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RADIONUCLIDE TRANSPORT IN A DOLOMITE AQUIFER*

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ABSTRACT

The most probable paths for radionuclide transport between the biosphere and the proposed bedded salt repository (WIPP) in South-eastern New Mexico are through dolomite formations which are the only currently water-bearing units overlying the repository horizon. This paper describes some of the experimental work performed to determine the potential for radionuclide migration in these formations. Included are the results of radionuclide sorption studies on natural dolomites (Magenta and Culebra) and on synthetic dolomite (protodolomite). Sorption on natural dolomites was evaluated with respect to core sample location, groundwater composition, nuclide concentration, and water volume to rock mass ratios used in making the measurements. The results show that a discrete value such as a distribution coefficient (K_d) assigned to a given radionuclide does not accurately describe its interactions with site-specific geological formation.

INTRODUCTION

The final links in the most probable path for radionuclide transport between the biosphere and the proposed bedded salt repository (WIPP) are dolomite formations which represent the only currently water-bearing units overlying the repository horizon. Batch distribution coefficient (K_d) experiments have shown that radionuclides are efficiently absorbed by dolomites under some

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conditions [1]. Based in part on some of this data, mathematical modeling associated with safety assessment efforts predicts significant retardation of radionuclides in groundwater relative to groundwater movement. This study was initiated to obtain a better understanding of the sorption process on dolomite and thus contribute to the reliability of mathematical extrapolation of observed phenomena. The results show that a discrete value such as a K_d assigned to a given radionuclide does not accurately describe its interactions with a site-specific geological formation.

RADIONUCLIDE SORPTION ON NATURAL DOLOMITE

Two water-bearing dolomite beds are recognized in the WIPP site area and range between 20 and 30 feet thick. The upper dolomite member, Magenta, is a finely crystalline, dense dolomite and the lower, Culebra, is vuggy and commonly associated with anhydrite [2]. Since the formations are not homogeneous, measured sorption properties of radionuclides on these formations are dependent on both the borehole location and depth from which core samples used in a particular measurement were obtained. Table I gives some sorption coefficients (K_d) for Cs, Sr and Pu on Magenta and Culebra dolomite obtained from different boreholes near the WIPP site. Techniques used in determining and expressing the K_d values are described elsewhere [1]. The water used for the aqueous phase was a simulant containing approximately 10,000 ppm of dissolved solids with a composition similar to that of water obtained from boreholes H-2b and H-2c in the Culebra formation [3]. The results in Table I were extracted from a larger body of data describing the variability of sorption properties in Magenta and Culebra dolomite [4] and represent the range of sorption behavior observed for these particular nuclides.

TABLE I
Nuclide Sorption on Magenta and Culebra Samples
From Various Locations at the WIPP Site

<u>Borehole/Depth</u>	<u>Formation</u>	<u>K_d, ml/g</u>		
		<u>Cs</u>	<u>Sr</u>	<u>Eu</u>
H5A 800'	Magenta	215	2	280
H5A 811'	Magenta	10	9	126
H5A 818'	Magenta	0.5	22	24
H4B 517'	Culebra	9	0.6	1100
H4B 526'	Culebra	1.2	32	530
H5B 900'	Culebra	68	0.6	4460

RADIONUCLIDE SORPTION ON SYNTHETIC DOLOMITE (PROTO-DOLOMITE)

The variability of the sorption results on natural dolomite suggests that sorption is associated in part with minor or trace mineral phases in the dolomite. This heterogeneity in sorption properties was demonstrated in electron microprobe examinations of Magenta which had been equilibrated with concentrated solutions of stable isotopes of some of the fission product elements [5]. A synthetic dolomite, proto-dolomite, prepared by the method of Gaines [6] with analytical grade reagents, was used in an attempt to determine the sorption properties of the matrix of Magenta and Culebra. Two materials were prepared and were shown to be a mixture of proto-dolomite and brucite (Prep 1) and pure proto-dolomite (Prep 2), respectively, by comparison of their x-ray diffraction patterns with previously published data [7,8]. Sorption coefficients for several radionuclides on the synthesized materials are given in Table II. Sorption coefficients for natural dolomite measured under the same conditions are included for comparison. The data show that the sorption properties of the natural and synthetic materials are very similar, suggesting that the dolomite matrix of Culebra and Magenta can contribute to radionuclide sorption.

There are several probable explanations for the apparent discrepancy between the microprobe study showing heterogeneous sorption and the proto-dolomite work indicating sorption on the dolomite matrix. High solution concentrations (≥ 50 ppm to 1 M) of stable fission product isotopes used in the microprobe work probably led to precipitation in localized areas where solubility products were exceeded. Strontium sorption, for example, was associated with gypsum inclusions in the natural dolomite. Impurities, such as

TABLE II

Comparison of the Radionuclide Sorption Properties of Natural Dolomite and Synthetic Proto-dolomite

	Proto-dolomite	Kd, ml/g	Natural dolomite	
	Prep #1*	Prep #2**	Culebra	Magenta
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
Am	7×10^3	2×10^4	2×10^4	2×10^3
Tc	0	0	1	1.5

*XRD patterns showed mixture of proto-dolomite and brucite.

**XRD patterns showed only proto-dolomite.

clay minerals, with higher exchange capacities per unit volume than the matrix material would also contribute to apparent heterogeneous sorption, particularly if the concentrations of sorbed species on the dolomite matrix were below microprobe detection limits.

THE EFFECT OF GROUNDWATER COMPOSITION AND NUCLIDE CONCENTRATION ON RADIONUCLIDE SORPTION

Both groundwater composition and nuclide concentration are important parameters in sorption studies associated with radionuclide migration since most natural materials exhibit low cation exchange capacities and non-linear absorption isotherms. Shiao, Rafferty and Meyer [9] found in studies with montmorillonite clays, that the K_d values for Cs, Sr and Eu decreased gradually with increasing concentrations until approximately 10% of the total exchange capacity of the clay was achieved. This was followed by a more precipitous decrease at higher loadings. Similar behavior was noted in this work in the case of Cs sorption on Culebra dolomite and is evidenced by the results given in Table III.

The problem presented by this behavior in terms of current

TABLE III

Dependence of Cs Distribution Coefficients
on Culebra Dolomite on Cs Concentrations

1. Initial Cs Concentration Range: 8.4×10^{-11} to $8.4 \times 10^{-8} M$

$[Cs]_{\text{initial, mole/l}}$	$K_d, \text{ml/g}$	$K', \text{ml/g}$
8.4×10^{-11}	34	1.4
8.4×10^{-10}	24	1.4
8.4×10^{-9}	21	1.7
8.4×10^{-8}	12	1.3

$$K' = [Cs]_{\text{rock}} / [Cs]_{\text{liquid}}^{87}$$

2. Initial Cs Concentration Range: 8.4×10^{-8} to $7.5 \times 10^{-4} M$

$[Cs]_{\text{initial, moles/l}}$	$K_d, \text{ml/g}$	$K'', \text{ml/g}$
8.4×10^{-8}	12	0.19
7.6×10^{-7}	6.4	0.18
7.5×10^{-6}	3.2	0.16
3.8×10^{-5}	2.3	0.18
7.5×10^{-5}	1.8	0.17
7.5×10^{-4}	1.2	0.20

$$K'' = [Cs]_{\text{rock}} / [Cs]_{\text{liquid}}^{75}$$

transport modeling lies in choosing a discrete value of K_d to describe the sorption of Cs on Culebra. This purpose would be better served using empirical constants, K' and K'' , where $K' = [Cs]_{rock}/[Cs]_{liquid}^{107}$ and $K'' = [Cs]_{rock}/[Cs]_{liquid}^{175}$ over initial Cs concentration ranges of 8.4×10^{-11} to 8.4×10^{-8} and 8.4×10^{-8} to $7.5 \times 10^{-4} M$, respectively. Average values of 1.5 ± 0.1 ml/g and 0.18 ± 0.01 ml/g were found for K' and K'' , respectively.

The effect of groundwater composition on K_d is of particular importance in the case of repositories planned for halite formations where any water escaping from the repository would most likely be a saturated brine. Subsequent dilution in other groundwaters could result in widely varying compositions, particularly with respect to sodium concentrations. Values of distribution coefficients of greater than 600 are observed for Cs on Magenta dolomite in de-ionized water. The effect of sodium ion concentration on Cs sorption on Magenta is shown in Table IV over a sodium concentration range of 0.25 to 5.0 M. This range was produced by adding varying amounts of brine representing water in contact with a halite zone to a synthetic groundwater typical of the WIPP site area. Again, an empirical relationship, $K''' = [Cs]_{rock}/[Cs]_{liquid} \times [Na]^{0.52}$ can be used to describe sorption as a function of sodium concentration, where an empirical constant, K''' , was found to be 57 ± 4 for the concentration range studied.

THE EFFECT OF LIQUID TO SOLID RATIOS USED IN LABORATORY SORPTION MEASUREMENTS

The liquid to solid ratio used in measuring distribution coefficients by batch contacting of a groundwater containing dissolved radionuclides with a solid has been shown to effect experimental results. Due to practical considerations such as the need for liquid-solid phase separation prior to analyses and limited availability of core sample, the tendency is to use liquid to solid ratios (>10 ml/g) which are much higher than those found in typical geological formations ($<<1$ ml/g). An example of the influence of this ratio for the sorption of U(VI) on Magenta and Culebra dolomites is shown in Table V. The liquid phase used in these measurements was Solution C [1], a groundwater simulant typical of the WIPP area and was doped with a mixture of ^{235}U and ^{237}U to a concentration of $8 \times 10^{-10} M$ U(VI). The ^{237}U to ^{235}U isotopic ratio was 1.8×10^{-4} . The solid phases were -200 mesh Magenta and Culebra dolomite from the 749' depth of the AEC#8 borehole and the 500' depth of the HSB borehole, respectively. Two sets of experiments were done using as-received dry core material and the same material which had been pre-washed with the groundwater simulant prior to contact with the doped simulant. Liquid phase U(VI) concentrations were determined by gamma spectroscopy using the 208 Kev peak of ^{237}U .

TABLE IV
The Effect of the Presence of Sodium on Sorption
of Cesium on Magenta Dolomite

<u>[Na], mole/liter</u>	<u>Kd, ml/g</u>	<u>K'', $\frac{\text{ml} \cdot \text{mole}}{\text{g} \cdot \text{liter}}$</u>
0.25	101	50
0.50	80	56
0.75	66	57
1.0	59	59
1.25	55	62
2.0	43	61
2.5	38	61
3.75	27	54
5.0	22	50

$$K''' = Kd \times [\text{Na}]^{0.52}$$

TABLE V
The Effect of Liquid to Solid Ratios on Distribution
Coefficients for U(VI) on Dolomites

Material	<u>Borehole/Depth</u>	<u>Liquid to Solid ratio, ml/g</u>				
		<u>5</u>	<u>15</u>	<u>25</u>	<u>50</u>	<u>100</u>
Culebra As-received	H5B 900'	2.1* (8.0)**	4.4 (8.0)	5.6 (7.7)	13.6 (7.7)	38 (8.2)
Culebra Pre-washed	H5B 900'	7.8 (7.6)	13.6 (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)	17.4 (7.7)	43 (8.0)
Magenta Pre-washed	AEC#8 749'	13 (7.7)	20 (7.5)	29 (7.4)	52 (7.4)	132 (7.3)

*The Kd values are given in units of ml/g.

**The values under the Kd in parentheses are the final pH values.

A significant trend of decreasing K_d with decreasing liquid to solid ratios was observed in all cases. The generally higher values observed for the pre-washed core sample may reflect a lower solution ionic strength due to removal of highly soluble components of the core sample which occurs during the pre-wash. There is no apparent correlation of K_d with pH as these values either remain nearly constant or increase slightly as the liquid to solid ratio decreases. Increasing pH is generally associated with increasing rather than decreasing sorption coefficients for cations on inorganic materials. The data of Table V suggests that interaction of U(VI) with dolomite involve precipitation (described by a solubility product and independent of the liquid to solid ratio) rather than an ion exchange sorption equilibrium.

This trend raises questions about the validity of extrapolating laboratory results to field conditions since U(VI) sorption appears to decrease as field conditions are approached. However, Cs sorption does appear to be dependent on liquid to solid ratios. Cs distribution coefficients determined in laboratory experiments using liquid to solid ratios in the range of 50 to 100 have been successfully used to predict transport velocity through one inch thicknesses of monolithic Magenta core sample [10]. The liquid to solid ratio in saturated Magenta core is approximately 0.15.

SUMMARY

The results presented in this paper show that a discrete value for the distribution coefficient assigned to a given radionuclide does not accurately describe its interaction with a site-specific geological formation. Empirical relationships such as those given above can account for changes in solution chemical parameters such as nuclide concentration and groundwater composition. If variations in parameters such as liquid to solid ratios which are unique to laboratory measurements are determined to be important for a given set of conditions, their effects can probably be minimized by designing experiments which approximate field conditions as closely as practicable. Variation in sorption properties with changes in the geological formation being studied and the local hydrology is a more difficult problem and additional information is needed in this area to provide a sound basis for evaluating potential radionuclide migration associated with a repository site.

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