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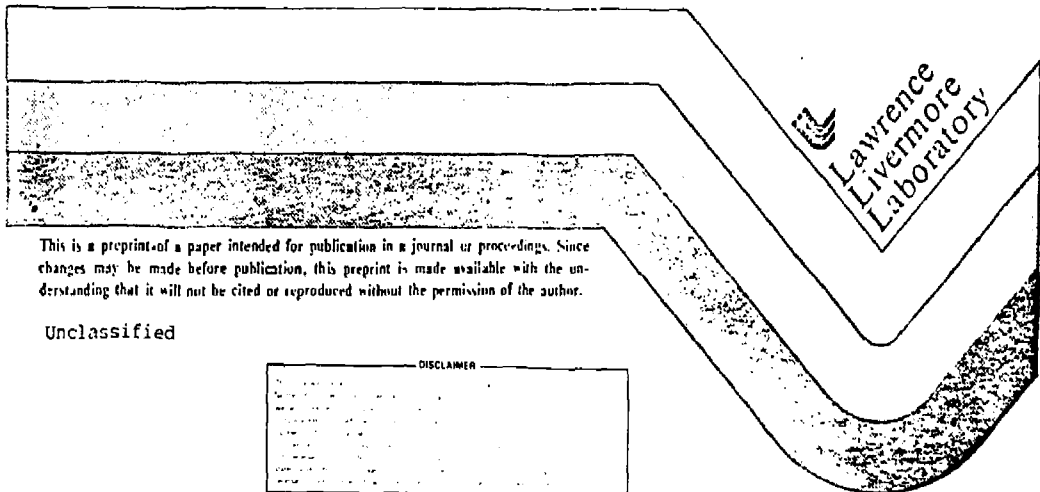
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RADIONUCLIDE TRANSPORT IN SANDSTONES
WITH WIPP BRINE

H. C. Weed, F. Bazan, J. Fontanilla
J. Garrison, J. Rego, and A. M. Winslow

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H. C. Weed, F. Bazan, J. Fontanilla
J. Garrison, J. Rego, and A. M. Winslow

Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA. 94550

ABSTRACT

Retardation factors (R) have been measured for the transport of ^3H , ^{95}mTc , and ^{85}Sr in WIPP brine using St. Peter, Berea, Kayenta, and San Felipe sandstone cores. If tritium is assumed to have $R=1$, ^{95}mTc has $R=1.0$ to 1.3 and therefore is essentially not retarded. Strontium-85 has $R = 1.0$ to 1.3 on St. Peter, Berea, and Kayenta, but $R=3$ on San Felipe. This is attributed to sorption on the matrix material of San Felipe, which has 45 volume % matrix compared with 1-10 volume % for the others. Retardation factors (R_s) for ^{85}Sr calculated from static sorption measurements are unity for all the sandstones. Therefore, the static and transport results for ^{85}Sr disagree in the case of San Felipe, but agree for St. Peter, Berea, and Kayenta.

INTRODUCTION

The work described in this report was performed under Task 3 of the Waste/Rock Interaction Technology (WRIT) program during FY 80. An important goal of the program is to provide defensible models of radionuclide transport behavior in the vicinity of waste repositories. Since an experimental data base is required for these models, this study is designed to directly measure radionuclide retardation factors for the data base and to compare them with those calculated from static sorption ratio measurements on the same rock/solution systems. Sandstones and (WIPP) Waste Isolation Pilot Plant Brine B were chosen because salt deposits suitable for repositories usually have sandstone aquifers associated with them. Other recent core transport measurements have been reported on dolomite (Lynch, 1979) granite, and tuff (Daniels et al., 1980).

EXPERIMENTAL WORK

Starting Materials

The solution used in the transport measurements was WIPP Brine B diluted with deionized water to 80% of the original concentration. Table 1 shows the composition of the diluted brine. Before use in the core transport experiments it was filtered through a 0.2 μ m pore size Nuclepore filter and then stored under laboratory atmosphere. No attempt was made to control Eh or pH.

TABLE 1

COMPOSITION OF 80% WIPP BRINE B SOLUTION FOR CORE TRANSPORT STUDIES

<u>Compound</u>	<u>C, g/l</u>	<u>Compound</u>	<u>C, g/l</u>
NaCl	229.6	Na ₂ B ₄ O ₇ · 10H ₂ O	0.013
Na ₂ SO ₄	5.0	NaHCO ₃	0.011
CaCl ₂	2.07	KI	0.010
NaBr	0.42	FeCl ₃ · 6H ₂ O	0.008
KCl	0.023	RbCl	0.00058
SrCl ₂ · 6H ₂ O	0.036		

The sandstones used were St. Peter, Berea, and Kayenta quartz arenites, and San Felipe subarkose. They are described briefly elsewhere (Coles et al. 1980) on the basis of X-ray diffraction data on powders. Core samples and the powdered samples used for static sorption measurements were prepared from the same blocks of material in order to minimize the effects of rock variability. They were right circular cylinders 25 mm diameter x 25.5 mm length.

Spike solutions contained ^{85}Sr , $^{95\text{m}}\text{Tc}$, and ^3H . They were prepared by pipetting appropriate amounts of the individual radionuclide stock solutions into a volumetric flask, evaporating them to dryness under an IR lamp with a gentle stream of filtered, compressed air, and then redissolving them in the 80% WIPP Brine B. Tritium was added as a water solution before final dilution to volume with the brine. An aliquot of the solution was evaporated to dryness on a filter paper and then γ - counted in the LLNL Nuclear Chemistry Division's γ - analysis facility in order to determine the $^{95\text{m}}\text{Tc}$ and ^{85}Sr concentrations; ^3H concentrations were determined by scintillation counting on the distillate from another aliquot of the spike solution.

Apparatus

The basic design of the transport apparatus has been described elsewhere (Coles et al. 1980). This design was used for the present study with only minor changes. A Canberra 30 pulse height analyzer and NaI (Tl) well counter were used for $^{95\text{m}}\text{Tc}$ and ^{85}Sr analyses, and a Packard Tri-Carb liquid scintillation counter for ^3H analyses.

Procedure

The following procedure was used for experimental runs: confining pressure on the sample was set at 10 MPa, steady state flow was established, 0.5 cm^3 of spike solution was injected into the inlet stream, the effluent radionuclide concentration was monitored as a function of time, and the run was continued until it appeared that at least one of the radionuclides (usually, $^{95\text{m}}\text{Tc}$) had been completely transported through the core. After the run the core was blown dry with compressed air, and the dry core was removed from the sample holder and jacket and impregnated with EPON/TEEA resin. The core was sectioned perpendicular to the core axis, and γ - counted. Also, the

parts of the disassembled system were rinsed with 6M HNO_3 and the rinse liquid γ -counted. Unfortunately, it was later found that the rinse liquids and all the cores except San Felipe were not counted long enough to get good statistics. The results cannot be used to determine the concentration profile or the amount of activity left in the system. The San Felipe core sections were counted in the LLNL Nuclear Chemistry Division's γ -counting facility so that the total amount of ^{85}Sr activity in them is known within 1.3% and the very small amount of ^{95}Tc activity within 9%. Effluent samples containing the $^{95\text{m}}\text{Tc}$ peak were distilled to remove the brine salts and analyzed for ^3H by scintillation counting of the distillate. Runs were performed at 25°C.

DISCUSSION AND CONCLUSIONS

Experimental results for the effluent solutions are expressed in terms of C/C_0 vs. N_e , where C/C_0 is the ratio of radionuclide concentrations in the effluent solution and the original spike solution, and N_e is the number of static pore volumes of effluent. In order to calculate the retardation factors, we have used the analytic solution of the one-dimensional advection-dispersion equation (Scheidegger 1974) for constant pore velocity v , an injected pulse of negligible width compared with the transport path, and an infinite homogeneous medium. This is a moving Gaussian of the form

$$C(x, t') = \frac{(\text{const.})}{\sqrt{Dt'}} \exp \left[\frac{-(x-vt')^2}{4Dt'} \right] \quad (1)$$

where x is the axial coordinate, $t' = t/R$ is the time scale for a nuclide with retardation factor R , t is the time, and D is the dispersion coefficient. We normalize $C(x, t')$ so that the integral over volume is equal to the number of injected tracer atoms.

Rewriting Equation (1) in terms of the number of pore volumes and applying it at the space position $x = L$, the exit face of the sample, we get an asymmetric function of pore volume N' :

$$\left(\frac{C}{C_0}\right) = \frac{B}{\sqrt{DN'}} \exp \left[-\left(\frac{Lv}{4D}\right) \frac{(1-N')^2}{N'} \right] \quad (2)$$

where

B = a normalization factor with a theoretical value of

$$B = (V_0/V_s) \sqrt{Lv/4D},$$

V_0 = the initial spike volume,

V_s = the static pore volume.

Equation (2) has a single maximum with a steep rise and a more gradual fall according to the value of the Peclet number (Lv/D).

Differentiating Equation (2) with respect to N' in order to locate the maximum in (C/C_0) and rearranging:

$$N'_{\max} = \sqrt{(D/Lv)^2 + 1} - (D/Lv). \quad (3)$$

For two nuclides, one unretarded and the other retarded, the ratio of pore volumes is

$$\frac{N}{N'} = \frac{vt/L}{vt'/L} = \frac{t}{t'} = R. \quad (4)$$

N is related to experimental quantities by:

$$N = N_e - N_r \quad (5)$$

where

$$N_e = V/V_s,$$

V = the total volume of effluent,

N_r = the reference value of N_e which corresponds to the origin of the theoretical curve at $N' = 0$ in Equation (2).

Substituting (3) and (5) into (4),

$$R = \frac{(N_{e \max} - N_r)}{\sqrt{(D/Lv)^2 + 1} - (D/Lv)}. \quad (6)$$

In this treatment it is assumed that the dynamic pore volume is equal to the static pore volume. Although the flow inside the core is not strictly one-dimensional, Equation (2) can be fitted to the data, and R calculated from Equation (6). Equation (2) was fitted to the data by means of the routine CURVE on the Livermore Time-Sharing System. This routine displays data points superimposed on a graph of Equation (2) and the quantities B_e , N_r and D are adjusted to fit the graph to the data by inspection. Assuming that $R = 1$ for a reference nuclide, (usually ^3H), R for other nuclides can be calculated from Equation (6) using values of $N_{e \max}$, N_r and D from the curve-fitting routine.

The estimated error in the retardation factors is 20%. The estimated experimental error in the (C/C_0) data for Sr and Tc due to weighing of samples, γ -counting, and the uncertainty in the value of C_0 is between 8% and 11% in the peak regions. The estimated experimental error for ^3H data is 10% to 20%. No ^3H data are reported for San Felipe sandstone since they are too irregular to serve as a reference standard for $^{95\text{m}}\text{Tc}$ and ^{85}Sr . Although some problems exist in the ^3H analysis of the brine solutions, we are using ^3H as a reference nuclide because it is widely accepted as a standard (Payne 1972). We believe that the experimental errors affect the peak heights but not the peak locations ($N_{e \max}$). Similar considerations apply to $^{95\text{m}}\text{Tc}$ and ^{85}Sr ; though some of the experiments show low fractional recovery of the nuclides, the main effect is on the peak heights rather than the peak locations ($N_{e \max}$). Values of the retardation factors and other parameters are shown in Table 2.

TABLE 2.

VALUES OF FITTING PARAMETERS AND RETARDATION FACTORS FOR
 ^3H , $^{95\text{m}}\text{Tc}$, AND ^{85}Sr IN SANDSTONES WITH WIPP BRINE B

Sandstone	Nuclide	Time, min	$10^4 v$ cm/s	$10^4 D$ cm ² /s	$10^3 B_e$	N_r	N_e max	R ^(a)	F.E.
St. Peter 10	^3H	10107	4.69	2.6	2.2	3.92	4.73	1.0	.7
	$^{95\text{m}}\text{Tc}$				2.3	3.86	4.71	1.1	1
	^{85}Sr				2.0	3.74	4.79	1.3	1
St. Peter 4	^3H	7215	24.3	30.	5.3	4.42	5.05	1.0	.9
	$^{95\text{m}}\text{Tc}$				50.	4.65	5.16	1.1	.9
	^{85}Sr				50.	4.70	5.26	1.2	.7
Kayenta	^3H	2859	3.39	.80	1.2	5.35	6.25	1.0	.8
	$^{95\text{m}}\text{Tc}$				1.2	5.27	6.22	1.0	.7
	^{85}Sr				1.2	5.20	6.25	1.2	.8
Berea	^3H	2634	1.08	.16	.64	.58	1.52	1.0	.5
	$^{95\text{m}}\text{Tc}$.76	.46	1.42	1.0	.8
	^{85}Sr				.80	.37	1.45	1.2	.9
San Felipe	$^{95\text{m}}\text{Tc}$	3938	1.43	0.6	.74	.95	1.93	1.2	.5
	^{85}Sr				.20	.45	3.07	3	.5

\emptyset = fractional porosity based on static pore volume

ρ = bulk density, g/cm³

F.E. = fraction of spike activity recovered in effluent.

(a) Estimated error 20%

In Figures 1-5, the curves are calculated from Equation (2) and the values of R, B_e , N_r , and D are in Table 2. The vertical arrows indicate the time of spike injection. The delay between injection and appearance of the leading edge of the peak is due to dead volume effects in the system. The retardation factors (R) for $^{95\text{m}}\text{Tc}$ and ^{85}Sr vary from 1.0 to 1.3, so that they are essentially unretarded relative to ^3H in St. Peter, Kayenta, and Berea sandstones. In the case of St. Peter 10 sandstone the curves for all

three nuclides lie close together (Figure 1). The ^3H peak was not sampled completely which caused the low fractional recovery in the effluent. In Figure 2, the effluent curves for St. Peter 4 sandstone have a steeper rise and a more gradual fall than those for St. Peter 10. This is due to the higher pore velocity and higher dispersion coefficient required to fit the theoretical curves to the data. In Figure 3, the effluent curves for Kayenta sandstone agree very closely with each other and are more symmetrical than those for the St. Peter sandstones. The curves for Berea sandstone in Figure 4 are fitted to the data at the rise and fall of the peak since the data at $N_e = 1.5$ appear anomalously low compared with the rest. The apparent delay of the ^3H peak relative to the others is .07 to 0.1 pore volume, which is considered to be within the limits of experimental error for N_e .

There is no obvious correlation between the retardation factors and mineralogical characteristics of St. Peter, Kayenta and Berea sandstones. St. Peter has 1 volume % matrix material, while Kayenta and Berea have 10 volume %, the rest being mostly quartz. Technetium-95m is considered to be unretarded because of the scarcity of anion adsorbers in rock materials. Strontium-85 may be unretarded because of occupation of Sr sorption sites by the Sr in the WHP Brine B, or because the matrix material has a low selectivity ratio K_{Na}^{Sr} .

In the case of San Felipe sandstone, ^{95m}Tc shows little retardation ($R = 1.2$) but ^{85}Sr behaves very differently. It shows definite retardation ($R = 3$) and the theoretical curve fits the data quite well below about 5.5 pore volumes, but thereafter the data and the curve diverge. About 11% of the originally injected ^{85}Sr is distributed along the core with an essentially uniform profile, but there is less than 1% ^{95m}Tc . Since the core has 45 volume % matrix material, the observed retardation may be due to irreversible sorption

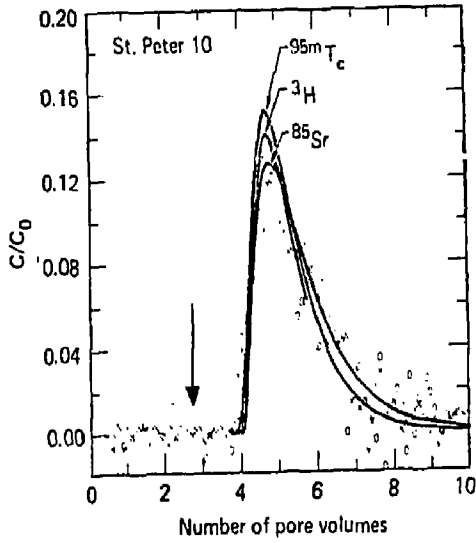


FIGURE 1. C/C_0 vs. N_e for St. Peter Sandstone 10
 \times ^{85}Sr , \circ ^{95m}Tc , $+$ ^3H

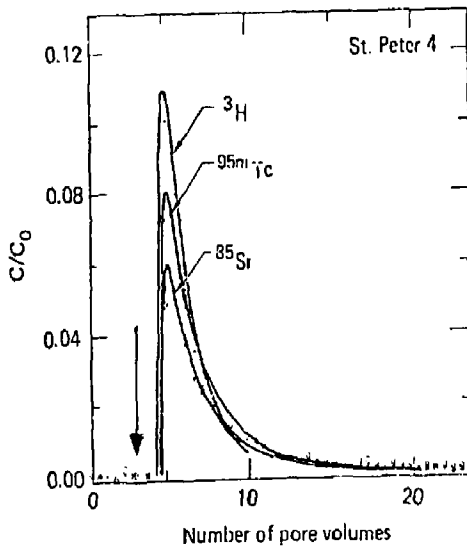


FIGURE 2. C/C_0 vs. N_e for St. Peter Sandstone 4

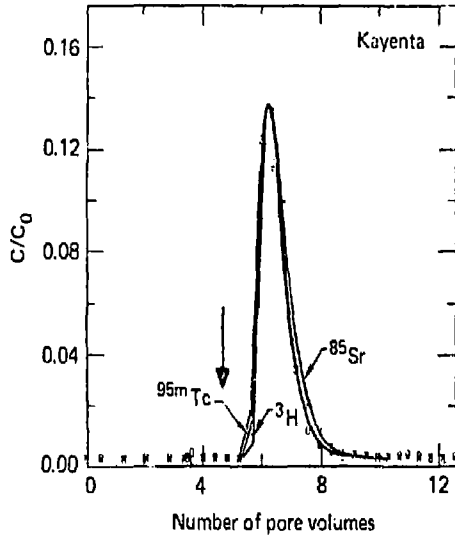


FIGURE 3. C/C_0 vs. N_e for Kayenta Sandstone

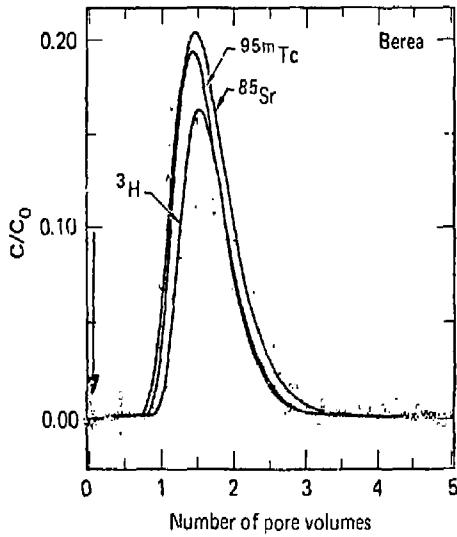


FIGURE 4. C/C_0 vs. N_e for Berea Sandstone

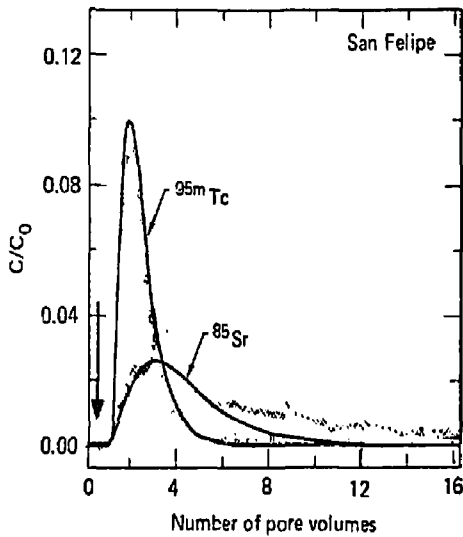


FIGURE 5. C/C_0 vs. N_p for San Felipe Sandstone

of the ^{85}Sr by the clay in the matrix. Also, if small amounts of colloidal clay particles transport ^{85}Sr in the solution, this may account for the additional ^{85}Sr appearing in the effluent after the initial peak. We have no definite explanation for the low fractional recovery of $^{95\text{m}}\text{Tc}$ and ^{85}Sr . Some possible causes are incomplete filling of the spike loop, or leakage at the spike valve or high pressure inlet fittings.

Retardation factors for ^{85}Sr calculated from static sorption measurements in Coles et al. (1980) on the sandstones in this study all have the value $R_s = 1$. Agreement between core transport and static sorption values is good for all the sandstones except for San Felipe, where the static sorption value is $R_s = 1$ compared with $R = 3$

from core transport measurements. Also, the static sorption experiments give no indication of the complexities in the behavior of ^{85}Sr shown in Figure 5.

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