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TITLE

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SORPTION OF RADIONUCLIDES ON YUCCA MOUNTAIN TUFFS

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ABSTRACT

A substantial database of sorption coefficients for important radionuclides on Yucca Mountain tuffs has been obtained by Los Alamos National Laboratory over the past ten years. Current sorption studies are focused on validation questions and augmentation of the existing database. Validation questions concern the effects of (1) the use of crushed instead of solid rock samples in the batch experiments, (2) the use of oversaturated stock solutions, and (3) variations in water/rock ratios. Sorption mechanisms are also being investigated. Database augmentation activities include determination of sorption coefficients for elements with low sorption potential, sorption on psuedocolloids, sorption on fracture lining minerals, and sorption kinetics.

Sorption can provide an important barrier to the potential migration of radionuclides from the proposed repository within Yucca Mountain to the accessible environment. In order to quantify this barrier, sorption coefficients appropriate for the Yucca Mountain groundwater system must be obtained for each of the important radionuclides in nuclear waste[1]. Los Alamos National Laboratories has conducted numerous batch (crushed-rock) sorption experiments over the past ten years to develop a sorption coefficient database for the Yucca Mountain site[2]. In the present site characterization phase, the main goals of the sorption test program will be to validate critical sorption coefficients and to augment the existing database where important data are lacking.

DATABASE VALIDATION

The sorption coefficient database available at the present time[2] suggests that for all but a few of the important elements (i.e., U, Tc, Np) sorption coefficients are sufficiently large (i.e., >> 10 ml/g) to make sorption an important barrier to the migration of radionuclides in Yucca Mountain under most conditions anticipated for the site. An important question is, "Are the coefficients included in the database appropriate for modeling radionuclide migration in the Yucca Mountain ground water system? For example, "Could crushing of the rock material used in the batch experiments artificially enhance the value of the sorption coefficient obtained for a given element? For the alkali and alkaline earth elements (e.g., Cs, Ba, Sr), the latter question can be answered with some certainty. Sorption of these elements on Yucca Mountain tuffs is dominated by ion exchange reactions involving zeolites and clays[3]. Ion exchange reactions on these phases are fairly well understood. Further, because these phases have large intracrystalline exchange capacities and because the crystal sizes are much smaller than the (crushed-rock) particle sizes used in the experiments, crushing should not substantially influence the sorption coefficients. This is borne out by comparisons of batch sorption coefficients obtained on crushed and solid samples of several rock types[1]. Because zeolites and clays are relatively abundant along flow paths between the proposed repository and the accessible environment[4], we can say with some confidence that sorption coefficients for the alkali and alkaline earth elements will generally be large over the ranges of environmental conditions and radionuclide concentrations anticipated in the far-field of the proposed repository[2].

For the actinides and lanthanides, the sorption reactions are not as well understood even though measured sorption coefficients are large for many of these elements[2]. Because the stable compounds of Am, and presumably Ce and Eu, have very low solubilities in Yucca Mountain ground waters[5], some question exists as to whether the large sorption coefficient values listed in the present database for these elements[2] could simply reflect precipitation reactions. For example, the solubility limited concentration of Am in Yucca Mountain ground waters is on the order of 10^{-9}M[5]. Because the sorption experiments reported in the database[2] were

TABLE I

Am SORPTION ON DEVITRIFIED TUFF/J-13

Sample no.	Rd (sorption) (ml/g)	Rd (desorption) (ml/g)	Initial Concentration
GU3-688	14,000		6.9 X 10 M
G1-1833	4,200-5,300	5,900-8,900	1.0 X 10 M
GU3-433	2,900-3,800	6,000-14,000	2.1 X 10 M
JA-32	79-230	1,500-2,800	1.0 X 10 M
YM-22	1,100-1,500	1,900-3,100	1.0 X 10 M
YM-54	150-160	400-690	1.0 X 10 M

Solubility of Solid $AmOHCO_3$ = 10 to 10 M

carried out with stock solutions containing 10^{-6} to 10^{-7} M Am, if Am did not sorb onto Yucca Mountain tuffs, precipitation in the sorption experiments could produce an apparent sorption coefficient in the range of 10^3 ml/g. To investigate this possibility, a new set of experiments was carried out with solution concentrations of 6.9 X 10^{-12} M, well below the estimated solubility limited concentration level. At this concentration, normal counting techniques are not appropriate and a mass spectrometric isotope dilution technique was utilized. Preliminary results for a devitrified welded tuff from Yucca Mountain (GU3-688) are shown in Table I. Fortunately, the newly measured sorption coefficient is as large as the largest value measured in the earlier experiments on this type of rock (Table I). In fact, the formation of colloids[6] in the earlier experiments (e.g., samples JA-32, YM-54) may have resulted in a lowering of measured sorption coefficients due to imperfect separation of colloids from the solution phase[5].

Although the new Am results indicate that sorption coefficients for this element should be large in Yucca Mountain tuffs, the batch experiments that produced these results do not provide much indication of the mechanism(s) by which Am is sorbed onto the tuffs. Some knowledge of such sorption mechanisms would not only enhance our confidence in the experimental results obtained to date but would also provide some basis for extrapolation of these results to environmental conditions not directly addressed by the experiments. As a start in this direction, a series of experiments have been initiated to determine the mechanism(s) by which neptunium sorbs to individual mineral phases found in Yucca Mountain tuffs[4]. Np was chosen as the first actinide element to be studied because it has a relatively high solubility in Yucca Mountain ground waters[8] and is therefore easier to analyze. Preliminary results of batch experiments with Np and pure mineral phases are shown in Table II. These experiments were carried out to identify the mineral phase(s) with the greatest affinity for Np under conditions appropriate to the Yucca Mountain ground water system. Once such phases are identified, the mechanism(s) by which Np sorbs to each phase will be investigated in detail. The sorption coefficients listed in Table II have not been corrected for possible differences in the surface areas of the mineral samples although these differences are thought to be of second order. For example, the difference in the Np sorption coefficient measured for synthetic and natural calcite may reflect differences in surface areas for these two samples. Clearly, of the minerals listed in Table II, the iron oxides and oxyhydroxides have the greatest affinity for Np, followed by Mn oxides (romanechite and cryptomelane), the aluminosilicates montmorillonite and clinoptilolite, and finally calcite. Synthetic samples were used instead

TABLE II

Sorption of Np on Pure Minerals

Mineral	Rd (ml/g)
Hematite (synthetic)	5.1 X 10
Goethite (synthetic)	5.1 X 10
Cryptomelane (natural)	7.8 X 10
Romanechite (natural)	1.5 X 10
Calcite (natural)	390
Calcite (synthetic)	21
Montmorillonite (natural)	78
Clinoptilolite (natural)	30

Distilled water buffered at pH = 8.5

of natural samples because the latter are are often "contaminated" with small fractions of other mineral phases, complicating interpretation of the experimental data. Full details of these experiments will be presented elsewhere.

An important part of defining the mechanism(s) by which a given element sorbs to a mineral surface is the experimental characterization of the species of the element attached to the mineral surface. Spectroscopic techniques of the type required to characterize these species have only recently been applied to geochemical problems[7]. As part of an preliminary effort to apply these techniques to the investigation of sorption mechanisms of actinides on Yucca Mountain tuffs, we have designed an experiment involving Np sorbed onto goethite. Although hematite (Fe_2O_3) appears to be the most abundant secondary iron oxide mineral in Yucca Mountain[8], goethite (FeOOH) was chosen for these experiments because well-characterized pure samples were available and because the experimental group had experience with this phase[7]. Np was chosen as the adsorbate because its compounds have relatively high solubilities in Yucca Mountain ground waters as noted above[5]. High solubilities are necessary to permit the transfer of a sufficient number of Np atoms onto the goethite surface, from an undersaturated solution, to obtain a reliable EXAFS signal. An adsorption edge for Np on goethite was obtained (Figure 1) to allow selection of an appropriate pH for the preparation of the EXAFS sample and to provide a basis for future surface complexation modeling efforts[9]. Similar experiments will be carried out with other elements and substrates.

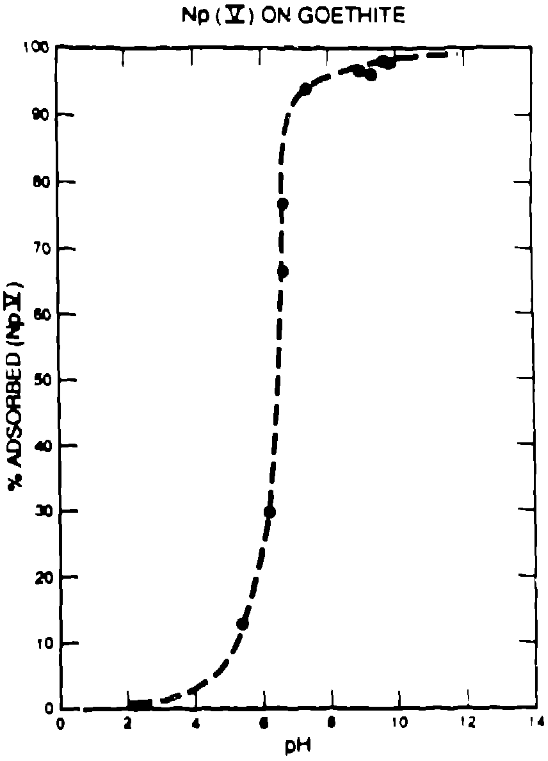

Figure 1. Neptunium absorbed onto synthetic goethite. Initial concentration of neptunium in solution was 5.0 X 10^{-3}M.

TABLE III
WATER/ROCK RATIO EXPERIMENTS
Zeolitic Tuff (G4-1502)/J-13

Ultracentrifugation Experiments

Rd's (ml/g)

W/R Ratio	Ba	Cs	Sr
5:1	6,970 (2,400)	14,600 (4,200)	>10,500
10:1	46,700 (14,000)	13,900 (1,400)	>32,400
20:1	81,100 (3,900)	23,800 (2,200)	>27,900
30:1	123,000 (25,000)	31,100 (770)	108,000 (40,000)

Ultrafiltration Experiments

Rd's (ml/g)

W/R Ratio	Ba	Cs	Sr
5:1	69,200 (4,900)	17,900 (800)	92,500 (55,900)
10:1	106,000 (25,400)	33,500 (3,100)	169,600 (10,900)
20:1	236,000 (4,100)	43,200 (3,700)	207,900 (9,050)
30:1	433,800 (70,300)	44,700 (2,150)	322,100 (5,100)

The influence of different water/rock ratios on sorption coefficients is another validation question needing resolution[10]. The question is, "Could the relatively large water/rock ratios used in the experimental program bias the measured sorption coefficients in a nonconservative direction?" Theoretically, isotherm measurements should provide sufficient information to allow a correction to be made for differences in water/rock ratios in the experiments versus the site. Indeed this seems to be the case for experiments involving devitrified tuffs from Yucca Mountain[3]. However, for zeolitic tuffs the situation is less clear. As shown in Table III, sorption coefficients for Ba, Cs, and Sr on zeolitic tuffs increase with water/rock ratios contrary to theoretical expectation. If this trend is real and not some experimental artifact, it could have important implications for radionuclides which have small sorption coefficients (e.g., Tc, Np, U) as these coefficients might be even smaller at the lower water/rock ratios common to Yucca Mountain. Interestingly, the results for experiments in which solutions were separated from solids by ultrafiltration seem to be more in line with theoretical expectation than those in which ultracentrifugation was the separation method (Table II), although neither technique produced sorption coefficients that decreased with increasing water/rock ratios. A new set of experiments have been initiated using larger samples and larger filtration areas to attempt to resolve this question.

DATABASE AUGMENTATION

Additional batch sorption coefficient data are needed for elements with small sorption coefficients (e.g., Np, Pu, Tc, and U) because the errors associated with the determination of these coefficients are typically a larger fraction of the coefficient than the errors associated with larger coefficients. Experiments are planned to identify the phases with the greatest affinity for these elements. Once identified, the details of the mechanisms by which each of these elements sorb to these phases will be investigated. The results of these investigations should provide a basis for critical evaluations of whole rock sorption coefficients for these elements and thereby allow the derivation of more realistic error estimates.

In addition to sorption coefficient data, other types of information are required to fully quantify the influence of sorption processes on the potential rates of migration of radionuclides from the proposed repository in Yucca Mountain. These include sorption coefficients that pertain to fracture flow, sorption of radionuclides on psuedocolloids that may be present in the ground water system, and the kinetics of sorption reactions. Sorption coefficients that pertain to fracture flow will be estimated by weighting of sorption coefficients measured for each of the important radionuclides on pure mineral phases identified as fracture fillings in cores from Yucca Mountain. The sorption of radionuclides on psuedocolloids will be investigated through batch experiments, once the colloids present in Yucca Mountain ground waters have been characterized. The question of the kinetics of sorption reactions has been partially addressed (Rundberg)[11]. He concluded the kinetics of sorption reactions involving the alkali and alkaline earth elements were sufficiently fast to provide a large margin of safety given the large values measured for the sorption coefficients for these elements. For the actinides and presumably the lanthanides, the situation was less clear partly because the very little is known about the mechanisms by which these elements sorb onto Yucca Mountain tuffs. Plans for the investigation of sorption reaction kinetics and sorption mechanisms for these elements are in place.

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