LA-UR-93- 437

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DE93 007323

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Submitted to: 1993 INTERNATIONAL HIGH-LEVEL RADIOACTIVE WASTE MANAGEMENT CONFERENCE
April 26-30, 1993 - Las Vegas, Nevada

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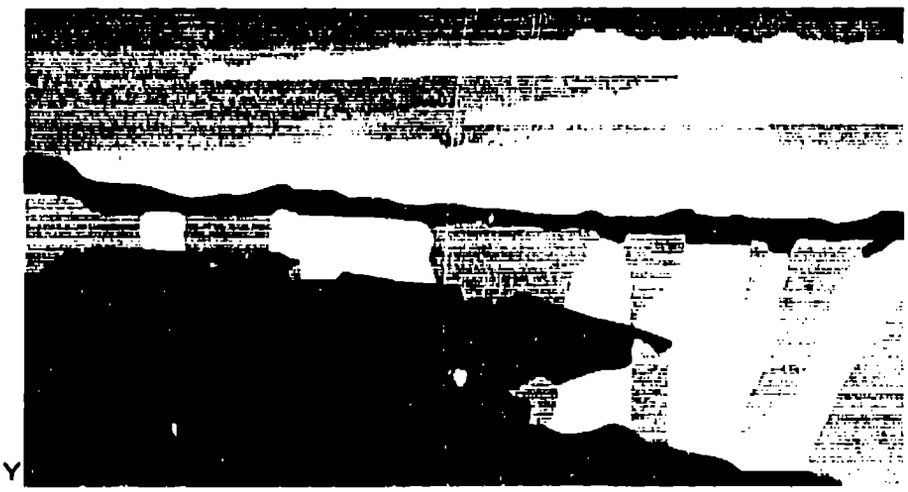

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DIFFUSION OF SORBING AND NON-SORBING RADIONUCLIDES

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ABSTRACT

Diffusion is considered one of the most important retardation mechanisms in fractured media. The diffusion experiments conducted involved solid tuff and groundwater from Yucca Mountain. The uptake of radionuclides by the tuff was studied utilizing containers made of tuff in the form of beakers. The solution containing the radionuclides of interest was placed in the tuff beaker cavity and the uptake of the radionuclides by the tuff was measured as a function of time. Our results indicate that the diffusion coefficient for nonsorbing radionuclides into saturated Yucca Mountain tuff is on the order of 10^{-6} cm^2/s. Large anions, such as pertechnetate are excluded from tuff pores and their diffusion coefficients are on the order of $10^{-7}cm^2/s$. Comparison of the predictions for the uptake of sorbing radionuclides by the tuff with the actual data obtained indicates that conservative transport calculations will result from predicting diffusion using the batch sorption coefficient for the sorbing radionuclide and the diffusion coefficient obtained for tritiated water.

INTRODUCTION

A model for matrix and fracture flow regimes in unsaturated, fractured porous media at Yucca Mountain was provided by Nitao.[1] This model provides a framework for assessment of the importance of matrix diffusion at Yucca Mountain. Solute transport in fractured rock in a potential radionuclide waste repository has been discussed by Neretnieks,[2] who concluded that most rocks (even dense rocks such as granites) have small fissures between the crystals. These microfissures interconnect the pore system containing water. Small molecules of radioactive materials can diffuse in and out of this pore system. The inner surfaces in the rock matrix are much larger than the surfaces in the fractures in which the water flows. The volume of water in the microfissures is much larger than the volume in fractures. Consequently, over a long time scale diffusion can play an important role in radionuclide retardation.

The objective of the diffusion experiments conducted was to provide diffusion information for nonsorbing neutral molecules and anions and sorbing radionuclides. Since the uptake of radionuclides by tuff is measured as a function of time, these experiments also yield information on kinetics of sorption.

EXPERIMENTAL

The experimental technique involves fabricating containers in the form of a beaker (made of tuff). The rock beaker sits on a Plexiglas container (surrounded by a layer of groundwater on the sides). A stopper is utilized to prevent evaporation. The beaker has a cavity with a radius of approximately 1.4 cm and length of 2.5 cm. The rock beaker has a length of approximately 5 cm and a radius of 3.1 cm. Figure 1 shows a cross section of a rock beaker encapsulated in a Plexiglas container.

The radionuclides utilized for these experiments were H-3, Tc-95m, Np-237, Am-241, Sr-85, Cs-137, and Ba-133. A solution (prepared with groundwater from the well J-13) containing the radionuclides of interest was placed in the cavity of the rock beakers. Aliquots of the solution containing the radionuclides of interest were taken as a function of time and analyzed for radionuclide concentration.

Batch sorption experiments were performed utilizing the tuffs being studied. The batch sorption

procedure consisted of pretreating 1 g of tuff with 20 ml of a J-13 solution for two weeks, separating the phases, adding 20 ml of the J-13 solution containing the radionuclides of interest to the pretreated tuff, separating the phases by centrifugation, and determining the amount of radionuclide in both phases.

DATA ANALYSIS

The results of the rock beaker experiments were modeled using TRACRN.[3] Due to the complex geometry of the rock beaker, an analytical solution is not available for this system. The concentration profiles of the diffusing tracer are fitted to Equation (1).

$$\nabla\bullet(\varepsilon D \nabla C) = \varepsilon \partial C/\partial t + Q, \qquad (1)$$

where

ε = porosity of the tuff,
D = diffusion coefficient through tuff,
C = concentration of diffusing tracer in solution,
t = time,
Q = 0 for a non-reactive tracer,
$Q = \rho_b \partial F/\partial t$ for a sorbing solute,
ρ_b = bulk tuff density, and
F = amount of tracer sorbed per unit mass of solid.

The mechanism of sorption determines the relationship between F and C. When sorption is linear, reversible, and instantaneous, the relationship between F and C is given by Equation (2), where Kd is the sorption distribution coefficient.

$$F/C = Kd \qquad (2)$$

Substitution of Equation (2) into Equation (1) yields Equation (3). Equation (4) provides a means of comparing results for sorption coefficients obtained under diffusive conditions with the sorption coefficients obtained utilizing batch sorption experiments. The expression for the retardation factor R_f (given in equation 4) is only valid if sorption is linear, reversible, and instantaneous. The Langmuir and the Freundlich isotherms are examples of non-linear relationships between F and C.

$$\nabla\bullet(\varepsilon D \nabla C) = \varepsilon R_f \partial C/\partial t \qquad (3)$$

$$R_f = 1 + (\rho_b/\varepsilon) Kd \qquad (4)$$

Consequently, fitting of concentration profiles for non-sorbing tracers will allow determination of the diffusion coefficient and fitting concentration profiles for the sorbing tracers will allow the determination of sorption parameters such as Kd.

RESULTS AND DISCUSSION

Figure 2 shows the concentration left in the solution in the cavity of the rock beaker (made with tuff G4-737) divided by the initial concentration of the solution placed in the rock beaker as a function of time elapsed after the J-13 solution was placed in the cavity. The diffusion data were fitted to the diffusion equation, given by Equation (1), utilizing the transport code TRACRN.[3] Figure 3 shows the fits obtained (solid lines) utilizing TRACRN for nonsorbing radionuclides (H-3 and Tc-95m) in a beaker made of tuff G4-737. The diffusion coefficients obtained for the nonsorbing radionuclides in all the tuffs studied are given in Table 1. Large anions such as pertechnetate are excluded from tuff pores because of their size and charge. The diffusion coefficients obtained for nonsorbing radionuclides agree well with previous results.[4]

The relationship between F and C describes the sorption mechanism that is observed for the sorbing radionuclides. If sorption is linear, reversible, and instantaneous, then F/C is equal to a sorption coefficient (K_d). In order to test this assumption, batch sorption experiments were performed utilizing the tuffs under study. The sorption coefficients (K_d) determined by batch sorption techniques are given in Table 2.

The diffusion of the sorbing radionuclides could not be fitted assuming reversible, instantaneous, and linear sorption. Figure 4 shows the fit that would be obtained assuming the diffusion coefficient determined for tritiated water in tuff G4-737 and the sorption coefficient determined for each sorbing radionuclide in tuff G4-737. Comparison of the fits for the sorbing radionuclides with the actual data obtained (see example in Figure 5) indicates that conservative transport calculations will result from a batch sorption K_d and the diffusion coefficient obtained for tritiated water.

The results obtained from rock beaker experiments agree with previous results.[5] Tuff water experiments were utilized to study the uptake of sorbing radionuclides by tuff. The rate constants for uptake of the sorbing cations on tuff were consistent with a model that is diffusion limited (where diffusion occurs in two stages). First, the cations diffuse into rock through water filled pores and then the cations diffuse into narrower intracrystalline channels. This dif-

Figure 1: Sample Rock Beaker

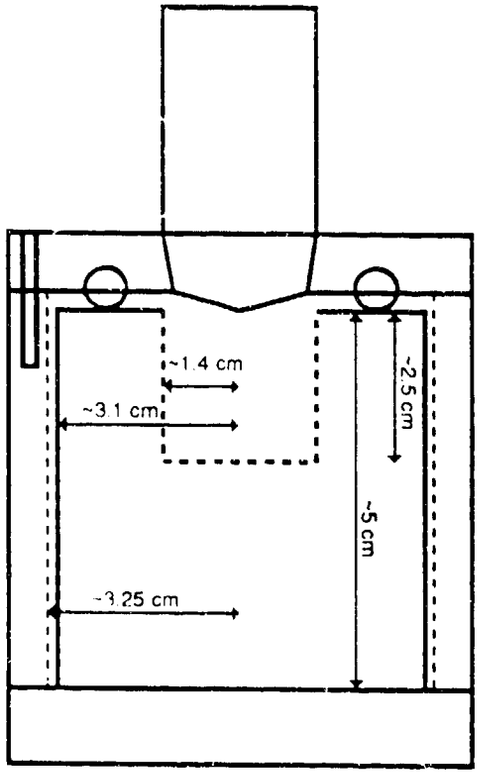


Figure 2: Diffusion Data for Rock Beaker G4-737.

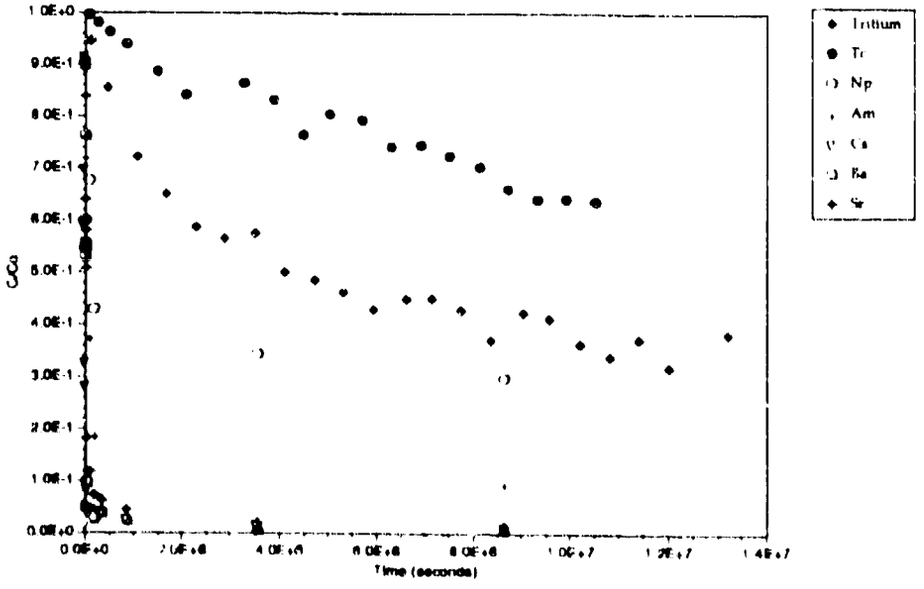


Figure 3: Fits (solid lines) to Diffusion Data for Rock Beaker G4-737.

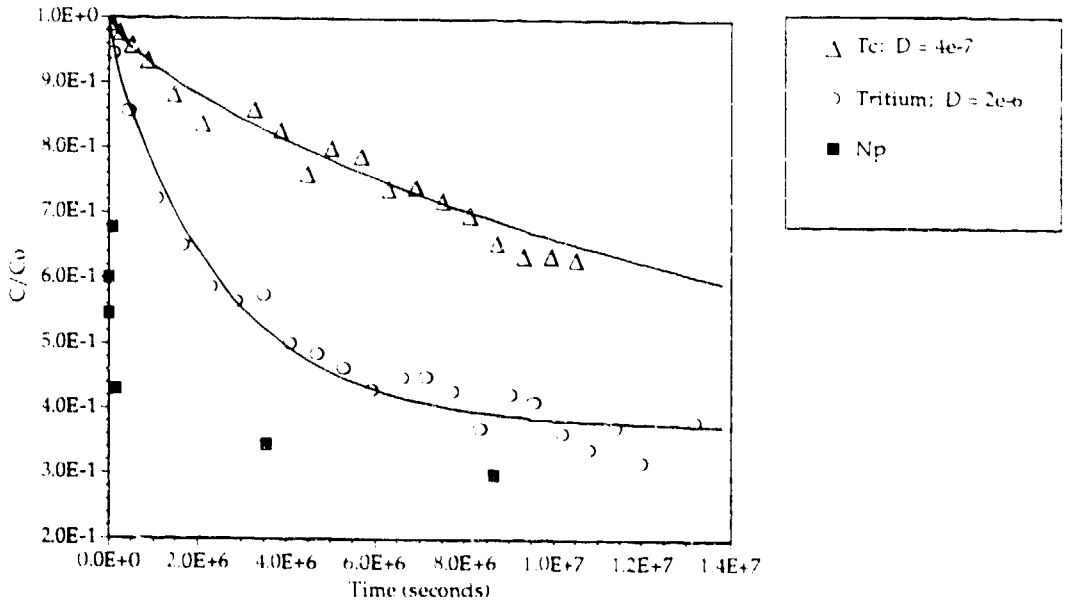


Table 1: Diffusion Results.

Tuff Sample	Major Minerals, %	Porosity	D (cm^2/s)	
			HTO	TcO_4^-
G4-737	alkali feldspar, 68 cristobalite, 28	0.07	2.2×10^{-6}	3.9×10^{-7}
GU3-304 #1	alkali feldspar, 75	0.06	1.5×10^{-6}	3.0×10^{-7}
GU3-304 #2	cristobalite, 25		1.6×10^{-6}	3.0×10^{-7}
GU3-433	alkali feldspar, 76 cristobalite, 15	0.10	3.5×10^{-6}	
GU3-1119	alkali feldspar, 70 quartz, 19	0.10	2.0×10^{-6}	4.9×10^{-7}
Topopah Outcrop	alkali feldspar, 59 cristobalite, 23 quartz, 12	0.07	1.0×10^{-6}	1.0×10^{-7}

Table 2: Sorption Results.

Tuff Sample	Major Mineral, %	K_d (ml/g)				
		Np	Am	Cs	Sr	Ba
G4-737	alkali feldspar, 68 cristobalite, 28	8	134	532	52	28
GU3-304	alkali feldspar, 75 cristobalite, 25	8		342	18	19
GU3-433	alkali feldspar, 76 cristobalite, 15	9	154	1264	20	61
GU3-1119	alkali feldspar, 70 quartz, 19	8	136	494	42	27
Topopah Outcrop	alkali feldspar, 59 cristobalite, 23 quartz, 12	9		465	20	25

Figure 4: Calculated Diffusion Data for Rock Beaker G4-737.

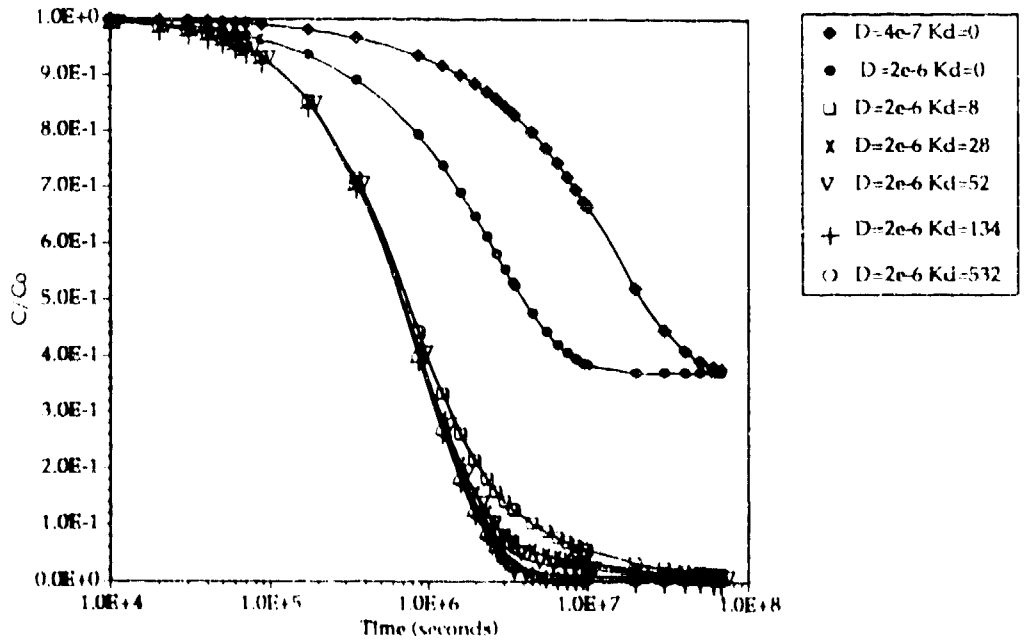
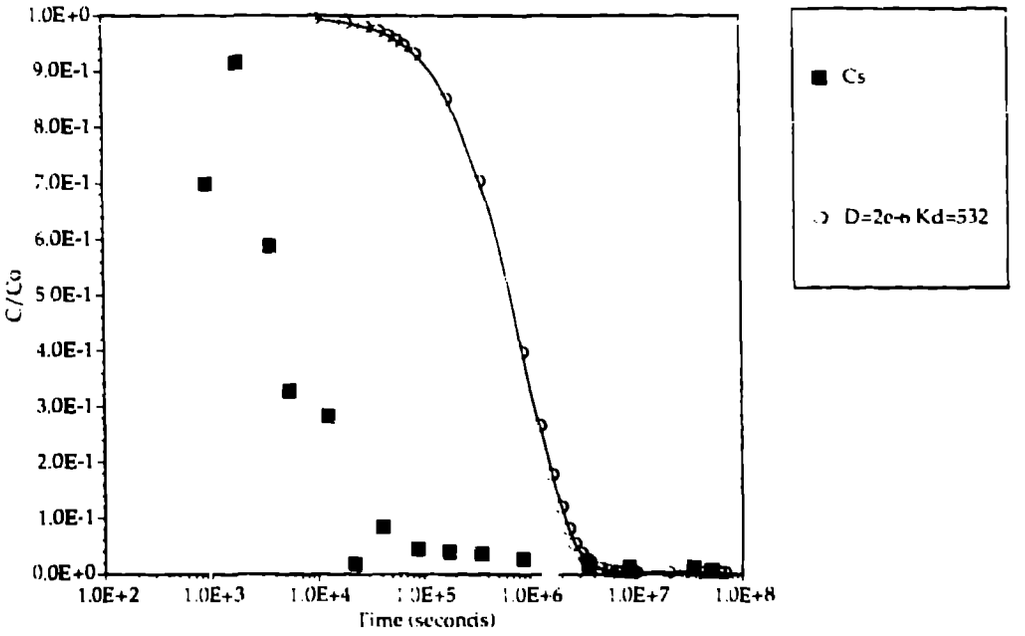


Figure 5: Comparison of Fit Obtained (solid line) with Actual Cs Data (solid squares) for Rock Beaker G4-737.



fusion model yielded sorption coefficients that agree well with sorption coefficients determined by batch techniques for the cations Cs, Sr, and Ba.

ACKNOWLEDGEMENTS

This work was supported by the Yucca Mountain Site Characterization Project Office as part of the Civilian Radioactive Waste Management Program. This Project is managed by the U.S. Department of Energy, Yucca Mountain Site Characterization Project.

The XRD data presented in this work was obtained by David Bish and Steve Chipera.

The data utilized to compile this document is referenced in Notebook TWS-INC11-9/88-6.

The code TRACRN used for data analysis has not been fully qualified per the Yucca Mountain Site Characterization Project Software Quality Assurance Plan

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