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ASSESSMENT OF POTENTIAL RADIONUCLIDE
TRANSPORT IN SITE-SPECIFIC GEOLOGIC
FORMATIONS

MASTER

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Assessment of Potential Radionuclide Transport in Site-Specific Geologic Formations

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Associated with the development of deep, geologic repositories for nuclear waste isolation is a need for safety assessments of the potential for nuclide migration. Frequently used in estimating migration rates is a parameter generally known as a distribution coefficient, K_d , which describes the distribution of a radionuclide between a solid (rock) and a liquid (groundwater) phase. This report is intended to emphasize that the use of K_d must be coupled with a knowledge of the geology and release scenarios applicable to a repository. Selected K_d values involving rock samples from and groundwater/brine simulants typical of two potential repository sites, WIPP and NTS, are used to illustrate this concern. Experimental parameters used in K_d measurements including nuclide concentration, site sampling/rock composition, and liquid-to-solid ratios are discussed.

The solubility of U(VI) in WIPP brine/groundwater was addressed in order to assess the potential contribution of this phenomena to K_d values. The results showed a general decrease in solubility with increasing pH as well as a dependence on the total amount of U(VI) initially present in solution (1-50 ppm range). Also indicated was the formation of a U(VI) particulate which passed an 0.8 μm filter but was retained on a 0.2 μm filter. This behavior was observed in a simulant with a composition based on brine from a halite zone in the vicinity of WIPP.

Understanding mechanisms of sorption of radionuclides on rocks would lead to a better predictive capability. In most instances, these are not clearly defined and sorption is attributed to the presence of trace constituents (often unidentified) in rocks, i.e., clay or hydrous oxide materials. An attempt was made to determine if this applied to WIPP dolomite rocks by comparing sorption behavior of the natural material with that of

a synthetic dolomite prepared in the laboratory with reagent grade chemicals. The results were inconclusive as K_d values for Cs, Sr, Eu and Pu were comparable or higher on the synthetic material.

The results of a study of Tc sorption by an argillite sample from the Calico Hills formation at NTS under ambient laboratory conditions were more conclusive. The Tc sorption was found to be associated with elemental carbon, which comprised approximately 1% by weight of the rock. Available evidence points to a reduction mechanism leading to the apparent sorption of Tc on the solid phase.

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INTRODUCTION

Nuclear waste generated both in Defense Programs and in the commercial sector is currently being stored in surface facilities in the U. S. These facilities were not designed to provide isolation of long-lived nuclides from the biosphere for long periods of time. Among the alternatives being considered is permanent disposal in geologic formations located deep beneath the surface of the earth. The most probable scenario for radionuclide release from a deep geologic repository assumes an infusion of groundwater into the repository, leaching of the solid waste therein, and subsequent transport of the dissolved waste to surrounding geologic formations. Although site selection criteria may be designed to give an extremely low probability of occurrence to this scenario, the safety assessment for a specific site must include some evaluation of potential releases of radioactivity to the biosphere.

If groundwater containing dissolved radionuclides from the waste should enter the surrounding geologic formation, reactions such as sorption on rock surfaces or precipitation resulting from changes in solution chemistry can retard nuclide transport. The formation thus acts as a barrier to nuclide transport and, for

safety assessment, it is desirable to quantify this effect. Both site geology and hydrology are obviously very important in nuclide transport modeling. However, this paper deals only with the sorption phenomena.

Ideally, sorption measurements would be made in situ, at the field repository site. However, practical considerations dictate first approximations be made from simple laboratory measurements using core samples and groundwater simulants which are representative of site geology and hydrology. The measured parameter generally representing sorption in transport models is the distribution coefficient, K_d , which denotes the equilibrium distribution of a given nuclide between a solid phase (rock) and a liquid phase (groundwater), expressed in units of ml/gram.

In measuring K_d 's, solution-rock contact times are generally based on the time necessary for the system to reach a constant distribution and can vary from hours to weeks (1). Sorption can and probably does occur on more than one mineral phase in a given rock sample. Precipitation or sorption onto container surfaces can also result in the loss of a nuclide from the liquid phase. In practice, reported K_d values generally include all applicable sorption mechanisms and are in that sense empirical values denoting a nuclide distribution valid only for a specific set of experimental conditions. Nevertheless, the K_d represents the best available means of comparing the sorption properties of rocks from potential repository sites if the measurements are performed under identical conditions. The importance of controlling these

conditions is emphasized in the results of a study initiated by Relya and Serne (2) in which eight laboratories were given "identical" rock samples and solution compositions to be used in measuring K_d for Pu, Sr, and Cs. Other parameters were left to the discretion of the participants. Variations of two to three orders of magnitude in some of the reported K_d values for a given nuclide and rock were attributed to the differences in the experimental procedures used.

In site-specific sorption studies, the choice of experimental parameters is narrowed by the availability of specific field information applicable to the site. This includes groundwater chemistry and mineralogy of the rocks and variations that can be expected to occur based on site characterization studies and reasonable accident scenarios. In this paper, the influence of these parameters representing the environment and other more arbitrary experimental parameters, such as initial tracer concentration and solution-volume to rock-mass ratio, on sorption properties is discussed. Experimental results obtained in our laboratories and by others will be used to emphasize the fact that a discrete value in the form of a K_d assigned to a given radionuclide cannot adequately describe its interaction with a complex geologic environment.

DISTRIBUTION COEFFICIENT MEASUREMENTS

Experimental procedures used in determining K_d generally fall into one of two general types: 1.) a static method represented by batch contact of monolithic or powdered rock with a liquid phase, and 2.) dynamic methods where the liquid phase

flows through monolithic or aggregate rock columns. Both techniques are used in our laboratory; however, the static method using powdered rock is experimentally preferred for the majority of the work. The large number of measurements needed to evaluate the effects of various parameters on K_d values are done more efficiently by the batch method in terms of time, laboratory space, and consumption of limited quantities of core sample. Once potential reactions have been characterized, a limited number of flow experiments must be performed to assess the effects of changes in sorption kinetics, surface area, and surface mineralogy which may have resulted from grinding or other size-reduction and homogenizing techniques.

Rock samples used in the batch K_d 's reported in this paper were prepared by reducing a representative section of a core sample to a $\leq 74 \mu$ maximum-particle-dimension powder. This was accomplished by continued grinding or ball-milling in alumina or tungsten carbide apparatuses until the entire sample passed through a U.S. standard sieve with an average opening of 74μ . Liquid-to-solid ratios during batch contacting were in the range of 30 to 50 ml/gram unless otherwise noted. Radioisotopes were added to groundwater simulants by air-drying the desired quantity of a stock solution of the tracer at ambient temperature in a borosilicate glass container contacting the residue with a groundwater simulant for a minimum period of one day, and then filtering the solution through a 0.8μ filter (Acropore from Gelman Instr. Corp., Ann Arbor, Michigan). This method was found to be more satisfactory than the direct addition of the stock solution as

simulant pH was not altered and changes in "feed" solution activities with time were minimized or eliminated. Simulants were traced with only one nuclide for any given measurement. All solutions were assumed to be initially in equilibrium with the atmosphere and no attempt was made to control Eh during the measurements.

Batch contacting was done in screw-top polyethylene dropper bottles. Polyethylene film was placed over the bottle opening prior to replacing the top to prevent leakage. Sample bottles were agitated during contact times using a wrist-action shaker. Samples of the liquid phase were taken for analyses by placing an 0.8 μ filter (Acropor^R) over the bottle opening, replacing the dropper cap, and compressing the bottle to force the liquid through the filter. The liquid/filter contact times were on the order of 10-15 seconds, and no bias in results due to sorption of the radionuclides on the filter material was observed when the filters were used in this manner.

Kd values were based on liquid-phase analyses, i.e., solid-phase activities were calculated from the difference in activity between a control sample and a sample of the liquid contacted with a rock. With the exception that control solutions were not contacted with rock, they were subjected to the same experimental conditions as were the sample solutions. Pu, Am, and Tc activities were determined by liquid scintillation using Packard Insta-Gel scintillation cocktail and a Packard Model A3255 liquid scintillation counter. All other isotopes were analyzed by gamma spectroscopy using a 3 x 3 inch sodium iodide well detector with a Searle Model 1185 automatic gamma counting system.

GEOLOGICAL SAMPLES AND GROUNDWATER SIMULANTS

Rocks used included dolomites from the Los Medanos area in southeastern New Mexico (WIPP site) and argillaceous rock from the Nevada Test Site (NTS). Laboratory samples were taken from core samples obtained from boreholes in these areas.

The dolomites, subsequently referred to as Magenta and Culebra, were from two water-bearing dolomite units, which are part of the Rustler Formation at the WIPP site, and overlie the repository horizon, which is deep in the Salado Formation. The upper dolomite unit, Magenta, is a fine crystalline, dense dolomite and the lower, Culebra, is vuggy and commonly associated with anhydrite (3,4). Both are approximately 20-30 feet in thickness. Specific boreholes and depths from which samples were taken are included in subsequent discussions.

Argillite was from the Fleana Formation at NTS. Laboratory samples were from the 1805-ft. level of Hole UF17e in the Syncline Ridge area and the 1018-ft. level of Hole UF25A #3 in the Calico Hills area (5).

Groundwater simulants used in work with the dolomites are referred to as Solutions A, B, C and Culebra water. These compositions are given in Table 1. A brief description of these simulants is as follows: 1) Solution A - a brine with high concentrations of K and Mg to simulate a solution formed by water in contact with potash deposits in the vicinity of the WIPP site, 2) Solution B - a brine used to simulate a solution formed by water flooding of the former lower repository horizon at WIPP,

TABLE 1

Nominal Compositions of Groundwater/Brine Simulants

Species*	Solution A	Solution B	Solution C	Culebra H ₂ O	NTS H ₂ O
Na	42,000	115,000	100	2,850	16
K	30,000	15	5	105	6.4
Mg	35,000	10	200	140	25
Ca	600	900	600	685	79
Fe	2	2	1	0.07	0.03
Sr	5	15	15	--	0.42
Li	20	--	--	--	--
Rb	20	1	1	--	--
Cs	1	1	1	--	--
Mn	--	--	--	0.17	--
Si	--	--	--	2.6	31
Cl	190,000	175,000	200	3,750	13
Br	400	400	--	--	--
I	10	10	--	--	--
F	--	--	--	1.4	0.4
SO ₄ ⁼	3,500	3,500	1,750	1,100	6.2
B (BO ₃ ⁼)	1,200	10	--	9.8	--
HCO ₃ ⁻	700	10	100	59.5	280
NO ₃ ⁻	--	--	20	0.99	--
pH	6.5	6.5	7.5	7.5	7.2

* All concentrations given in units of mg/liter.

3) Solution C - a simulant intended to represent potable groundwaters, used for agricultural purposes, from the dolomite units in the Los Medaños area, and 4) Culebra water - a simulant with a composition based on the averaged compositions of non-potable brine found in the Culebra dolomite in boreholes H-2b and H-2c near the site (6).

Groundwater simulant used with the argillite had a composition similar to water from Tippipah limestone and uppermost quartzite in the Eleana Formation at NTS. The composition is given in Table 1 and the method of preparation of this simulant is described elsewhere (7).

VARIATION IN K_d WITHIN GEOLOGICAL FORMATIONS

The initial step in doing sorption studies related to a site-specific geologic formation is choosing samples to represent various rock units in the formation. Rock samples taken from various depths in a number of boreholes in the Culebra and Magenta members were available for study in the form of 2-in. or 4 in. diameter cores approximately 6 in. in length. Powdered samples of these cores were contacted with Culebra water containing Cs, Sr, or Pu(IV) tracer at concentrations of 0.01 $\mu\text{Ci/ml}$ and K_d values as a function of sample location are given in Table 2. These results were extracted from a larger body of data dealing with sorption properties in Magenta and Culebra (8) and represent the range of values observed for these particular nuclides.

Comparison of Cs, Sr, and Pu(IV) K_d 's on Syncline Ridge and Calico Hills argillite showed variations of less than a factor

of two for Cs and Sr, and less than an order of magnitude for Pu (9). However, Tc Kd's differed by more than an order of magnitude on the two materials, i.e., at Tc concentrations of 0.001 $\mu\text{Ci/ml}$, a Kd of 6.5×10^3 was found for the Calico Hills argillite and 200 for the Syncline Ridge material. The sorption of Tc on the argillite from Calico Hills is discussed in more detail in a subsequent section concerned with sorption mechanisms.

SOLUTION CHEMISTRY EFFECTS ON Kd

Nuclide Concentration and Groundwater Composition

Both groundwater composition and nuclide concentration are important parameters since many rocks exhibit low cation exchange capacity and non-linear sorption isotherms. Shiao, et al. (10), in studies with montmorillonite clays, found Kd values for Cs, Sr and Pu decreased gradually with increasing nuclide concentration until a loading of approximately 10% of the total exchange capacity of the clay was achieved. A more precipitous decrease followed at higher loading.

Similar behavior was noted in this work for Cs sorption from Solution C on Culebra dolomite and from NTS water on Syncline Ridge argillite (Fig. 1). The sorption behavior of Cs on argillite may parallel the observation of Shiao as the material contained significant quantities of clay minerals including approximately 5 volume percent of montmorillonite. The concentration range in which Kd is rapidly decreasing ($>10^{-4} \text{ M Cs}^+$) is probably unrealistically high in terms of concentrations which may be expected due to a repository failure unless natural Cs concentrations are high in the groundwaters.

For Cs sorption on dolomite, the change in K_d (Fig. 1) with nuclide concentration is significant in a lower concentration range. The problem presented by this behavior in terms of current transport modeling lies in using a discrete value of K_d to describe the sorption of Cs on Culebra dolomite; obviously this sorption isotherm is nonlinear. This purpose would be better served using empirical a partition ratio which is a function of nuclide concentration. Two such expressions derived to fit the

Figure 1. Distribution coefficients (K_d) for Cs on argillite from Syncline Ridge and Magenta dolomite are plotted as a function of the initial Cs concentration in moles/liter.

Cs sorption data in Figure 1 are $K' = [Cs]_{\text{rock}}/[Cs]_{\text{liquid}}^{.87}$ and $K'' = [Cs]_{\text{rock}}/[Cs]_{\text{liquid}}^{.75}$ over initial Cs concentration ranges of 8.4×10^{-11} to 8.4×10^{-8} M and 8.4×10^{-8} to 7.5×10^{-4} M, respectively. Average values of 1.5 ± 0.1 and 0.18 ± 0.01 were found for K' and K'' , respectively.

The need for two empirical expressions to describe the sorption behavior of Cs on Culebra dolomite as a function of concentration is not understood. If the phenomena is related to exchange capacity, either a low capacity or sorption on a minor component of the dolomite is suggested. Another explanation may be that multiple mechanisms and/or minerals are involved in Cs sorption. The latter was postulated by Erickson in explaining similar observations for sorption of Cs on smectite-rich red clay from the North Pacific (11).

Groundwater composition is of particular importance for repositories planned for halite formations, where any water exiting a repository would most likely be a saturated brine. Subsequent dilution in other groundwaters could result in widely varying compositions, particularly with respect to sodium content. A decrease in nuclide K_d 's with increasing sodium concentration is expected for ion exchange sorption mechanisms. Beall and co-workers (12) observed this trend in studying the sorption of Cs, Rb, and the trivalent lanthanides/actinides on the clay minerals attapulgite, montmorillonite, and kaolinite as a function of sodium concentration.

Similar behavior was observed in our work for sorption of Cs on Magenta dolomite where K_d 's decreased from greater than 600 in deionized water to approximately 20 in simulants containing

5 M Na^+ concentrations. Over a range of 0.25 M to 5.0 M Na^+ produced by the addition of varying amount of Solution B to Solution C, a five-fold decrease in Cs K_d was observed. Again, an empirical relationship, $K' = K_d [\text{Na}]^{-.52}$, can be used to describe Cs sorption, in this case as a function of Na concentration. A value of 57 ± 4 was found for K' over the sodium concentration range cited above.

Hydrogen Ion Concentration

The importance of groundwater pH in radionuclide transport is a difficult parameter to assess. Certainly, the pH plays an important role in determining the solubility and speciation of some of the radionuclides. Water exiting a repository with a pH substantially different than water in the surrounding geology may also alter the mineralogy of the rocks.

The nominal pH of WIPP solutions A, B, and C were 6.5, 6.5, and 7.5 respectively, based on pH measurements of the waters on which the simulant concentrations were based. After contacting powdered Cu²⁺ ore and Magenta dolomites, typical pH values of 6.9, 7.6, and 8.2 are found for Solutions A, B, and C, respectively. Neither the difference in Ph between the three solutions nor the pH changes which occurred during contact with dolomite could be simply correlated with observed K_d values.

A simple procedure used in our work to look for potential pH effects involves consecutive K_d measurements made by contacting two samples of a given rock with the same liquid phase. Effects such as rock alteration, nuclide precipitation, or changes in nuclide species which may result from a pH change during the

initial rock-solution contact should be evidenced by a change in observed Kd during a subsequent contact of the same liquid phase with a fresh sample of the same rock. Applicability of this test extends only to those nuclides which have a linear absorption isotherm in the concentration range involved.

The results of one such test for the sorption of Pu(IV) in Solution B on Culebra dolomite are shown in Table 3. Dolomite samples were contacted with as-prepared Solution B (pH = 6.6) and Solution B which had been pre-equilibrated with powdered Culebra dolomite and filtered through an 0.9 μ filter (pH = 7.8), both of which contained approximately 1.4×10^{-3} ppm of $^{238}\text{Pu(IV)}$. The initial contact time was seven days, after which the solutions were filtered with 0.8 μ filters and analyzed. The filtrates were then contacted with fresh samples of Culebra dolomite for twelve days, filtered with 0.8 μ filters, and analyzed. The overall agreement between the first and second Kd values is considered to be good, particularly for the pre-equilibrated simulant. The difference in Kd's in the as-prepared simulant may be attributed to pH effects or changes in the system which resulted in pH changes; however deviations of this magnitude, less than a factor of two, are commonly observed in duplicate Kd measurements.

Both pH and solution composition effects were apparent in a recently completed study on the interaction of U(VI) with Culebra and Magenta dolomite, and argillite (13). As a part of this work, U(VI) solubility measurements were done in Solutions A, B. and

TABLE 2
Nuclide Sorption on Magenta and Culebra
From Various Boreholes/Depths at the WIPP Site

Borehole/Depth	Member	Kd, ml/g (1)		
		Cs	Sr	Pu(IV)
AEC #8 743'	Magenta	220	30	450
H5A 818'	Magenta	0.6	22	24
H4A 399'	Magenta	60	1.5	830
H4B 517'	Culebra	9	0.6	200
H4B 526'	Culebra	1.2	32	80
H5B 900'	Culebra	26	0.3	390

- 1) One gram samples of rock were contacted with 30 ml. of solution for a period of two weeks.

TABLE 3
Consecutive Kd Determinations: Pu(IV) on
Culebra Dolomite

	<u>[Pu(IV)] initial (1)</u>	<u>Kd (2), ml/g</u>
As-Received Core Solution B		
First Contact	$5.9 \times 10^{-9} \text{ M}$ (6.6)	1.26×10^3 (7.7)
		1.33×10^3 (7.7)
Second Contact	$1.3 \times 10^{-10} \text{ M}$ (7.7)	8.6×10^2
		8.8×10^2
Pre-washed Core Solution B		
First Contact	$5.9 \times 10^{-9} \text{ M}$ (7.8)	1.20×10^3 (7.7)
		1.17×10^3 (7.7)
Second Contact	$1.0 \times 10^{-10} \text{ M}$ (7.7)	1.13×10^3
		1.07×10^3

- The pH of the Pu(IV) - Solution B feed solutions are given in parentheses.
- The results of duplicate experiments are listed. "Equilibrium" pH values are given in parentheses.

C as a function of pH and initial U(VI) concentration. The solutions initially contained 1, 10, or 50 ppm of $^{238}\text{U(VI)}$ traced with $^{237}\text{U(VI)}$. Samples of each concentration were adjusted to a pH of 7, 8, or 9. After five days, the pH was again measured and analytical samples were taken thru both 0.2 μ and 0.8 μ filters (Gelman Acropor^R). A partial summary of the results is given in Tables 4 and 5, however, the trends observed are applicable to all the measurements.

Two potential sources of error, sorption on container and/or filter materials, were found to be negligible in this work. Variation in the final pH from the nominal values reflect changes which occurred during the five day equilibration period. The analytical results show an expected decrease in U(VI) solubility with increasing pH and also point out the complexity of U(VI) solubility, which cannot be expressed by a simple solubility product. Solid precipitates were visually observed in only two samples, both containing solution A at 10ppm U(VI) - pH 8.8 and 50 ppm U(VI) - pH 8.48, respectively. In both cases the quantity of solid was too great to be attributed solely to U(VI) and most likely resulted from solution supersaturation during pH adjustment. However, some phenomena which occurred in Solutions B and C, but not in A, resulted in the formation of U(VI) species that could be differentiated by 0.8 μ and 0.2 μ filters.

The results of U(VI) Kd measurements on Culebra dolomite in four simulants are given in Table 6. Concentrations of 1.4×10^{-3} ppm U(VI) comprised of a mixture of ^{236}U and ^{237}U were used in all of the measurements.

TABLE 4
Concentration and pH Dependence of U(VI)
Solubility in Solution A

<u>Initial [U(VI)], ppm</u>	<u>Final pH</u>	<u>[U(VI)] in Filtrate, ppm</u>	
		<u>0.2μ filter</u>	<u>0.8μ filter</u>
50	7.1	49	50
50	8.0	29	29
50	8.5	1.3	1.1
10	7.1	9.7	9.7
10	7.9	4.9	4.7
10	8.8	0.5	0.5
1	7.0	1.0	1.0
1	8.0	0.8	0.7
1	8.9	0.02	0.08

TABLE 5
pH Dependence of U(VI) Solubility in Solutions A, B, and C
for Initial U(VI) Concentrations of 10 ppm

<u>Solution</u>	<u>Final pH</u>	<u>[U(VI)] in Filtrate, ppm</u>	
		<u>0.2μ Filter</u>	<u>0.8μ Filter</u>
A	7.1	9.7	9.7
A	7.9	4.9	4.7
A	8.8	0.5	0.5
B	6.8	3.3	8.6
B	7.4	1.9	8.9
B	8.8	0.4	5.0
C	6.4	4.9	8.7
C	7.1	1.1	4.4
C	8.5	0.7	2.3

Immediately apparent is the variation in K_d 's with sample location reflecting mineralogical variations and the dependence of K_d and, thus, potential U(VI) transport on the composition of the water. K_d 's in the Culebra H_2O simulant and Solution A are, in general, much lower than those observed in Solution B, a halite brine, and in the groundwater simulant C. The pH values are fairly consistent for a given solution, but variations of greater than one pH unit are seen for different solutions. There appears to be little correlation between K_d and pH solutions with the highest and lowest average pH, Culebra H_2O and Solution A, both exhibit K_d values lower than B and C, which have intermediate pH values.

The formation of U(VI) species in Solutions B and C which were differentiated by 0.2 μ and 0.8 μ filters in the solubility studies does not appear to be a factor in the K_d values. Filters with 0.8 μ pore size were used for liquid solid phase separations, yet the K_d values were generally higher in Solutions B and C than those observed in A. Either the species did not form or formed more slowly at the lower U(VI) concentration, or it was absorbed or influenced in some other manner by the dolomite interacting with the solutions in a different manner. The general trend toward decreasing K_d in Solutions B and C between the four day and seven day measurements (also observed for Magenta dolomite) may be due to a slow change in U(VI) speciation. The lower K_d values observed in Solution A as compared to B and C could result from the higher Mg concentration in A which could reduce the number of potential sorption sites available to U(VI) ion. There is no apparent explanation for the low values

in the Cluebra water, which has a composition bounded by those of Solution B and Solution C, but having a pH equivalent to Solution C initially.

LIQUID TO SOLIDS RATIOS IN Kd MEASUREMENTS

The liquid-to-solid ratio used in measuring Kd by the batch contact method has been shown to affect the experimental results under some conditions. Due to practical considerations, such as the need for liquid/solid separation prior to analyses and the limited availability of core sample, the tendency is to use ratios (10ml/g) which are much higher than those found in typical geologic environments (1ml/g). An example of the influence of this ratio on the sorption of U(VI) on Magenta, Culebra, and argillite from Calico Hills is shown in Table 7.

The liquid phase used for the dolomite rocks was Solution C doped with 8×10^{-10} M U(VI) and that used for the argillite was the NTS simulant containing the same U(VI) concentration. Both solutions were traced with $^{237}\text{U(VI)}$. The Magenta and Culebra dolomites were from the 749' depth of AEC #8 borehole and the 900' depth of the HSB borehole, respectively. Two sets of experiments were done with the dolomites using powders of as-received dry core material and the same material which had been pre-washed three times with Solution C prior to contact with Solution C containing U(VI). This was done by contacting the rock with Solution C using the same liquid-to-solid ratio used in the Kd measurement, centrifuging, and decanting of the liquid. Liquid phase U(VI) concentrations were determined by gamma spectroscopy using the 208 keV peak of $^{237}\text{U(VI)}$ tracer.

A significant trend of decreasing K_d with decreasing liquid-to-solid ratios was observed in all the dolomite measurements. The generally higher K_d 's observed on the pre-washed dolomite may reflect a lower solution ionic strength due to removal of highly soluble components of the core sample during the pre-wash step or possibly changes in the dolomite rock. In these samples there is no apparent correlation of K_d with pH as these values either remain constant or increase slightly as the liquid-to-solid ratio decreases. Increasing pH generally associated with increasing rather than decreasing sorption of cations on inorganic materials (14). The results suggest that U(VI) sorption on dolomite is governed by a solubility product relationship rather than an ion exchange equilibrium.

The trend toward decreasing U(VI) sorption on dolomite as field conditions are approached raises questions as to the validity of extrapolating laboratory data to field conditions. However, the U(VI) results cannot be arbitrarily applied to the sorption of other radionuclides on dolomites. For example, K_d 's determined in batch contact experiments with liquid-to-solid ratios in the range of 50 to 100 ml/g have been adequate to predict Cs transport velocities through one-inch thicknesses of monolithic Magenta core (15), where the liquid-to-solid ratio of the saturated core is approximately 0.15 ml/g.

Similar constraints in generalizing the effect of liquid-to-solid ratios must be applied to argillites. The results in Table 7 indicate that U(VI) sorption on Calico Hills material is not dependent on the liquid-to-solid ratio. However, ^{99}Tc

TABLE 6

U(VI) Distribution Coefficients on Culebra Dolomite

Borehole/ Depth	Contact Time	K _d , ml/g			
		Culebra H ₂ O	Sol. A	Sol. B	Sol. C
H5B 900'	4 day K _d	2.1	0	10	38
	7 day K _d (pH)	2.3 (8.2)	1.6 (7.0)	9.9 (7.6)	31 (8.2)
H55/906'	4 day K _d	5.7	1.8	32	98
	7 day K _d (pH)	7.4 (8.2)	1.3 (7.0)	27 (7.6)	69 (8.1)
H43 517'	4 day K _d	2.5	0	1.5	14
	7 day K _d (pH)	1.1 (8.3)	0.9 (7.0)	2.6 (7.2)	13 (8.3)
H4B/526'	4 day K _d	0.6	0	608	224
	7 day K _d (pH)	0.9 (8.1)	0.3 (7.0)	227 (7.2)	112 (7.3)

TABLE 7

The Effect of Liquid To Solid Ratios On Distribution Coefficients For U(VI) On Dolomites And Argillite and For TcO₄⁻ on Argillite*

Material	Borehole/Depth	U(VI)				
		5	15	25	50	100
Calico Hills Argillite	UE 25A #3 1081'	19	13	10	7.5	11
			(8.5)	(8.3)	(8.2)	(7.8)
Culebra As-Received	H5B 900'	2.1 (8.0)	4.4 (8.0)	5.6 (7.7)	14 (7.7)	38 (8.2)
Culebra Pre-washed	H5B 900'	7.8 (7.6)	14 (7.5)	18 (7.4)	34 (7.4)	80 (7.2)
Magenta As-received	AEC #8 749'	2.3 (8.1)	5.1 (7.9)	8.5 (7.9)	17 (7.7)	43 (8.0)
Magenta Pre-washed	AEC #8 749'	13 (7.7)	20 (7.5)	29 (7.4)	52 (7.4)	130 (7.3)
Tc(VII)						
Calico Hills Argillite	UE 25A #3 1081'	2 (-)	7.5 (7.8)	15 (7.6)	30 (7.6)	60 (7.7)

*The K_d values are given in units of ml/g. The values under the K_d in parentheses are the final pH values. The underlined values at the top are liquid to solid ratios in units of ml/g.

Kd values determined with the same material and simulant decreased significantly over a range of liquid-to-solid ratios of 60 to 2 ml/g (Table 7).

SORPTION MECHANISMS OF GEOLOGICAL MATERIALS

Ideally, site-specific sorption studies would include investigations into mechanisms which result in the sorption of a given nuclide or group of nuclides (i.e. trivalent lanthanides and actinides) on a rock. Many studies have been devoted to ion exchange mechanisms leading to sorption on natural materials such as soils, clay minerals, and zeolites (16). However, information concerning sorption mechanisms associated with deep geologic environments is sparse, a condition which probably reflects a relatively recent interest in these phenomena. The wide variations in nuclide sorption properties of geologic materials which can be described by identical generic nomenclature points out the need for information of this kind. A knowledge of sorption mechanisms would lead to much greater certainty in predicting the influence of repository-related parameters such as those discussed above on potential radionuclide migration.

In this section, the results to date of sorption mechanism studies on dolomites from the WIPP Site and argillite from Calico Hills are summarized. The purpose for including these is to point out some of the problems associated with determining mechanisms (dolomite sorption) and the potential benefits of these studies (Tc sorption on argillite).

The variability of the sorption results on natural dolomite suggests that sorption may be associated in part with minor or

trace mineral phases in the dolomite. Heterogeneity in dolomite sorption properties was demonstrated by autoradiography of monolithic core samples which had been contacted with solutions containing tracer level concentrations ($< 10^{-6}M$) of nuclides (17) and in electron microprobe examinations of core sample which had been contacted with concentrated solutions ($\geq 0.05M$) of stable isotopes of some of the fission product elements (18). Prior to trying to isolate "impurities" associated with heterogeneous sorption on Magenta and Culebra, an attempt was made to determine the sorption properties of the dolomite matrix. Chemically pure, synthetic dolomite (protodolomite) was prepared from reagent-grade chemicals using the method of Gaines (19). Two separate syntheses resulted in materials shown to be a mixture of protodolomite and brucite, $Mg(OH)_2$, and protodolomite, respectively, by comparison of their X-ray diffraction patterns with previously published data (20,21). Distribution coefficients for several nuclides on the synthesized materials are compared with those measured on a natural dolomite in Table 8. The results show that the overall sorption properties of the natural and synthetic materials are similar, indicating that the dolomite matrix of Culebra and Magenta can contribute to nuclide sorption.

There is an apparent disparity between these results and the autoradiography and microprobe data which indicate heterogeneous sorption. A possible explanation may be that impurities such as clay minerals (tentatively identified by microprobe data) in the natural dolomites tend to concentrate the nuclides as a result of higher exchange capacities rather than higher affinities for the

nuclides. This could lead to an erroneous conclusion that nuclide sorption is associated only with impurities in the dolomite. The combined microprobe, autoradiography, and protodolomite experiments definitely lead to the conclusion that nuclide sorption on natural dolomite cannot be attributed to a single mineral phase, but occurs on at least two different phases (possibly by different mechanisms) and possibly more depending on the number and character of the trace constituents present.

The results of a study of the mechanism of Tc sorption on argillite from Calico Hills were more definitive, as sorption was found to be associated with a minor ($\leq 1\%$) carbon phase in the material. Technetium, present in solution as the oxyanion, TcO_4^- , under oxidizing conditions, has shown little tendency to sorb on deep geologic materials (22). Bondietti and Francis (23) observed apparent absorption of Tc on igneous rocks under reducing conditions which they attributed to a reduction of TcO_4^- to form the sparingly soluble oxide, TcO_2 . Fried and co-workers observed absorption of up to 99+% of TcO_4^- tracer on various sulfide minerals, a result which they suggested may be due to redox reactions and/or formation of insoluble sulfide compounds. The high K_d values for Tc on argillite from Calico Hills were observed under oxidizing Eh in our work and prompted an investigation into the mechanism involved. The results of the work are described below and summarized in Table 9.

The as-received core sample contained 1.35% C (organic), 0.032% S, and ferrous iron in the form of siderite in the range of 1-10% by weight. These constituents were of interest because

TABLE 8

Radionuclide Sorption Properties
of Natural Dolomite and Synthetic Protodolomite

	Proto-dolomite K_d , ml/g		Natural dolomite K_d , ml/g	
	<u>Prep #1*</u>	<u>Prep #2**</u>	<u>Culebra</u>	<u>Magenta</u>
Cs	25	76	9	4
Sr	16	9	5	5
Eu	5×10^4	4×10^5	1×10^4	1×10^4
Pu	5×10^3	2×10^3	7×10^3	2×10^3
Tc	0	0	1	1.5

* XRD Patterns Showed Mixture of Protodolomite and Brucite.

** XRD Patterns Showed Only Protodolomite

TABLE 9

Technetium - 99 Sorption on Calico Hill Argillite

<u>As-Received Core</u>	<u>K_d, ml/g</u>	<u>C, % by weight</u>	<u>S, % by weight</u>
HE 25A #3 1081'	2.6×10^3	1.35	0.032
<u>Initial Dissolution</u> <u>(~ 90% Total Weight Loss)</u>			
HF	4.3×10^4	6.8	0.24
HF + HNO ₃	24	4.2	0.17
<u>Final Dissolution</u> <u>(~ 99% Total Weight Loss)</u>			
HF + (HCl + H ₃ BO ₃) ⁽¹⁾	8.5×10^4	~98	ND ⁽²⁾

1) Residue from initial HF dissolution contacted with HCl + H₃BO₃ solution

2) S and Hydrocarbons not detected by GC/MS analysis.

they represent potential reducing agents or precipitants for Tc.

Samples of the core were contacted with HF or HF-HNO₃ solutions at 70°C which resulted in dissolution of approximately 90% of the material. X-ray diffraction analyses showed the residues to be primarily (K, Na) MgAlF₆, a compound which formed during dissolution as it was not observed in the as-received core. Emission spectrographic analyses showed only trace amounts (0-1% by weight) of iron remaining in the residues. Both dissolution techniques resulted in the loss of some of the organic carbon, an effect that was greater in the HF-HNO₃ solution as would be expected due to the presence of the oxidizing acid. The increase in S content in the HF residue correlated with weight loss, however, the HF-HNO₃ dissolution resulted in the loss of some of the S, again due to oxidation. Hydrocarbons were not detected in the residues by infrared spectroscopy or gas chromatography/mass spectrometry.

The most obvious difference in the residues was in their Tc sorption properties. The K_d of the HF residue for Tc correlated reasonably well with the observed weight loss while the Tc sorption properties of the HF-HNO₃ mixture caused a greater decrease in the K_d for Tc than was observed under the same time and temperature conditions for H₂O₂ solutions (K_d = 80) and aqua regia (K_d = 1.5×10^3). No effect on Tc K_d was observed as a result of contacting the argillite with HCl, either as a 1:1 HCl solution or in combination with HF.

Contact of the HF residue with a $\text{HCl} - \text{H}_3\text{BO}_3$ solution resulted in further dissolution leaving a residue which represented approximately 1% by weight of the original argillite sample. The Tc Kd of this residue again increased, however, not by an order of magnitude as would be expected based on weight loss alone. X-ray diffraction, infrared spectroscopy, and gas chromatographic/mass spectrographic analyses did not detect the presence of crystalline material, hydrocarbons, or sulfur. The residue was identified as carbon containing less than 2% non-volatile material when heated in air at 600°C.

The study led to the conclusion that Tc sorption on argillite from Calico Hills under oxidizing conditions was associated with a relatively pure carbon fraction comprising 1% by weight of the core sample. The use of activated carbon to sorb Tc has been reported (25), and tests in our laboratory with activated carbon materials from three sources (Barnebey-Cheney Co., Columbus, Ohio; Mallinkrodt Co., St. Louis Mo., and Matheson, Coleman and Bell, Cincinnati, Ohio) showed Tc Kd's of 170, 7.6×10^3 , and 6×10^3 under the same conditions used in the argillite study.

The chemistry involved in the sorption of TcO_4^- on the "argillite carbon" has not been determined. The results of Landa and co-workers (26) who attributed Tc sorption observed on soil samples to living and/or non-living organic fractions in the soil and Steigman and co-workers (27) who observed reduction of TcO_4^- in dilute alkaline solutions in the presence of polyhydric alcohols and polyhydroxy acids suggest a reduction reaction involving active groups on the carbon surface. The

significant decrease in Tc sorption on argillite subjected to the strongly oxidizing environments of hot HNO_3 and H_2O_2 solutions also suggests a reduction reaction. Electrochemical and ESCA studies being conducted in an attempt to resolve the mechanism have not been completed, but initial results point toward a reduction mechanism.

SUMMARY

The results presented in this paper are intended to reinforce a general observation of a number of investigators working in the area of nuclide transport in geologic environments. That is, a discrete value, such as a distribution coefficient, cannot be assigned to a given radionuclide to adequately describe its interaction with a specific rock type. Empirical relationships may be derived to account for chemical solution parameters such as nuclide concentration or groundwater composition. Parameters which are arbitrarily chosen for laboratory measurements, such as liquid-to-solid ratios and rock form (powder or monoliths) can be evaluated in terms of their importance for a given rock/fluid system and/or nuclide and minimized by subsequent experiment design.

Perhaps the most difficult unknown to account for in site-specific nuclide transport studies is heterogeneity in a geologic formation. Differences in sorption properties among samples from different areas and depths of members, such as the Culebra and Magenta, are as large or larger than those which can be induced by orders-of-magnitude variation in other sorption phenomena. In lieu of in situ transport measurements involving

representative samples of a geologic unit, which are very difficult in terms of accessibility, cost, and experimental duration, there would appear to be two other general approaches to overcoming the problem of heterogeneity.

The first would involve exhaustive site-specific sampling coupled with laboratory studies to determine nuclide sorption properties to gain an understanding of the mechanisms involved. The migration of Tc in argillite, for example, should be a workable problem given that retardation is probably related to a minor carbon phase in the rock and that the distribution of this phase and the hydrology, particularly with respect to oxidation reactions, of the environment could be characterized.

The second approach would involve a change in emphasis from far-field studies to studies of near-field geology and engineered barriers designed to prevent or significantly delay the movement of any aqueous-borne nuclides from the repository environment into the surrounding geology. This would reduce the scope of site-specific transport studies to a well defined regime which are more apt to be adequately characterized with current technology and resources. Far-field migration studies associated with a repository site should not be ignored, but could be deferred until such time that existing or new technology can be applied to the purpose of characterizing deep geologic environments.

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