MASTER

INTERACTION OF RADIONUCLIDES WITH GEOMEDIA

FROM THE NEVADA TEST SITE*

A. W. Lynch and R. G. Dosch

Sandia Laboratories**
Albuquerque, NM 87185

ABSTRACT

Aqueous/solid distribution coefficients have been measured for ^{137}Cs, ^{85}Sr, ^{99}Tc, ^{152}Eu, ^{144}Ce, ^{238}Pu, ^{243}Am and ^{244}Cm on powdered argillite and hornfels obtained from the Nevada Test Site. The fluid phases included a groundwater simulant and deionized water preequilibrated with powdered argillite. Distribution coefficients for lanthanides and actinides are generally high and Eleana Shale was found to effectively sorb technetium.

INTRODUCTION

Among the sites being investigated as a possible repository for radioactive waste are geologic formations at the Nevada Test Site (NTS). One of the studies included in the evaluation is the measurement of distribution coefficients (Kd's) of radionuclides in various aqueous media on the geomedia in the area. Argillite from two areas, Syncline Ridge and Calico Hills, and hornfels from Calico Hills were among the materials initially chosen for study. Both argillites are from the Eleana Formation and were chosen to test the variability of the distribution coefficients.

One concern of the safety assessment of any proposed nuclear waste repository is the potential for groundwater flowing to the waste to leach the waste form, and transport radionuclides to the biosphere. Sorption of the migrating radioisotopes by the surrounding rock could have a significant impact on the rate with which the radionuclides migrate. Distribution coefficients for

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^{137}Cs, ^{85}Sr, ^{99}Tc, ^{152}Eu, ^{243}Am and ^{238}Pu were measured for a simulated groundwater and both powdered hornfels and argillites. Additional measurements were made with argillite from Syncline Ridge in contact with several other groundwater simulants containing the above isotopes plus ^{144}Ce and ^{244}Cm.

The Kd values obtained in the measurements varied over a wide range depending on the rock, the radionuclide and its concentration in solution and the concentration of other ions in solution. Technetium for example did not sorb on hornfels but was strongly sorbed by argillite. The general trends observed were an increase in Kd with decreasing nuclide concentration and lower Kd's in the preequilibrated deionized water as compared to both preequilibrated and as-prepared NTS simulants. There were, however, a number of exceptions to these trends.

GEOMEDIA

The rock samples used were obtained from the following core samples drilled at the Nevada Test Site:

(1) Syncline Ridge argillite - borehole UE17E - 1805' horizon
(2) Calico Hills argillite - borehole UE25H#3 - 1801' horizon
(3) Calico Hills hornfels - borehole UE25H#3 - 1678' horizon

X-ray analysis[1] of the argillite from borehole UE17E - 1805' horizon showed the following constituents: quartz-SiO_2 and illite, a variable composition K-Al silicate along with lesser or trace quantities of chlorite, $(Mg, Fe, Al)_6(Al, Si_4) O_{10}(OH)_8$, ferroan dolomite - $Ca(Mg_xFe_{1-x})(CO_3)_2$, siderite - $FeCO_3$, microcline - $KAlSi_3O_8$, pyrophyllite - $Al_2Si_4O_{10}(OH)_2$ and sodic plagioclase - $(Na,Ca)(Al,Si) AlSi_2O_8$. A quantitative analysis is given elsewhere.[2]

Analyses by emission spectroscopy[2] which compared the argillite ith hornfels with Calico Hills showed no significant difference in qualitative elemental composition. A quantitive analysis[3] for carbon, sulfur and nitrogen gave the following results:

Rock	C	S	N
Hornfels	<0.05%	0.028%	<0.05%
Argillite	1.35%	0.032%	<0.05%

All rock samples used in this work were -200 mesh (<74 micron) powder. A piece of core (50 to 100 grams) was crushed in a tungsten carbide ball mill and/or an alumina mortar and pestle until it completely passed through a 200 mesh sieve.

LIQUID PHASE

The aqueous phase used in the majority of the measurements

was a simulated groundwater with a composition based on an analysis
from the Tippipah limestone which overlies the Eleana and uppermost
quartzite within the Eleana formation.[4] This simulant composition
represented a solution which may enter the repository through a
large fracture. Other solutions include the same simulant pre-
equilibrated with the sample rock to simulate a natural groundwater
solution that is slowly migrating through the area surrounding the
repository and a preequilibrated deionized water solution. Pre-
equilibration of the aqueous solutions with rock were accomplished
by continuously agitating a mixture of 20 grams of crushed argillite
(-200 mesh) with 1-liter of solution for 3 weeks, then filtering.
All measurements were made in solutions containing a single radion-
uclide. The distribution coefficients were determined at two or more
concentrations of each radionuclide. All the solutions were analyzed
prior to use and the results are given elsewhere.[5]

EXPERIMENTAL PROCEDURE

Samples of the argillite and hornfels (1 gram or less) were
weighed directly into 30 ml capacity polyethylene dropping bottles.
The solutions were doped with a single radioisotope in one or two
ways:
(1)   Addition of stock isotope solution directly to the simu-
      lant groundwaters, or
(2)   the stock isotope was dried at ambient temperatures
      then redissolved in the simulant groundwater.

Method (2) was used in an attempt to prevent precipitation in the
control solutions. All controls were filtered through 0.8μ (Gelman
Acropore) filters before adding them to the rock samples.

The measurements made on the argillite from Syncline Ridge
used method (1) exclusively. The liquid to solid ratio was 50
ml/g. The subsequent measurements on the Calico Hills materials
used doping method (1) for the Cs, Sr, Eu and Tc method (2) for
the Pu and Am and a liquid/solid ratio of 30 ml/g. Contact times
of one month were used for all samples.

Sampling involved placing an 0.8 micron filter over the
bottle opening, replacing the cap, and collapsing the bottle to
force the liquid through the filter. Known volumes of the clarified
solutions were used for analyses. Problems associated with multiple
sampling and competing ion effects were circumvented by using a
different simulant-argillite mixture containing a single radionuclide
for each measurement. Control volumes of each doped simulant
solution (containing no rock sample) were carried through an
experimental and sampling procedure identical to that used for the
mixtures. A more detailed description of the sampling procedure
may be found elsewhere.[6]

The fission product activities were determined by gamma ray spectroscopy, using a NaI well crystal. Actinide activities were determined by liquid scintillation counting.

DISTRIBUTION COEFFICIENTS

The Kd's presented in Table I were calculated using Equation 1,

$$Kd = \frac{\text{Control Activity} - \text{Final Activity}}{\text{Final Activity}} \times \frac{\text{Simulant Volume, ml}}{\text{Weight Solid, G}} \quad (1)$$

where activities refer to solution phase activity and the control and final activities refer to those in the control simulant and the filtered simulant-rock mixture, respectively. The Kd values calculated represent total sorption coefficients and are valid only for the conditions set forth in each individual experiment. Parameters such as hydrolysis and absorption on container walls may also contribute to the calculated Kd, however, control samples were used to minimize the latter. The results in most cases are given as both apparent Kd's and overall Kd's. The apparent Kd is the first value given in Table I and was calculated using the activity in the control simulant after the contact period. The values in parentheses were calculated using the initial activity as the control activity in Eq. (1). The Kd thus calculated includes all sorption mechanisms and are referred to as overall Kd's.

137Cesium

Little if any of the original activity added to the controls is lost, therefore the overall values compare closely with the apparent Kd's. All values are quite high (greater than 10^3) with the lowest value being obtained with argillite in equilibrated deionized water (1.3×10^3 ml/gm), and the highest value came from the argillite from Calico Hills in groundwater simulant. All values agree well within a factor of 10. The results indicate that no Cs concentration dependence is evident at the low levels of Cs (1.0 to 0.01 μCi/ml, 0.01 to .0001 ppm) added to the solutions.

Strontium

The results of the strontium Kd measurements vary widely and appear to be strongly dependent on the solution used in the experiment. The reason for the negative value given for the Sr in the preequilibrated NTS simulant is that more 85Sr activity was found in the sample solution than in the control after the 1 month equilibration. This suggests further solution changes may have occurred after contact with the rock. The Kd values ranged from 22 to 69 for all rocks in the simulant while an apparent Kd of 4.1×10^2 ml/gm was obtained with argillite in equilibrated DI water. Stable strontium is included in the simulants (~1 ppm) but

not in the equilibrated deionized water. The low ionic strength, as well as the lack of strontium in the equilibrated deionized water is probably the reason for the high Kd measured.

Technetium

One of the most significant results of the Kd survey was that technetium is removed from solution by the argillite under oxidizing conditions. This phenomenon appears to be fairly unique among the geomedia from the various potential repository sites around the country and is probably associated with the carbon found in the Eleana argillite.

While the hornfels is chemically very similar to the argillite lying above it in Calico Hills, it appears to have no affinity for technitium. A study to determine the mechanism for TeO_4 removal is in progress.

Europium and Cerium

Mechanisms other than sorption on the rock usually are a significant factor when making Kd measurements with europium. This is shown by the large difference between the apparent and overall Kd values for ^{152}Eu for argillite in the equilibrated solutions (37 vs 1.7×10^5 ml/gm). However, the problem was almost negligible in the experiments with as-prepared simulant.

Similar comments may be made about the cerium results. The results do indicate, however, that argillite is a very efficient getter for both cerium and europium (Kd $> 10^3$ ml/gm). The low Kd values given in the equilibrated solutions are a result of the loss of $> 99\%$ of the activity from the filtered control.

Americium

A wide range of Kd values was obtained for americium. The apparent Kd ranged from a low of 77 to a high 3.2×10^4. The low values (77, 78 ml/cm) are due to loss of control activity. Americium is efficiently absorbed on both argillite and hornfels. No ^{243}Am concentration dependence is evident.

Plutonium

Large Kd values were measured for all the samples in contact with the ^{238}Pu. Contrary to the results that might be expected from classical ion exchange processes the Kd's for argillite and hornfels with ^{238}Pu appear to increase with increasing ^{238}Pu concentration over the range of 0.01 to 1.0 $\mu Ci/ml$.

Curium

^{244}Cm was not contacted with the Calico Hills samples, however, the range of Kd values for ^{244}Cm on the argillite from Syncline Ridge appears to be similar to that of the Am and Pu. Loss of control activity is also a problem with Curium.

SUMMARY

The major factors controlling trace radionuclide distribution coefficients associated with the NTS samples are the same as those found with materials and solutions from the proposed WIPP site in New Mexico.[6] These include solution composition, radionuclide concentration and mechanisms which cause the loss of activity in control solutions. For nuclides which do not undergo hydrolysis in the pH range of interest (Cs, Sr and Tc), the overall Kd's agree generally well with the apparent Kd's. For the other isotopes studied solution composition was very important. Distribution coefficients for the lanthanides and actinides were generally found to be high. However, differences between the apparent and overall Kd's of up to five orders of magnitude were not uncommon.

The mechanism for the loss of activity in the control solutions may be hydrolysis, precipitation due to high pH, etc. However, neither the loss of activity from control solutions nor the final activity in the argillite-solution mixtures can be directly correlated with pH or pH changes during equilibration. The overall Kd's appear to provide the most useful empirical data because they include the effects of all mechanisms which result in the removal of radionuclides from the liquid phase.

Based on two samples taken a considerable distance from each other (Calico Hills and Syncline Ridge) Eleana argillite appears to react similarly with the radionuclides tested and is not sensitive to the area from which it was taken. Argillite and hornfels appear to have similar affinities for radionuclides tested with the exception of technetium. Technetium was effectively sorbed on Eleana argillite.

Table I. Distribution Coefficients[1]

Isotope/Rock	Non Equilibrated NTS Simulant			Argillite Equilibrated Solutions	
	1.0[2]	0.1[2]	0.01[2]	NTS Simulant 0.1[2]	D.I. Water 0.1[2]
^{137}Cs					
Argillite (S.R.)[3]	3.1×10^2	3.3×10^3	4.0×10^3	2.2×10^3	1.3×10^3
	(3.6×10^3)	(3.6×10^3)	(4.2×10^3)	(2.2×10^3)	(1.3×10^3)
Argillite (C.H.)[3]	--	5.1×10^3	5.1×10^3	--	--
Hornfels (C.H.)[3]	--	2.4×10^3	2.4×10^3	--	--
^{85}Sr					
Argillite (S.R.)	41	50	43	$\sim$[4]	4.1×10^2
	(53)	(58)	(57)	(287)	(2.1×10^3)
Argillite (C.H.)	--	65	69	--	--
Hornfels (C.H.)	--	22	23	--	--
^{152}Eu					
Argillite (S.R.)	--	1.4×10^4	4.5×10^3	37	18
		(4.2×10^4)	(7.8×10^4)	(1.7×10^5)	(3.3×10^3)
Argillite (C.H.)	--	9.2×10^4	5.8×10^4	--	--
		(9.7×10^4)	(6.6×10^4)		
Hornfels (C.H.)	--	8.3×10^4	9.7×10^4	--	--
		(9.4×10^4)	(1.1×10^5)	--	--
^{147}Ce					
Argillite (C.H.)	--	4.4×10^4	∞	2.9×10^4	26
		(9.0×10^4)	(∞)	(1.5×10^5)	(5.8×10^3)
^{237}Pu					
Argillite (S.R.)	3.3×10^4	2.0×10^3	1.1×10^3	1.4×10^2	9.3×10^2
	(1.1×10^5)	(1.2×10^5)	(1.1×10^5)	(5.5×10^4)	(1.8×10^4)
Argillite (C.H.)	--	1.6×10^4	6.8×10^3	--	--
		(2.0×10^4)	(8.3×10^3)		
Hornfels (C.H.)	--	3.0×10^4	7.4×10^3	--	--
		(3.8×10^4)	(9.2×10^3)		
^{243}Am					
Argillite (S.R.)	5.9×10^3	2.3×10^4	77	3.2×10^4	78
	(1.2×10^5)	(2.6×10^5)	(8.8×10^5)	$8.5 \times 10^4)$	(7.3×10^3)
Argillite (C.H.)	--	1.9×10^4	2.2×10^4	--	--
Hornfels (C.H.)	--	2.9×10^4	2.6×10^4	--	--

Table I. Distribution Coefficients[1] (cont.)

Isotope/Rock	Non Equilibrated NTS Simulant			Argillite Equilibrated Solutions NTS Simulant	D.I. Water
	$1.0^{(2)}$	$0.1^{(2)}$	$0.01^{(2)}$	$0.1^{(2)}$	$0.1^{(2)}$
^{244}Cm					
Argillite (S.R.)	4.8×10^4	--	2.6×10^2	9.0×10^2	1.2×10^2
	(2.8×10^5)	(8.0×10^3)	(1.1×10^5)	(2.2×10^5)	(1.5×10^4)
^{99}Tc		$\leq.01^{(2)}$	$0.001^{(2)}$	$0.001^{(2)}$	$0.001^{(2)}$
Argillite (S.R.)	--	16	196	72	38
		(30)	(244)	(80)	(36)
Argillite (C.H.)	--	155	6.5×10^3	--	--
Hornfels (C.H.)	--	0	0	--	--

(1) Distribution coefficients in ml/gm.
(2) Activity added in μCi/ml. (See ref. 5 for element concentration)
(3) S.R. - Syncline Ridge, Hole UE17E, 1805 feet deep.
    C.H. - Calico Hills argillite, UE25A #3, 1061 feet deep.
    Calico Hills hornfels, UE25A #3, 1678 feet deep.
(4) Final activity in control lower than final activity in sample.

Note: Final pH's ranged from a low of 7.6 in the non equilibrated simulant samples to a high of 8.8 in the equilibrated D.I. water samples.

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