

Sorption Characteristics of Radionuclides on Clays in Yucca Mountain Alluvium

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Abstract – Sorption of $^{237}\text{Np(V)}$ and $^{233}\text{U(VI)}$ was measured on clays separated from Yucca Mountain alluvium as a function of solution pH and aqueous actinide concentrations. Our results indicate that sorption of U and Np on the separated clay fraction depends strongly on solution pH. Np sorption on clays increases slowly with increasing pH from 3 to 7. Above pH 7, Np sorption on clays increases rapidly up to a pH of about 10. On the other hand, U sorption on clays reaches its maximum at a pH of about 6, with sorption decreasing as pH increases from 6 to 8 and then increasing again as pH increases further from 8 to about 10. Our results suggest that a Freundlich isotherm can be used to describe U and Np sorption on clays at pH above 5.5. The results of this study indicate that clay minerals play a very important role in the sorption of U and Np on Yucca Mountain alluvium. Indeed, the clay content of the alluvium is probably considerably more important than water chemistry in predicting the ability of the alluvium to attenuate the transport of these radionuclides.

I. INTRODUCTION

The long-term safety of the proposed Yucca Mountain repository relies on the performance of both engineered and natural barriers. The saturated alluvium south of Yucca Mountain represents the last natural barrier to radionuclide transport to the accessible environment in the Yucca Mountain. It is therefore important to evaluate the potential capability of Yucca Mountain alluvium in capturing and retarding the migration of radionuclides under conditions relevant to the field.

The alluvium consists primarily of materials that are of volcanic origin found near Yucca Mountain, with small amount of clays, mostly smectite, and zeolites. Our previous studies on transport of radionuclides in saturated Yucca Mountain alluvium suggested that fine particles, rich in smectite and clinoptilolite, possess a larger radionuclide retention capacity than the bulk alluvium material^[1,2]. Knowledge of the sorption characteristics of radionuclides onto clays in Yucca Mountain alluvium is important from two perspectives: Clays can significantly attenuate radionuclide transport as a result of their high sorption capacity, but they can also facilitate radionuclide transport if they become mobilized as colloids (with radionuclides strongly sorbed to them).

The objective of this study is to characterize the adsorption of U and Np onto clay minerals in the alluvium south of Yucca Mountain so that the contributions of these radionuclides to offsite dose can be more accurately assessed. Rather than using chemically synthesized clay minerals, we separated the clays from the alluvium (Figure 1) using a gravity-settling-velocity method. This method does not separate clays based on mineralogy, but

rather based on grain size and bulk density, so the “clay fraction” is significantly enriched in clays, but it is not entirely comprised of clays. The details of the separation methods and characterization of clay-rich particles can be found elsewhere². The experiments presented in this paper focus on the sorption of $^{237}\text{Np(V)}$ and $^{233}\text{U(VI)}$ onto the clay fraction as a function of pH and aqueous actinide concentration, with particular emphasis on pHs that are common for Yucca Mountain groundwaters.



Fig. 1. Photograph of clay fraction isolated from Yucca Mountain alluvium. The clays are light yellowish, gel-like, and transparent. Field of view is ~5cm.

Table I. Mineral abundance (in weight %) of the alluvium and its clay fraction

Sample	Smectite	Illite/Mica	Clinoptilolite	Quartz	K-Feldspar	Plagioclase	Kaolinite	Cristobalite	Calcite	Tridymite	Total
Alluvium	7±2	1±1	13±1	12±1	44±7	---	2±1	11±1	9±1	1±1	100±8
Clay fraction	68.5	27.9	3.5	0.2	2.4	2.1	---	---	0.4	---	104.8

II. MATERIALS AND METHODS

II.A. Materials

II.A.i. Alluvium and Clays

The alluvium from which the clays were separated is from well NC-EWDP-03S, located south of Yucca Mountain, and taken at depth of 60-65 feet below land surface. Quantitative X-ray Diffraction (QXRD) analysis results of the alluvium and clay fraction separated from the alluvium are listed in Table I. As shown in Table I, the alluvium consists primarily of quartz (SiO_2), cristobalite (SiO_2) and K-feldspar (KAISi_3O_8), with a significant amount of secondary minerals such as clays and zeolites. The clay fraction separated from the alluvium, used in all our experiments, consists primarily of smectite and illite with small amounts of clinoptilolite, a zeolite.

II.A.ii. Radionuclides

$^{237}\text{Np(V)}$ and $^{233}\text{U(VI)}$ were used in this study because the long half-lives (^{237}Np : $T_{1/2} = 2.14 \times 10^6$ years; ^{233}U : $T_{1/2} = 1.592 \times 10^5$ years) as well as the very long half-lives of other U isotopes, combined with the relatively high solubility and weak sorption to volcanic tuffs under oxidizing conditions of these radionuclides, potentially result in significant contributions to long term offsite doses. $^{237}\text{Np(V)}$ tracer solution was prepared by diluting a concentrated $^{237}\text{Np(V)}$ solution (NpO_2^+ in HCl) with distilled water to make a stock solution of 2×10^{-4} mol·L⁻¹ ^{237}Np . Lower concentrations of Np tracer solution were prepared by diluting this stock solution with 0.1 mol·L⁻¹ NaNO_3 . $^{233}\text{U(VI)}$ tracer solution was prepared by diluting a $^{233}\text{U(VI)}$ standard (as Uranyl Nitrate in dilute Nitric acid, Isotope Products Laboratories, an Eckert & Ziegler Company) in distilled water to make a stock solution of 1×10^{-4} mol·L⁻¹ ^{233}U . Lower concentrations of U tracer solutions were prepared by diluting this stock solution with 0.1 mol·L⁻¹ NaNO_3 .

II.B. Methods

Batch sorption tests were conducted over a pH range between about 3 and 10. The ionic strength of the solutions was kept constant at ~ 0.1 M through the use of 0.1 mol·L⁻¹ NaNO_3 solution, and the solution pH was adjusted using HNO_3 or NaOH . Generally, the clays were introduced into 300 ml of 0.1 mol/L NaNO_3 solution, followed by adjusting the suspension to the required pH. After allowing the suspension to sit for one day, the pH was checked and adjusted if needed. Equilibration of clays in the NaNO_3 solution was considered to be reached if the suspension pH remained constant for more than three days. Fourteen ml of the suspension solution was pipetted into polyethylene test tubes. In each test tube a small volume of known activity of either ^{233}U or ^{237}Np solution was added making the total volume of the mixture about 14.5 ml. The tubes were put in a shaker and agitated at a speed of ~ 150 rpm for a week. Centrifuging was used to separate solution from the suspension. A Packard 2550 Tri-Carb Liquid Scintillation Counter (LSC) was used to measure the ^{233}U and ^{237}Np activities in solution.

III. Results and Discussions

III.A. Effect of Solution pH

U and Np partition coefficients (K_d values) associated with the alluvium clay fraction as a function of final solution pH are plotted in Figures 2 and 3. The K_d value is defined as;

$$K_d (\text{ml} \cdot \text{g}^{-1}) = C_s / C \quad (1)$$

where C_s is the concentration of sorbate on the solid (CPM/g), and C is the concentration of sorbate in solution (CPM/ml) (CPM is Counts Per Minute).

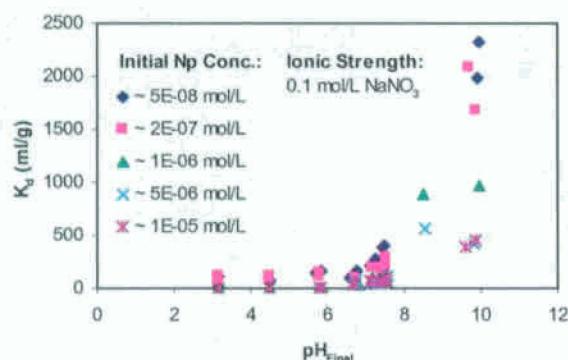


Fig.2. $^{237}\text{Np(V)}$ adsorption on clays as a function of final solution pH.

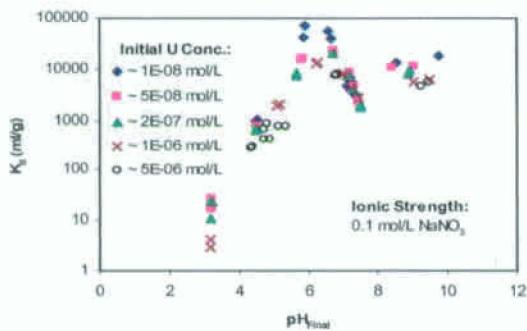


Fig.3. $^{233}\text{U(VI)}$ adsorption on clays as a function of final solution pH.

As is shown in Figures 2 and 3, the sorption of U and Np on clays depends strongly on solution pH. Np sorption on clays increases with increasing pH from 3 to 10. However, U adsorption on clays reaches its maximum at pH of 6. Below pH 6, sorption of U decreases with decreasing solution pH. Above pH 6 and below pH 8, sorption of U decreases with increasing pH, which may be related to the formation of uranyl (UO_2^{2+}) carbonate species in solution. Above pH 8, sorption of U increases again, but only slightly, with increasing pH. This result may be due to surface precipitation⁽⁴⁻⁶⁾ of uranyl (UO_2^{2+}) species at high pH. Increasing sorption of Np above pH 7 may also be attributable to the same process. Another important finding from these experiments is that the distribution coefficients (K_d's) of U on clays are much larger than those of Np at comparable experimental conditions (Table II). The K_d (ml/g) values of U measured at pHs of 6 and 7 range from 4275 ml/g to 21582 ml/g, whereas those for Np at the same pH are considerably smaller with values from 36ml/g to 239ml/g. These

values tend to agree well with those reported previously^(7,8) for U(VI) and Np(V) sorption onto Na-montmorillonite.

TABLE II. Measured K_d values of U and Np on clays at pH of 6 and 7.

Initial concentration (mol/L)	K _d (ml/g) of Np		K _d (ml/g) of U	
	pH 6	pH 7	pH 6	pH 7
5E-08	135	239	21582	7955
2E-07	88	193	20201	7439
1E-06	36	84	12943	4275

III.B. Effect of Aqueous Actinide Concentration

The amount of a solute sorbed as a function of its final concentration in solution measured at constant temperature is called a sorption isotherm³. Many solutes follow a Freundlich isotherm, which can be written as follows:

$$\frac{x}{m} = KC^n \quad (2)$$

where x/m is the mass of solute sorbed divided by the mass of sorbent (CPM/g), C is the final concentration of species in solution in CPM·L⁻¹, K is the Freundlich coefficient, and n is the Freundlich exponent.

Equation (2) can be transformed to:

$$\log(x/m) = \log K + n \log C \quad (3)$$

When n = 1, the isotherm is said to be linear, and the Freundlich coefficient becomes the linear K_d value.

Plots of log (x/m) as a function of final Np and U concentration in solution are shown in Figures 4 and 5. As shown by Figure 4, sorption isotherms of Np on clays at pHs of 6.7, 7.2, 7.4, 7.5, and 9.8 exhibit Freundlich behavior (linear sorption on a log-log plot). Similarly, Figure 5 shows that sorption isotherms of U on clays at pHs of 5.6, 6.7, 7.1, 7.3, 7.5, and 9.2 also exhibit Freundlich behavior.

Table III summarizes the Freundlich isotherm constants for Np and U. This table also indicates that, in general, the sorption capacity of Np on clays is lower than that of U by 1 to 2 orders of magnitude as indicated by the difference of their log K value.

At pHs lower than about 5, our test results suggest that sorption behavior of both Np and U on to clays can not be described by either a Freundlich isotherm equation or a Langmuir isotherm.

Table III. Isotherm constants and characteristics of Np and U sorption on clays

	pH	Log K*	n**	r***
Np	6.7	2.85	0.78	0.96
	7.2	3.24	0.72	0.98
	7.4	3.11	0.75	0.97
	7.5	3.45	0.68	0.97
	9.8	4.14	0.71	0.99
U	5.6	5.34	0.49	0.97
	6.7	5.42	0.57	0.92
	7.1	4.93	0.66	0.88
	7.3	4.57	0.77	0.96
	7.5	3.73	1.11	0.96
	9.2	4.78	0.84	1.00

* K is the Freundlich constant;

** n is the a the Freundlich defined in Eq 2.;

*** r² is the regression correlation coefficient.

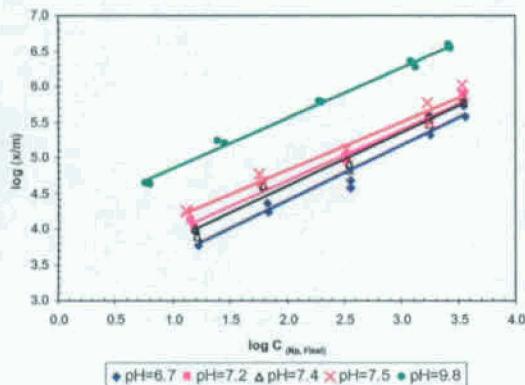


Fig.4. Sorption isotherms of Np onto alluvium clay fraction. C (CPM/ml) is the Np activity in solution after one week adsorption. The initial Np concentration in these experiments was 5×10^{-8} to 5×10^{-5} mol·L⁻¹. X is the amount of Np sorbed on the clay fraction (CPM), and m is the mass of clay used in the experiment (g). The ionic strength of the solutions was 0.1 mol·L⁻¹ NaNO₃. The liquid to solid ratio in the experiments was about 1000 ml·g⁻¹.

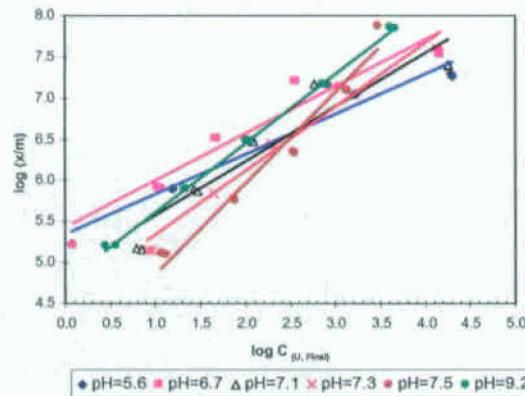


Fig.5. Sorption isotherms of U onto clays. C (CPM/ml) is U activity in solution after one week adsorption. The initial U concentration in these experiments was 1×10^{-8} to 1×10^{-6} mol·L⁻¹. X is the amount of U sorbed on the clay fraction (CPM), and m is the amount of clay used in the experiment (g). The ionic strength of the solutions was 0.1 mol·L⁻¹ NaNO₃. The liquid to solid ratio in the experiments was about 1000 ml·g⁻¹.

III. CONCLUSIONS

The results of this study indicate that the distribution coefficients (K_d values, ml/g) of U and Np on clays in Yucca Mountain alluvium are much higher than those of the bulk alluvium. The range of K_d values associated with bulk alluvium are reported in our previous work^(1,2). This large contrast in K_d values indicates the importance of clay minerals in Yucca Mountain alluvium on the transport behavior of radionuclides in the saturated alluvium near Yucca Mountain.

The sorption of U and Np on clays in the alluvium depends strongly on solution pH, which determines the speciation and solubility of the solution species. Also, the sorption of U and Np on clays in Yucca Mountain alluvium can be described by a Freundlich isotherm between pH 5 and 10.

The results of this study enhances our knowledge of the role of clay minerals on transport of radionuclides in Yucca Mountain alluvium. The clay content of the alluvium is apparently considerably more important than water chemistry in predicting the ability of the alluvium to attenuate the transport of these radionuclides.

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REFERENCES

1. M.Ding, P.R. Reimus, S.D. Ware, A. Meijer, 2003, Experimental Studies of Radionuclide Migration in Yucca Mountain Alluvium, *Proceedings of 2003 International High Level Radioactive Waste Management Conference*, Las Vegas NV., 2003
2. M. Ding, S. Chipera, and P. Reimus, "Sorption and Attenuation of Uranium and Neptunium on Clays from Yucca Mountain Volcanics and Alluvium", proceedings of the International Conference on Energy, Environment and Disasters (INCEED 2005), Charlotte, North Carolina, July 24-30.
3. D. Langmuir, 1997, Aqueous Environmental Geochemistry, Prentice Hall, Upper Saddle River, New Jersey, 600p.
4. Sposito, G., 1984, The Surface Chemistry of Soils, Oxford University Press, NY.
5. Sposito, G., 1986, On Distinguishing Adsorption from Surface Precipitation, in *Geochemical Processes at Mineral Surfaces*, J.A.Davis and K.F. Hayes (eds.), ACS Symposium Series 323, American Chemical Society, Washington, D.C., pp217-228.
6. Farley, K.J., Dzombak, D.A., Morel, F.M.M., 1985, A Surface Precipitation Model for the Sorption of Cations on Metal Oxides, *J. Colloid Interface Science*, **106**, pp226-242.
7. Bertetti P.F., Pabalan R.T., Almendarez M.G., 1998, Studies of Neptunium^V Sorption on Quarze, Clinoptilolite, Montmorillonite, and α -Alumina, in Jenne E.A. editor, Adsorption of Metals by Geomedia, Academic Press, pp131-148.
8. Pabalan R.T., Turner D.R., Bertetti P.F., Prikryl J.D., 1998, Uranium^{VI} Sorption onto Selected Mineral Surfaces: Key Geochemical Parameters, in Jenne E.A. editor, Adsorption of Metals by Geomedia, Academic Press, pp99-130.