions were prepared by diluting a $^{233}\text{U}(\text{VI})$ (as $\text{UO}_2(\text{NO}_3)_2$ in dilute HNO_3) stock solution obtained from Isotope Products Laboratories in the groundwaters described above. The $^{237}\text{Np}(\text{V})$ tracer solutions were prepared by diluting a $^{237}\text{Np}(\text{V})$ (as NpO_2^+ in HCl) hydrochloric acid stock solution obtained from Los Alamos National Laboratory in distilled water to make a stock solution of $2\times 10^{-4} \text{ mol}\times\text{L}^{-1} \text{ }^{237}\text{Np}$. Lower concentrations of neptunium tracer solutions were made by dilution of the $2\times 10^{-4} \text{ mol}\times\text{L}^{-1} \text{ }^{237}\text{Np}$ stock solution with the groundwaters described above. The final concentrations of each of the $^{233}\text{U}(\text{IV})$ and $^{237}\text{Np}(\text{V})$ tracer solutions are given in Table II. The studies described herein were performed under ambient conditions and the groundwater/tracer solutions used in the experiments are assumed to be in equilibrium with the ambient atmosphere (oxidizing conditions, 0.033% CO_2). The Np solubility at these experimental conditions is approximately $1\times 10^{-5}\text{M}$. [6] Previous sorption control experiments with similar concentrations of Np (with no alluvium present) showed no evidence of precipitation or sorption to container walls. [3]

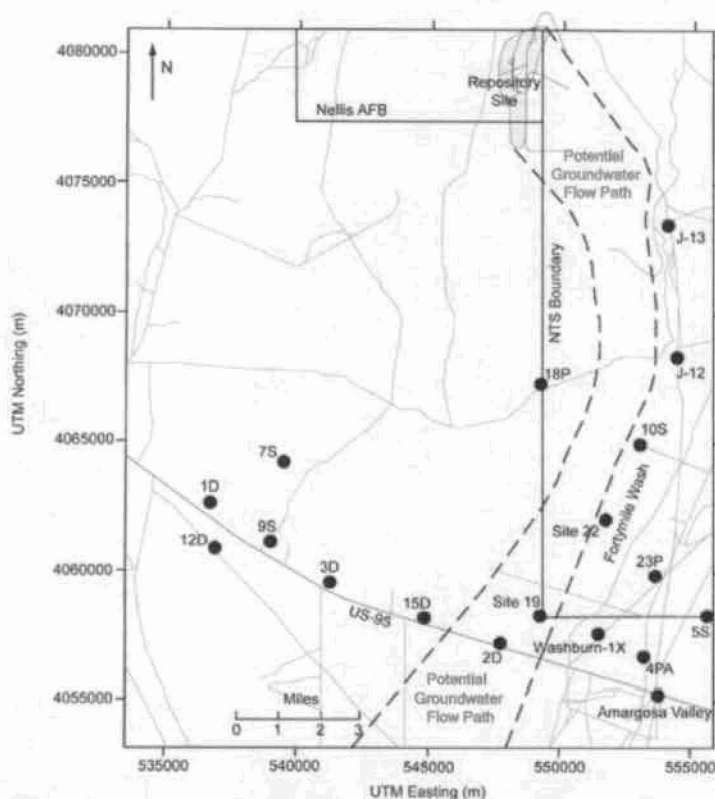


Figure 1. Map showing location of boreholes in relation to the repository site and a potential groundwater flow path. Wells NC-EWDP-19D and NC-EWDP-19IM1A are located in Site 19, NC-EWDP-22SA in Site 22 and NC-EWDP-10SA at the location denoted by 10S.

TABLE I. Quantitative X-ray Diffraction results for alluvium used in long-term uranium and neptunium desorption.

Mineral Phase	Well NC- EWDP- 191M1A (wt %)	Well NC- EWDP- 22SA (wt %)	Well NC- EWDP- 10SA (wt %)
Quartz	15.3	10.1	8.7
Plagioclase	23.0	28.4	26.0
K-Feldspar	24.4	17.5	30.6
Clinoptilolite	7.6	12.0	11.6
Mica	1.3	1.0	1.8
Kaolinite	0.5	0.2	0.4
Cristobalite	5.8	5.9	8.1
Tridymite	4.1	4.3	1.6
Opal-CT	13.6	---	---
Hematite	0.4	0.6	0.5
Smectite	4.6	19.4	8.0
Total	100.6	99.4	97.4

II.B. Long-term Desorption Experiments

Desorption rates were determined by long-term desorption of uranium and neptunium from the alluvium samples. First the alluvium was brought into contact with a tracer solution containing a single radionuclide of interest. The radionuclide was batch sorbed to the alluvium for one to fourteen days and the supernatant was decanted and either centrifuged or filtered to remove fine particles before being analyzed for radionuclide concentration to determine the partition coefficient (ratio of sorbed to nonsorbed radionuclide, or K_d value, ml/g). A partition coefficient implies a linear sorption isotherm, which should provide a good approximation of the sorption isotherm at the relatively low concentrations used in the experiments and the even lower concentrations that would likely occur in the saturated zone. Also, isotherm nonlinearity is expected to be a second-order effect compared to sorption heterogeneity due to variability in mineralogy and water chemistry in the alluvium. The radionuclide-bearing alluvium and tracer free groundwater were added to a small column and placed on a rocking shaker to maximize alluvium-solution contact. Tracer-free groundwater was eluted through the column and collected in fractions. The activity in the samples was measured by a Packard 2500TR liquid scintillation counter. The groundwater zone, sorption period, tracer solution concentration and liquid to solid ratio used for the experiments are listed in Table II.

II.C. Data Interpretation Methods

Results of long-term desorption of uranium after fourteen days of sorption were analyzed using a mathematical model written in FORTRAN that utilizes multiple sorption sites with different first-order forward and reverse reaction rate constants. The adjustable parameters are sorption rate constant, desorption rate constant, number of different types of reaction sites, and maximum sorption capacity for each type of site. The model was used to fit the concentrations in samples collected from desorption columns as a function of time, allowing for flow rate changes and flow interruptions. Equations (1) and (2) below are used in the model to fit the experimental column desorption data as activity desorbing as a function of time. The experimental data were fit as closely as possible using one type of sorption site. Additional site types were added as necessary to improve the fit, while balancing the amount of uranium on the alluvium after the sorption step and the cumulative amount of uranium desorbed from the alluvium.

$$\frac{dc}{dt} = \frac{1}{V} \left\{ Q(C_{in} - C) - \left[k_i \left(1 - \frac{s_i}{s_{i,max}} \right) \right] C + k_{ri} s_i \right\} \quad (1)$$

$$\frac{ds_i}{dt} = \left[\frac{k_i \left(1 - \frac{s_i}{s_{i,max}} \right) C - k_{ri} s_i}{M} \right] \quad (2)$$

where,

- C = concentration out of column, CPM/mL
- C_{in} = conc. in solution flowing into column, CPM/mL
- S_i = amount sorbed to site i , CPM/g
- $S_{i,max}$ = maximum sorption capacity of site i , CPM/g
- V = volume of solution in column, mL
- Q = flow rate through column, mL/hr
- M = mass of solid, g
- k_i = sorption rate constant for site i , mL/hr
- k_{ri} = desorption rate constant for site i , g/hr
- CPM = counts per minute.
- t = time, hr

II. RESULTS

To date, we have conducted 18 long-term uranium desorption experiments and 12 long-term neptunium desorption experiments (Table II). These experiments have been conducted with 3 different alluvium samples and 3 different waters collected from the alluvium south of Yucca Mountain. Each experiment has consisted of a

TABLE II. Experimental parameters used in uranium and neptunium batch sorption and long-term desorption column experiments.

Alluvium/ 19D Ground Water Zone	Sorption Period (days)	Radio- nuclide	Tracer Solution Conc. (M ⁻⁶)	Liquid: Solid Ratio (ml/g)
19IM1A/1	1	U-233	3	2.22:1
19IM1A/1	3	U-233	3	2.24:1
19IM1A/1	14#1	U-233	1	7.55:1
19IM1A/1	14#2	U-233	1	7.53:1
19IM1A/4	1	U-233	3	2.38:1
19IM1A/4	3	U-233	3	2.33:1
19IM1A/4	14#1	U-233	1	7.52:1
19IM1A/4	14#2	U-233	1	7.58:1
19IM1A/1	2	Np-237	3	2.38:1
19IM1A/1	4	Np-237	3	2.22:1
19IM1A/1	14	Np-237	3	1.76:1
19IM1A/4	2	Np-237	3	2.36:1
19IM1A/4	4	Np-237	3	2.38:1
19IM1A/4	14	Np-237	3	1.76:1
22SA/1	1	U-233	3	1.95:1
22SA /1	3	U-233	3	1.78:1
22SA /1	14#1	U-233	1	7.38:1
22SA /1	14#2	U-233	1	7.34:1
22SA /4	1	U-233	3	1.92:1
22SA /4	3	U-233	3	1.93:1
22SA /4	14#1	U-233	1	7.47:1
22SA /4	14#2	U-233	1	7.39:1
22SA /1	1	Np-237	3	2.00:1
22SA /1	3	Np-237	3	1.47:1
22SA /1	14	Np-237	3	1.73:1
22SA /4	1	Np-237	3	1.96:1
22SA /4	3	Np-237	3	2.00:1
22SA /4	14	Np-237	3	1.31:1
10SA	14#1	U-233	1	7.35:1
10SA	14#2	U-233	1	7.40:1

1- to 14-day sorption period (with sorption times being varied) followed by several months of desorption in the flow-through experimental apparatus. The experiments have consistently indicated that both uranium and neptunium initially desorb from the alluvium rather quickly, but their desorption rates eventually slow down and the ratio of sorption to desorption rates (i.e., effective K_d value) for the last 10-50% of the sorbed radionuclide is as much as two orders of magnitude higher than the initial ratio. Figure 2 shows the long-term desorption of uranium from the 19IM1A alluvium sample. For the Zone 1 groundwater (left plot) the long-term desorption results after one and three days of sorption show little difference; it is only after 14 days of sorption that there is a significant change in the amount of desorption. The Zone 4 groundwater (right plot) shows noticeable

differences in the amount of desorption after one, three and fourteen days of desorption. Figure 3 shows the long-term desorption of neptunium from the 19IM1A alluvium sample. The long-term desorption results indicate that for both the Zone 1 groundwater (left plot) and the Zone 4 groundwater (right plot) there is a significant difference in the amount of desorption after two, four and fourteen days of sorption.

Figure 4 shows fits of uranium desorption data with a multiple site/multiple reaction rate model that is consistent with the generalized sorption residence time distribution modeling approach mentioned above. The model fit shown in Figure 4 yielded desorption rate constant estimates that varied over nearly five orders of magnitude for the experiments with the 19D Zone 1 (lower carbonate) groundwater (upper plot) and over 2 orders of magnitude for the experiments with the 19D Zone 4 (higher carbonate) groundwater (lower plot), with the rates decreasing over time. The jumps in the data and model curves in Figure 4 correspond to flow rate changes in the desorption apparatus, including flow interruptions (both planned and unplanned) as indicated on the plots. The model fit for the experiment with 19D Zone 1 groundwater (red line, upper plot) was obtained using a four-site desorption model with rate constants ranging from .07 g/hr (early) to .000001 g/hr (late). Approximately 13% of the uranium initially in contact with the solid remained sorbed to the alluvium at the end of the long-term desorption. The model fit for the experiment with 19D Zone 4 groundwater (red line, lower plot) was obtained using a three-site desorption model with rate constants ranging from .04 g/hr (early) to .0001 g/hr (late). Approximately 6% of the uranium initially in contact with the solid remained sorbed to the alluvium at the end of the long-term desorption. The 19IM1A and 22SA paired column runs using the 19D Zone 1 water consistently result in a higher percentage of initial uranium sorption and a lower percentage of uranium desorbed as a function of time than the experiments utilizing the 19D Zone 4 water in all of the long-term desorption experiments conducted to date (Table III). These results are most likely due to the formation of negatively-charged uranyl carbonate and neptunyl carbonate complexes in solution, which should tend to decrease the tendency for the uranium and neptunium to sorb to the alluvium surfaces. In addition, the 22SA alluvium sample contains a higher weight percent of smectite (Table I) and results in greater partitioning of the radionuclide to the solid phase in the initial sorption, although not always the case after long term desorption (Table III).

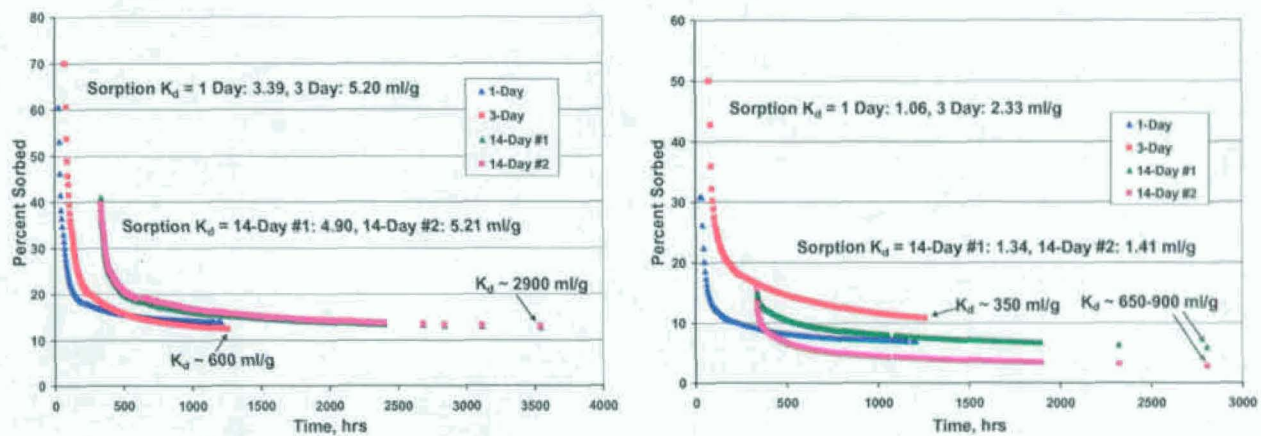


Figure 2. Percentages of uranium sorbed as a function of time in flow-through desorption experiments after different durations of sorption. Alluvium is from NC-EWDP-191M1A and water is from NC-EWDP-19D zone 1 (shallow – left plot) and zone 4 (deep – right plot). The zone 4 water has a higher pH and higher bicarbonate concentration, which suppresses uranium sorption because of carbonate complexation in solution. K_d values at end points are ratios of activity per gram on the solid to activity per milliliter in solution at the end of the long-term desorption. First point on each curve is the end of a sorption experiment.

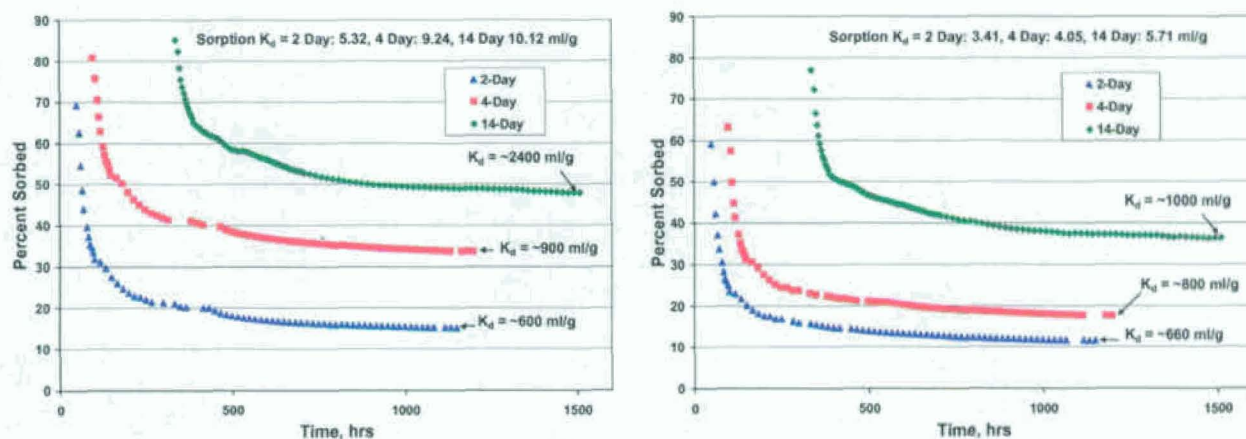


Figure 3. Percentages of neptunium sorbed as a function of time in flow-through desorption experiments after different durations of sorption. Alluvium is from NC-EWDP-191M1A and water is from NC-EWDP-19D zone 1 (shallow – left plot) and zone 4 (deep – right plot). The zone 4 water has a higher pH and higher bicarbonate concentration, which suppresses neptunium sorption because of carbonate complexation in solution. K_d values at end points are ratios of activity per gram on the solid to activity per milliliter in solution at the end of the long-term desorption. First point on each curve is the end of a sorption experiment.

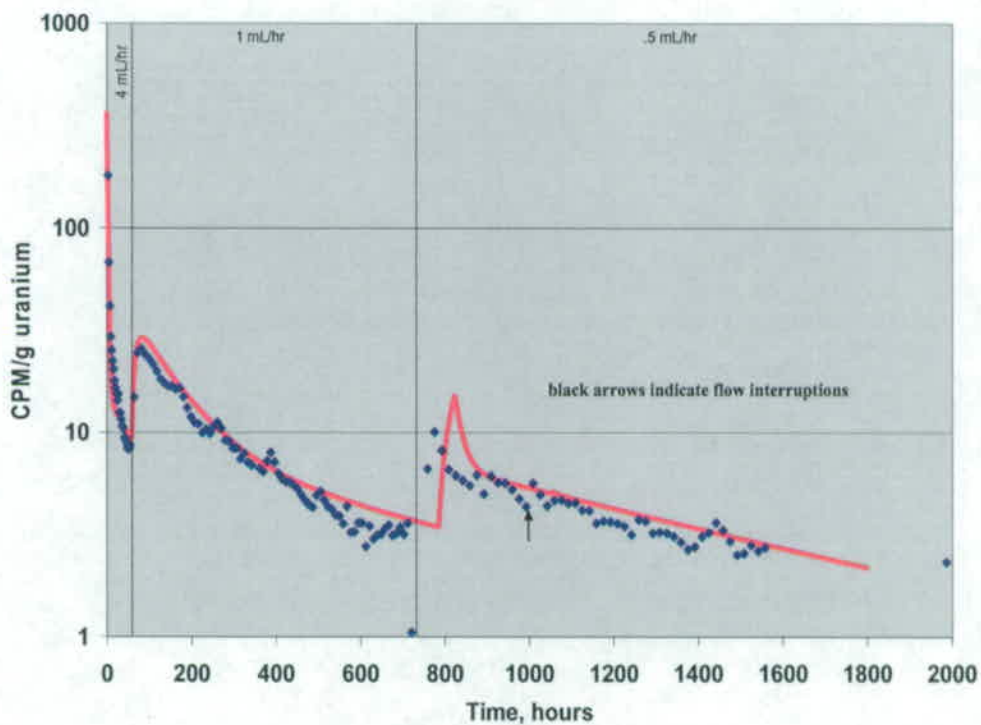
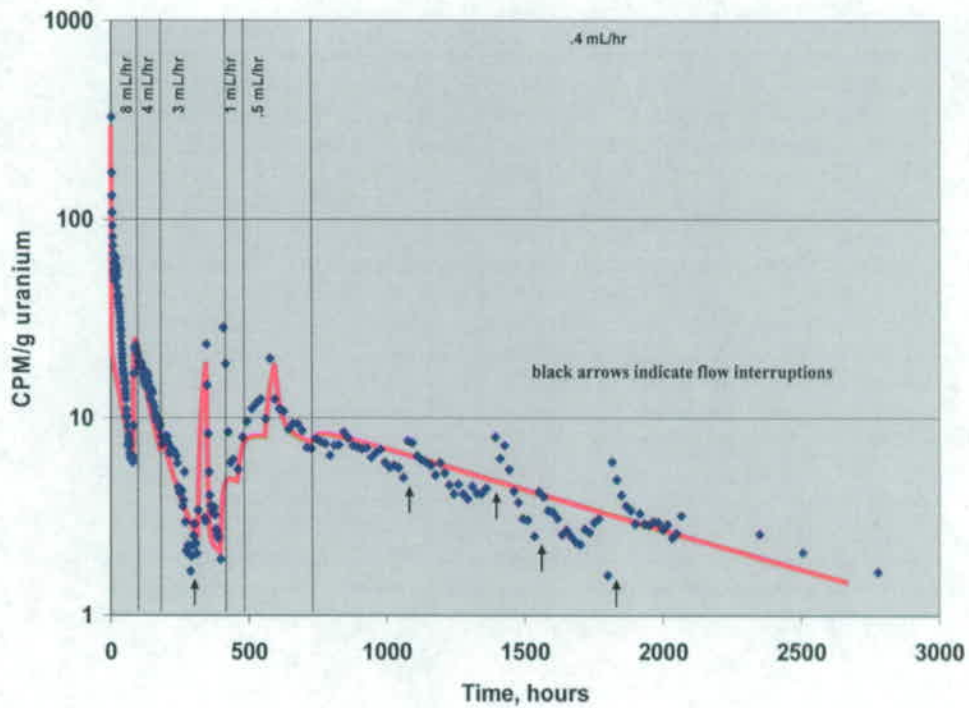


Figure 4. Counts per minute (CPM)/g uranium desorbed as a function of time. Alluvium is from NC-EWDP-19IM1A and water is from NC-EWDP-19D zone 1 (shallow – upper plot) and zone 4 (deep – lower plot). These are the same data as the green curves in the plots of Figure 2, but showing concentrations instead of percent sorbed, and also with time = 0 at the beginning of desorption rather than the beginning of sorption. Arrows indicate times of flow interruptions.

TABLE III. Results of uranium and neptunium long-term desorption column experiments. The 19IM1A and 22SA paired column runs using the 19D Zone 1 water consistently result in a higher percentage of initial uranium sorption and less desorption than the experiments utilizing the 19D Zone 4 water in all of the long-term desorption experiments conducted to date. Experimental parameters are given in Table II.

Alluvium/ 19D Ground Water Zone	Radio- nuclide	Sorption Period (days)	Sorption K_d (ml/g) ^a	Desorption Period (hours)	K_d (ml/g) at end of long-term desorption ^b	% remaining sorbed ^c
19IM1A/1	U-233	1	3.39	1209	1077	13.94
19IM1A/1	U-233	3	5.20	1257	617	12.40
19IM1A/1	U-233	14#1	5.21	3542	2896	12.74
19IM1A/1	U-233	14#2	5.21	3542	3031	13.04
19IM1A/4	U-233	1	1.06	1209	773	6.93
19IM1A/4	U-233	3	2.33	1257	362	10.76
19IM1A/4	U-233	14#1	1.34	2806	983	6.00
19IM1A/4	U-233	14#2	1.34	2806	400	2.73
19IM1A/1	Np-237	2	5.32	1149	603	14.96
19IM1A/1	Np-237	4	9.24	1197	926	33.50
19IM1A/1	Np-237	14	10.12	1507	2370	47.80
19IM1A/4	Np-237	2	3.41	1149	666	11.43
19IM1A/4	Np-237	4	4.05	1197	793	17.36
19IM1A/4	Np-237	14	5.71	1507	1000	36.30
22SA/1	U-233	1	27.04	1364	205	10.96
22SA/1	U-233	3	9.57	1412	217	12.73
22SA/1	U-233	14#1	9.92	679	197	19.95
22SA/1	U-233	14#2	9.92	679	204	20.93
22SA/4	U-233	1	1.97	1364	201	5.15
22SA/4	U-233	3	1.87	1412	155	5.74
22SA/4	U-233	14#1	3.13	2800	948	2.56
22SA/4	U-233	14#2	3.13	2800	140	0.91
22SA/1	Np-237	1	16.8	1276	611	30.14
22SA/1	Np-237	3	16.65	1324	659	30.96
22SA/1	Np-237	14	23.31	1340	332	41.00
22SA/4	Np-237	1	14.26	1276	585	27.00
22SA/4	Np-237	3	15.27	1324	409	32.80
22SA/4	Np-237	14	18.69	1340	576	43.10
10SA	U-233	14#1	5.14	664	158	20.44
10SA	U-233	14#2	5.14	664	128	11.66

^aReference is made to Table II for radionuclide tracer concentrations and liquid to solid ratios which effect sorption K_d values.

^b K_d values are ratios of activity per gram on the solid to activity per milliliter in solution at the end of the long-term desorption.

^cPercent of radionuclide initially sorbed to solid phase remaining sorbed at the end of the long-term desorption experiment.

III. DISCUSSION AND CONCLUSIONS

The results shown in Figures 2, 3 and 4 indicate that there is a very wide range of desorption rates from the alluvium, undoubtedly the result of many different reaction sites in the heterogeneous material. The slower rates (i.e., stronger sorption sites) are not normally apparent from batch sorption experimental results or from short-duration batch desorption experiments. The radionuclide K_d distributions used for YMP saturated

zone transport modeling [1] are almost exclusively derived from such experiments. By not investigating these slow rates, previous YMP experiments have yielded radionuclide K_d values that our experiments indicate may underestimate sorption/retardation in the alluvium. Specifically, the alluvium K_d values used for U and Np in Yucca Mountain models are at least 1-2 orders of magnitude lower than what our experiments would indicate over long time and distance scales. The same probably holds true for other radionuclides as well.

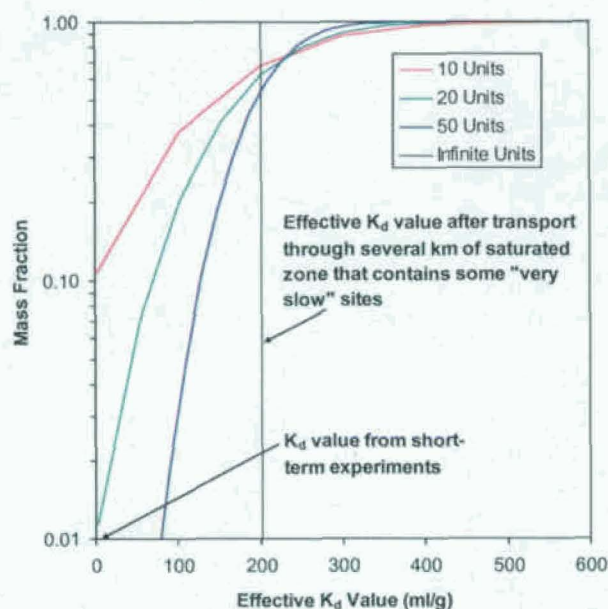


Figure 5. Fraction of radionuclide mass experiencing different K_d values as a function of number of distance units through which transport occurs. Calculations assume a simple two-site model with 80% of the sites having a K_d value of 3 ml/g and 20% of the sites having a K_d value of 1000 ml/g. See text for discussion.

Figure 5 shows the results of a simplistic analysis to illustrate the impact of our experimental results over long time and distance scales. In this example, we consider a simple two-site system in which the first site has a K_d value of 3 ml/g and represents 80% of the available sites, and the second site has a K_d value of 1000 ml/g and represents 20% of the available sites. These values are consistent with our results where frequently 20% or more of the sorbed radionuclide tends to desorb very slowly (i.e., high K_d value), but the slowly desorbing fraction would effectively not be noticed in a batch sorption experiment or short-duration desorption experiment. The apparent K_d value from such an experiment would be ~3 ml/g, or approximately the value corresponding to the weaker sorption site. If we assume that transport in alluvium over a small distance unit results in an 80:20 split of radionuclide mass experiencing the 3 and 1000 ml/g K_d values, respectively, then transport over n distance units will result in only 0.8^n of the radionuclide mass experiencing a K_d value of 3 ml/g, with the remaining radionuclide mass experiencing much greater K_d values. Figure 5 shows the fraction of mass experiencing different K_d values for different values of n , the number of distance units. For large values of n , all of the mass converges toward experiencing a weighted average of the K_d values, in this case $0.8(3) + 0.2(1000) = 202.4$ ml/g. That is, a K_d value of 3 ml/g will be

effectively experienced over 80% of the transport distance, while a K_d value of 1000 ml/g will be experienced over 20% of the transport distance. This simple analysis illustrates how effective K_d values will be much larger over long time and distance scales if the results of our experiments are considered rather than the results of batch sorption and short-duration desorption experiments.

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REFERENCES

1. BSC (Bechtel SAIC Company) 2004. *Site-Scale Saturated Zone Transport*. MDL-NBS-HS-000010 REV 02. Las Vegas, Nevada; Bechtel SAIC Company.
2. SCISM, C., REIMUS, P. AND DING, M. 2004. *Sorption and Desorption Behavior of Uranium in Yucca Mountain Alluvium*, LA-UR-04-7796, presented at Geological Society of America 2004 Annual Meeting, Denver, CO, November 2004.
3. LA0302MD831341.003. Neptunium-237 Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA Under Ambient Conditions. Submittal Date: 02/11/2003.
4. LA0302MD831341.004. Uranium Sorption in Alluvium from NC-EWDP Wells 19IM1A, 10SA, and 22SA Under Ambient Conditions. Submittal Date: 02/11/2003.
5. REIMUS, P., SCISM, C., AND DING, M. 2004. *Modeling of Early Breakthrough Behavior of ^{237}Np and ^{233}U in Yucca Mountain Alluvium*, LA-UR-04-7797, presented at Geological Society of America 2004 Annual Meeting, Denver, CO, November 2004.
6. EFURD, D. WES, WOLFGANG RUNDE, JOE C. BANAR, DAVID R. JANECKY, JOHN P. KASZUBA, PHILLIP D. PALMER, FRED R. ROENSCH, AND C. DREW TAIT. "Neptunium and Plutonium Solubilities in a Yucca Mountain Groundwater". *Environmental Science & Technology*, **32**, 3893 (1998).