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TITLE: OBSERVATION OF TIME DEPENDENT DISPERSION IN LABORATORY SCALE EXPERIMENTS WITH INTACT TUFF

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OBSERVATION OF TIME DEPENDENT DISPERSION IN LABORATORY SCALE EXPERIMENTS WITH INTACT TUFF

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The migration of radionuclides through intact tuff was studied using tuff from Yucca Mountain, Nevada. The tuff samples were both highly zeolitized ash-fall tuff from the Calico Hills and densely welded devitrified tuff from the Topopah Springs member of the Paintbrush tuff. Tritiated water and pertechnetate were used as conservative tracers. The sorbing tracers ^{85}Sr, ^{137}Cs, and ^{133}Ba were used with the devitrified tuff only. Greater tailing in the elution curves of the densely welded tuff samples was observed than could be fit by adjusting the dispersion coefficient in the conventional Advection Dispersion Equation, ADE. The curves could be fit using time dependent dispersion as was previously observed for sediments and alluvium by Dieulin, Matheron, and de Marsily. The peak of strontium concentration was expected to arrive after 1.5 years based on the conventional ADE and assuming a linear K_d of 26 ml/g. The observed elution had significant strontium in the first sample taken at 2 weeks after injection. The peak in the strontium elution occurred at 5 weeks. The correct arrival time for the strontium peak was achieved using a one dimensional analytic solution with time dependent dispersion. The dispersion coefficient as a function of time used to fit the conservative tracers was found to predict the peak arrival of the sorbing tracers. The K_d used was the K_d determined by the batch method on crushed tuff. These results will be discussed in the context of the relationship between the phenomenon of time dependent dispersion and the statistical properties of heterogeneous porous media.

Keywords: radionuclide, radionuclide migration, solute transport, dispersion, dispersivity, tuff, columns, technetium, tritium, strontium, cesium, and barium.

Introduction

The adsorption properties of Yucca Mountain tuff have been studied for many years[1] for the Yucca Mountain Project, YMP. This has been done as part of the overall evaluation of the site as a potential repository for the long term storage of nuclear waste. The past studies have been primarily batch sorption measurements of the distribution coefficients[2] for several radionuclides as a function of stratigraphic position. Other parameters affecting sorption measurements such as temperature, water composition, air composition, tracer concentration, and particle size have been varied and the sensitivity to these parameters evaluated for crushed tuff samples[3,4]. Crushed tuff columns have been used to verify the

prediction of retardation factors based on batch K_ds and found to be in good agreement provided the particle size distributions were controlled.[5] The experiments to be described are column experiments using saturated intact tuff samples. The use of intact tuff is necessary because one of the objections to the use of batch sorption measurements is that the crushing of tuff alters the mineral surfaces possibly resulting in an overly optimistic value for the K_d. The problem which arises from the use of intact tuff is that of the heterogeneity of natural samples. This heterogeneity leads to large values of dispersivity causing a shift in the breakthrough curve. This makes the determination of the retardation factor model dependent.

The theory of transport through porous media is well developed for chemical engineering (e. g., Sherwood, Pigford, and Wilke[6]). The theoretical methods have been developed with the principal purpose of designing efficient separations processes for the chemical industry using chromatographic columns. Chromatographic columns are generally homogeneous with respect to both of the hydraulic properties, i.e., porosity and permeability, and chemical properties. Transport in geologic media is on the other hand complex hydrologically and chemically. Some of difficulties which must be overcome in order to predict the hydrologic transport of radionuclides are: 1) the solubility of many radionuclides is too low to allow the direct determination of the chemical structure of solution species by spectroscopic methods 2) all of the chemical interactions between radionuclides and the minerals present in tuffaceaous rock have not been identified 3) all of the significant aqueous phase reactions occurring in groundwater have not been quantified 4) The effect of heterogeneity is not considered in column chromatography. With respect to fourth difficulty hydrologists have successfully applied the principles developed for column chromatography by the use of the simplifying assumption of a representative elementary volume, REV[7]. However, th · assumption of an REV is only valid under special circumstances. A general approach to modeling transport in complex hydrologic systems has yet to be developed.

The transport of solutes in porous media is most often considered a Fickian diffusive process described by the advection-diffusion equation[8],

$$div(D\ grad\ C - VC) = \epsilon R_f \frac{\partial C}{\partial t} \qquad (1)$$

where

D dispersion tensor;

C concentration of solute;

V Darcy's velocity vector;

ϵ effective porosity;

R_f retardation factor.

The dispersion tensor represents both diffusion and hydrodynamic dispersion. Hydrodynamic dispersion in this context refers both to dispersion caused by the variation in

water velocity across pores and the dispersion caused by heterogeneity in the permeability of the hydrologic system. The use of a diffusive mechanism to describe dispersion would appear justifiable in light of the concept of representative elementary volume.

The intact tuff columns approximate a one dimensional porous column. The solution for the above equation with continuous injection is:

$$C(x,t) = \frac{C_o}{2}\left[\mathrm{erfc}\left(\frac{x-(U/\epsilon R_f)t}{2\sqrt{Dt/\epsilon R_f}}\right) + \exp\left(\frac{Ux}{D}\right)\mathrm{erfc}\left(\frac{x+(U/\epsilon R_f)t}{2\sqrt{Dt/\epsilon R_f}}\right)\right] \quad (2)$$

When the tracer is injected as a pulse the concentration is,

$$C(x,t,\Delta t) = C(x,t) - C(x,t-\Delta t) \quad (3)$$

where Δt is the length of the pulse.

Modern stochastic models [9-11] capable of calculating the transport of conservative tracers describe the heterogeneity of aquifers in terms of the covariance of the permeability distribution. If the probability distribution of the velocity field is assumed to be gaussian the transport equation[12], given in eq. 2, can be written as,

$$\sum_j \sum_k \int_0^t C^{jk}(\tau)d\tau \frac{\partial^2 C}{\partial x^j \partial x^k} - \sum_j u^j \frac{\partial C}{\partial x_j} = \frac{\partial C}{\partial t} \quad (4)$$

where

C^{jk} = covariance matrix of the velocity field;

u^j = velocity.

These approaches predict increasing dispersion with time. Spatial covariance of hydraulic conductivity has been used to calculate macrodispersion[13-15]. However as de Marsily has pointed out the variation of chemical properties is also important. The spatial variation of the geochemical and/or sorptive properties with respect to transport has not been modeled. Of particular concern in terms of making accurate predictions of radionuclide migration is the covariance between permeability and sorption. For example, if the highly sorptive minerals, such as, smectites, were correlated with zones of low permeability the fastest moving radionuclides would in addition to having an above average water velocity would have a below average retardation factor. This could greatly increase the observed dispersion and lead to early breakthrough of small quantities of radioactive waste.

Experimental

The radioactive tracers were prepared from commercially available isotopes, from NEN and ICN corporations, diluted in J-13 water. All tuff columns were pretreated with J-13 water. Radioactive tracers were assayed using standard radiochemical procedures in accordance with the Los Alamos National Laboratory YMP QA manual. Gamma

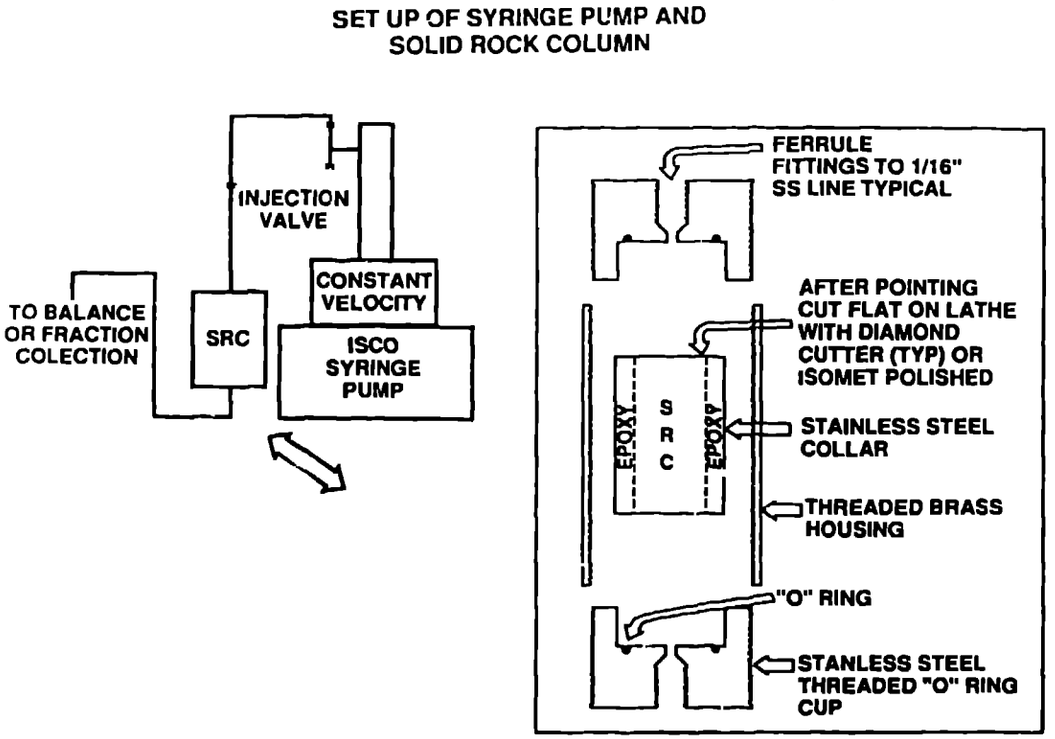

FIGURE 1 Diagram of the intact tuff column experiment apparatus.

ray emitters (^{95m}Tc, ^{85}Sr, ^{137}Cs, and ^{133}Ba) were analysed using an ORTEC hyperpure germanium well detector with a CANBERRA CI-80 multichannel pulse height analyser. Tritium was analysed by liquid scintillation counting using a PACKARD TRICARB 4530 spectrometer.

The apparatus used for the intact tuff columns is shown in Fig 1.; column dimensions, porosity, and flow parameters are shown in Table 1. The dead volumes listed in the tables were estimated by fitting the elution profiles. The columns are constructed in the following steps. A 1.66 cm diameter core is cored from a larger core sample or outcrop sample of tuff. The smaller core is then potted in BEUHLER epoxy in a stainless steel cylinder. The epoxy is a low viscosity resin which penetrates the tuff pore structure making a impermeable seal on the surface of the tuff. This procedure was used to prevent the possibility of water movement along the edge of the core. The core is then sealed into the confinement vessel with O rings to adapters which are designed to couple with standard high pressure chromatography fittings. The pump used to flow water through the tuff sample is an ISCO model 2600 high pressure precision syringe pump. The experiment performed had no confining pressure applied to the intact tuff columns other than provided by the steel jacket and epoxy.

The porosity was determined by taking the difference of sample weights after saturation (under vacuum) from the dry sample weights. The flow rates were determined by collecting water in test tubes over several 4-hour time periods and weighing the collected water. The fraction collectors were humidified to minimize evaporation. The mineralogy of the tuff samples are shown in Table 2. The Topopah Spring member tuffs (outcrop from Fran Ridge

Table 1

Experimental parameters for intact tuff columns

	Fran Ridge Outcrop	G4-1607	GU3-1119
Column length	4.71 cm	3.72 cm	4.56 cm
Column diameter	1.66 cm	1.66 cm	1.65 cm
Pore volume	1.59 ml	2.76 ml	0.64 ml
Porosity	0.156	0.343	0.065
Flow rate	1.32×10^{-5}ml/s	1.07×10^{-5}ml/s	1.19×10^{-5}ml/s
Dead volume	1.1 ml	0.7 ml	0.5 ml

Table 2

Mineralogic Composition of Tuff Samples

	Fran Ridge Outcrop[16]	USW-G4-1607[17]	USW-GU3-1119[18]
Smectite	2±1	6±2	-
Mica	tr	tr	~1
Quartz	12±1	5±2	19±3
Cristobalite	23±2	-	9±3
Clinoptilolite	-	68±6	-
Mordenite	-	3±1	-
Opal-CT	-	15±3	-
Feldspar	59±7	5±1	70±5
Calcite	1±1	-	-
Hematite	tr	-	

and USW-GU3-1119) are a densely welded tuffs, having a relatively low porosity and low permeability. The Calico Hills tuff sample, USW-G4-1608, is a highly zeolitized ash fall tuff having a high porosity and higher permeability. The tracer was injected into the column system via a RHEODYNE injection loop. The input pulses of tracer were 0.50 ml of solution. The samples of effluent from the column were collected in test tubes in a GILSON racetrack fraction collector. Tritiated water samples were collected in test tubes containing 3 ml of untraced water to further minimize evaporation. The runs using sorbing tracers, strontium, cesium, and barium were of such long duration that samples were collected in individual polyethylene scintillation vials rather than using the fraction collectors.

After the sorbing tracers were run through the Topopah outcrop samples for 78 weeks the experiment was terminated and the columns were sectioned using wire saw. The slices of tuff were counted in the germanium well counter.

Results

Samples of densely welded tuff from the Topopah Spring member, Yucca Mountain, Nevada have exhibited elution curves which cannot be fit to the conventional advection

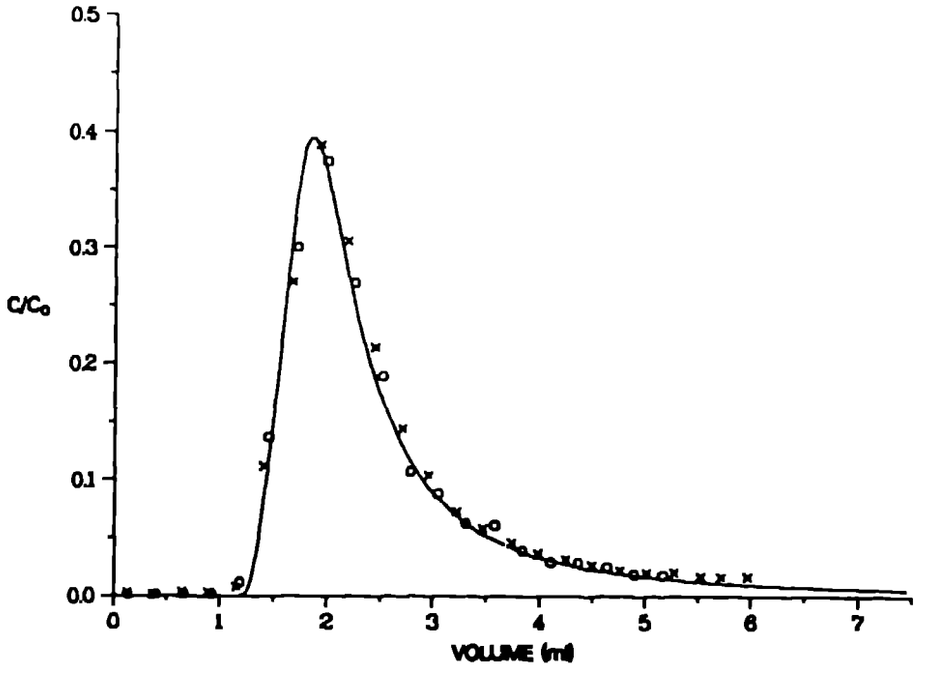

FIGURE 2 Comparison of predicted tritiated water elution, solid curve, with measured elutions, open circles for run 1 and x for run 2, through an intact Topopah Spring member outcrop tuff column.

dispersion equation, ADE[8]. The curves from the outcrop samples can be fit however with a time dependent equivalent dispersion coefficient[19]. This effect has been previously observed by Coats and Smith[20] and more recently by Herr et al[21]. These authors have attributed the effect to that of local heterogeneities or deadend pores (Coats and Smith). The effect of heterogeneity is more generally described by the methods advocated by De Marsily and his coauthors[9,12,10]. This phenomenon was theoretically shown to be the result of the spatial distribution of permeability by Matheron and de Marsily[9]. The tritiated water data was fit by approximating the time dependence of the dispersion coefficient with a power law expression.

$$D = D_1 + D_n t^n \tag{4}$$

The value for the exponent, n, which best fit the data in the case of the tritiated water was 1.0. The fits achieved using this approximation are shown in Fig. 2. In addition to duplicate tracer runs as shown in Fig. 2, duplicate columns of each tuff specimen were constructed and used. The results from duplicate columns were in good agreement for all tracers and tuff samples studied. The second set of topopah spring member tuff specimens from USW-GU3-1119 exhibited a time dependent dispersion which could not be fit with any value of n in eq. 4. The elutions in these columns shown in Fig. 3, exhibit two distinctly different flow paths as evidenced by a double peak elution curve. This implies the presence of permeable fractures in the tuff samples. The tritiated water elutions for the calico hills

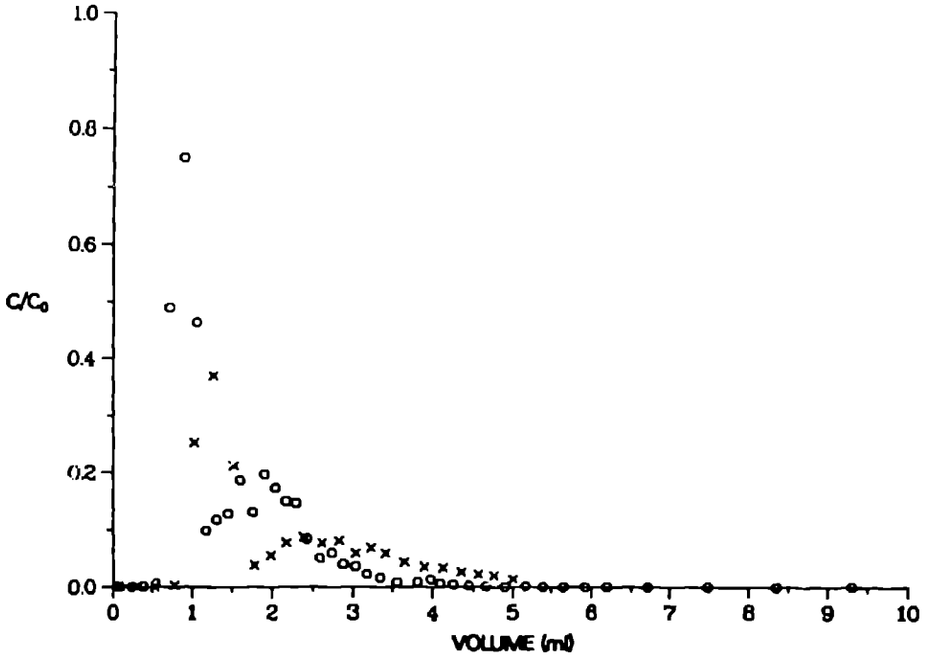

FIGURE 3 Tritiated water elutions, open circles for run 1 and x for run 2, through an intact Topopah Spring member tuff column, USW-G4-1119.

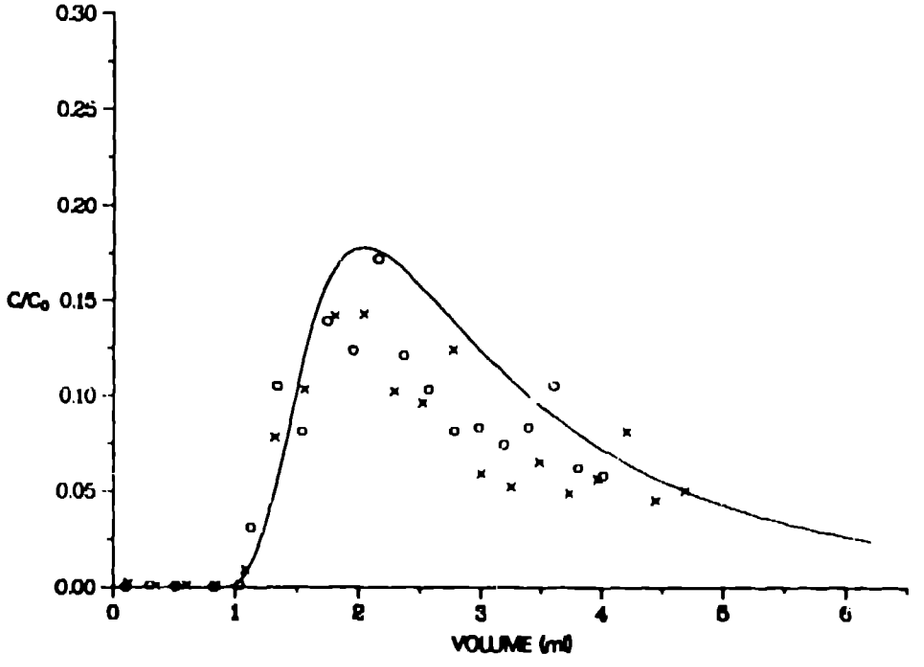

FIGURE 4 Comparison of predicted tritiated water elution, solid curve, with measured elutions, open circles for run 1 and x for run 2, through an intact Calico Hill tuff column, USW-G4-1608

samples from USW-G4-1608 were adequately fit by a time independent dispersion coefficient, Figs. 4. This tuff is more porous and evidently more uniform in hydraulic conductivity than the Topopah Springs member tuffs.

Pertechnetate was eluted under the same conditions as the tritiated water. The elution of pertechnetate exhibits anomalous behavior. In the case of the Topopah Spring member tuff (Fran Ridge outcrop) the shape of the elution curves are the same as the tritiated water elutions. The area under the curve however does not equal the amount of technetium injected. This loss cannot be explained at present. Possible explanations are adsorption on an unidentified trace mineral or uptake by microorganisms. Figures 5 show the shape of the technetium elution curves rescaled to compensate for the loss of technetium. The percentage loss of technetium is 51 percent and is not illustrated in the drawing. The Calico Hills tuff, USW-G4-1608, did not exhibit any loss or retention of the pertechnetate. However, the dispersivity required to fit the data was much higher, 6 cm as opposed to 1.4 cm in the case of tritiated water. The anion exclusion volume was 0.2 ml. The fit and the actual data are shown in fig. 6.

Prior to the injection of sorbing tracers, ^{137}Cs, ^{85}Sr, and ^{133}Ba, into the Fran Ridge outcrop samples batch measurements were made. One gram of crushed tuff was contacted with 20 ml of J-13 water containing the above tracers for a period of 11 days. The resulting K_ds are shown in table 3 along with the standard deviation of 8 batchs. These K_d were used in the fitting of the observed elutions. The retardation factor was calculated using the following expression[22],

$$R_f = 1 + \frac{K_d \rho_b}{\epsilon}, \tag{5}$$

where ρ_b is the dry bulk density.

The most dramatic consequence of the time dependent dispersion is the effect on the prediction of breakthrough times for sorbing tracers. If the conventional ADE is employed to predict the breakthrough of strontium the expected breakthrough in the solid tuff column would be at ~1.5 years, based on batch sorption measurements. The actual Sbreakthroughs, Fig. 7, occurs within a few weeks of the start of the experiment. This is a discrepancy of ~2 orders of magnitude. If the dispersion is given a time dependence the elution curve can be fit with the measured batch sorption coefficient. The distribution of residual radioactivity in the tuff columns was measured by sectioning the column after elutions were observed. The concentration of strontium, cesium, and barium as a function of distance from the column inlet is shown in Fig. 8. The distribution is nonuniform. The most localized tracers are the more strongly sorbed tracer because these tracers have not eluted to a significant extent. The heterogeneous distribution of sorbing minerals may be responsible, at least in part, for the reduced retardation. Dispersivities for the sorbing tracers are significantly greater than dispersivities for tritiated water in the same tuff columns.

The observation of time dependent dispersion in laboratory scale migration experiments has provided new insight into the effect of heterogeneity on the retardation of sorbing radionuclides. In order to calculate the time dependence a priori at the very least a statistical characterization of the spatial distribution of sorbing minerals and the distribution

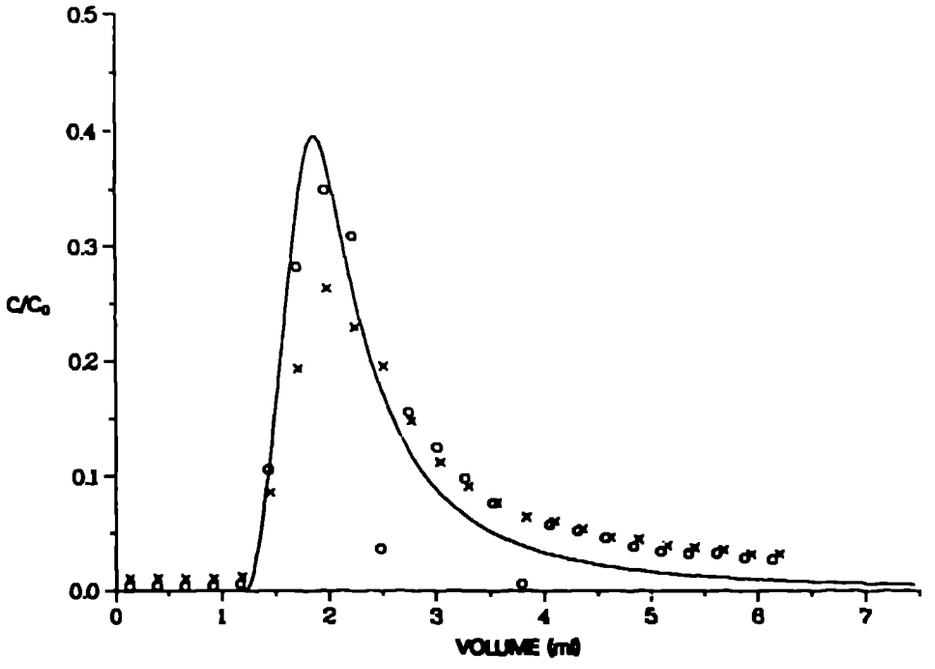

FIGURE 5 Comparison of predicted pertechnetate elution, solid curve, with measured elutions (rescaled to compensate for loss), open circles for run 1 and x for run 2, through an intact Topopah Spring member outcrop tuff column.

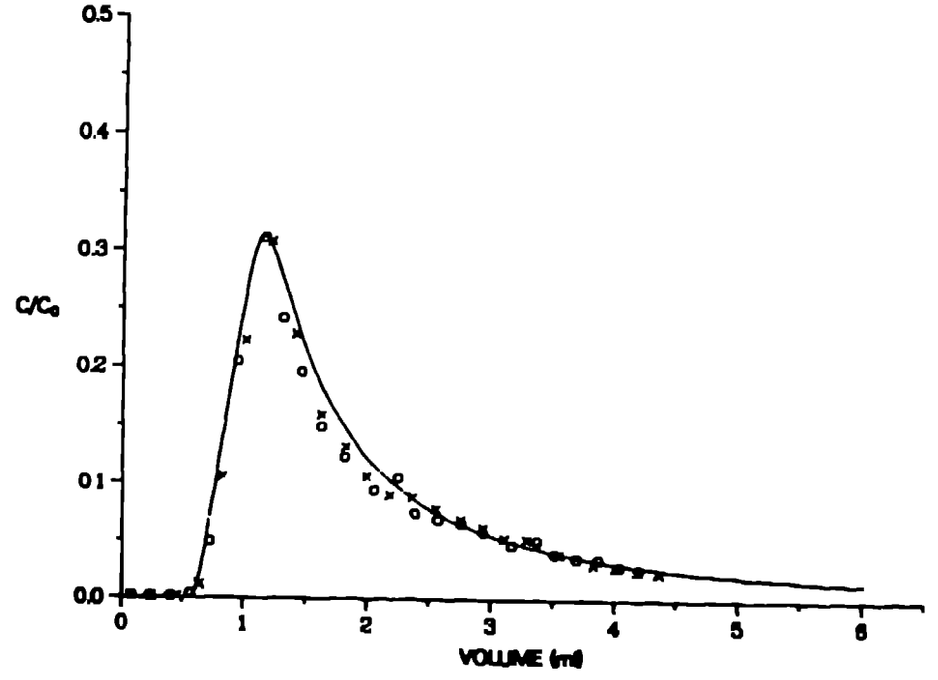

FIGURE 6 Comparison of predicted pertechnetate elution, solid curve, with measured elutions (rescaled to compensate for loss), open circles for run 1 and x for run 2, through an intact Calico Hills tuff column, USW-G4 1608.

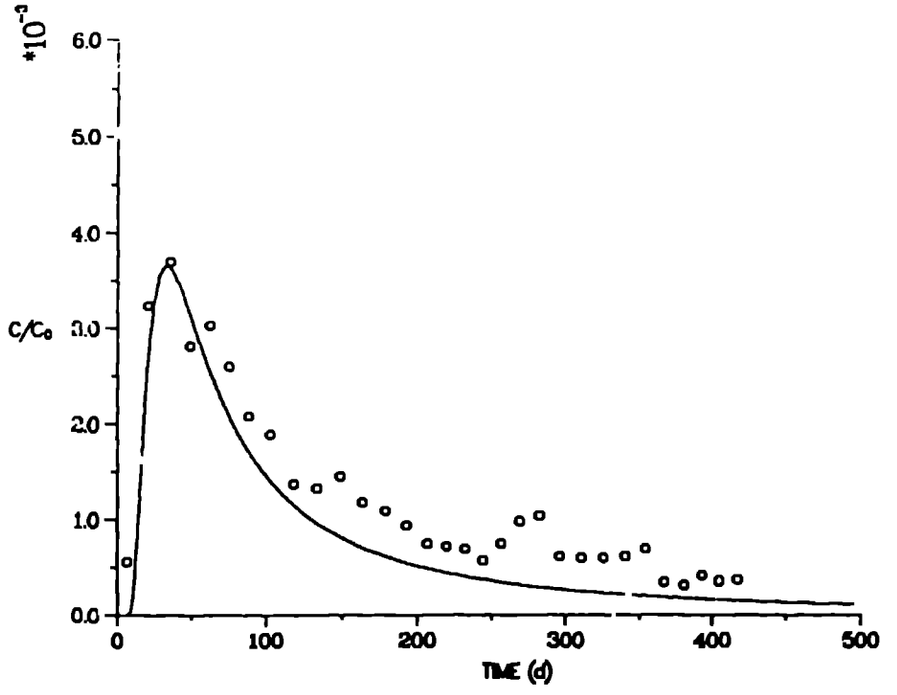

FIGURE 7 Fit to strontium elution, using time dependent dispersion, in intact Topopah Spring member tuff.

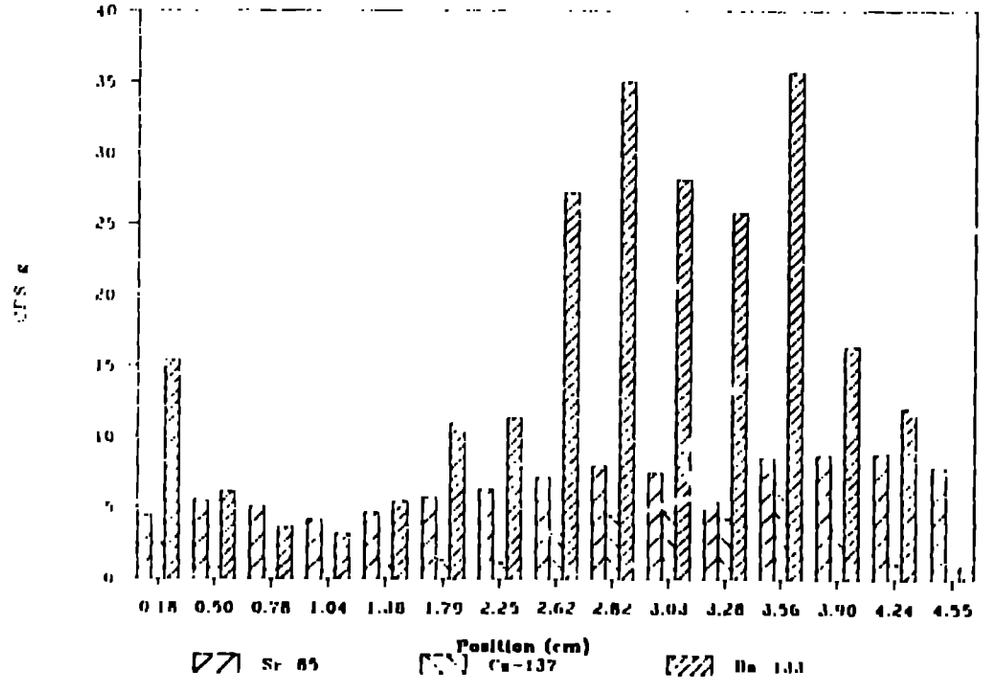

FIGURE 8 Distribution of sorbed strontium, cesium, and barium in an intact Topopah Spring member tuff column.

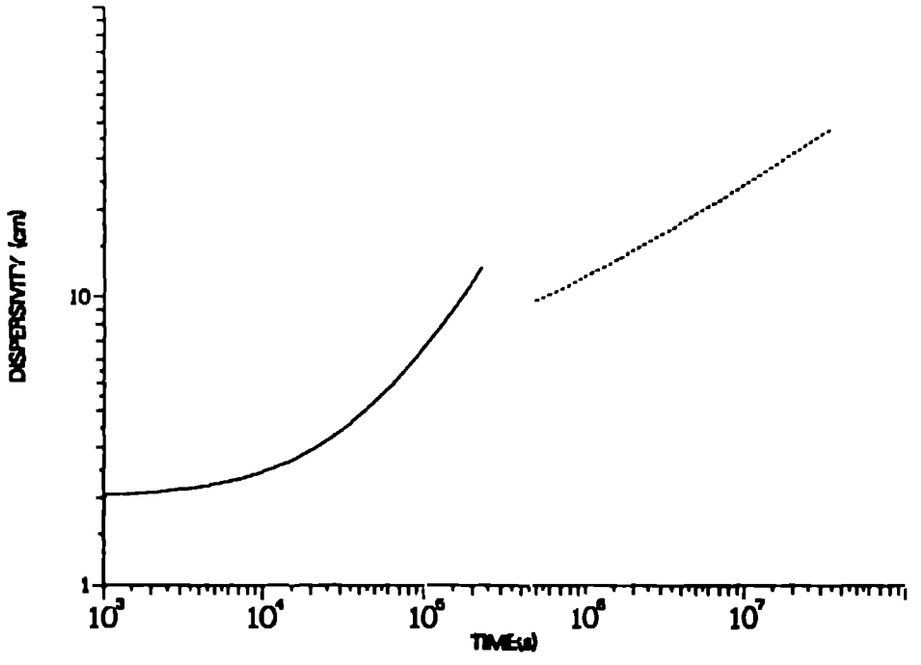

FIGURE 9 Dispersivity as a function of time used to fit the intact Topopah Spring member tuff column data, solid line is the dispersivity used to fit the tritiated water data and the dashed line for the strontium data.

of hydraulic conductivity must be made.

This effect will have an even greater importance as the scale of the hydrologic system increases to field and repository scales. Time dependent dispersion has been observed in the tritium and ^{36}Cl elutions from the CAMBRIC field test in tuffaceous alluvium on the Nevada Test Site for the Hydrology Radionuclide Migration project, HRMP[23]. The question which arises from considering these tuff column experiments is: when can one expect to observe the elution of sorbing radionuclides from CAMBRIC?

Conclusions

The intact tuff columns with densely welded tuff from the Topopah Spring member tuff have exhibited time dependent dispersion. This complicates the interpretation of these experiments in terms of the predictability of retardation given batch sorption, K_ds, measurements. The most important consequence of this observation is that without time dependent dispersion the elution of alkali metals and alkaline earths did not agree with batch sorption measurements. The apparent error in the predicted arrival time is greater than an order of magnitude. The results can be reconciled by giving the dispersion a time dependence and allowing the sorbing tracer to have a different time dependence from the conservative tracer tritiated water. The dispersion as a function of time used to fit the tritiated water data and the strontium data are shown in Fig. 9. The strontium elution required a dispersion that had a dependence on time of a power less than one, i.e. $n = 0.4$

Although in this sample the value of tritiated water dispersion extrapolated to the times relevant for the strontium elution would provide a conservative value of the dispersion this is probably not generally true. The actual dispersion for a sorbing tracer depends both on the covariance of the hydraulic conductivity and the cross correlation between the conductivity and the sorbing minerals. For example if the sorption anticorrelated with the hydraulic conductivity then the variance of the tracer velocity would be greater than the variance of the water velocity divided by the retardation factor. The pertechnetate tracer elution agreed with the dispersion observed with tritiated water in the Fran Ridge sample. But did not in the zeolitized Calico Hills tuff, USW-G4-1608. This again indicates that the dispersion depends not only on the hydraulic properties of the rock but on the chemical properties as well.

This observation points to the need for a more detailed characterization of the hydrologic and geochemical properties of Yucca Mountain tuff. Future experiments will utilize optical and scanning electron microscopy along with microautoradiography to attempt to provide a forward basis for predicting the time dependence of the dispersion in the radionuclide migration.

The Yucca Mountain site being investigated as a potential repository is largely above the water table. Lack of saturation would be expected to have an effect on the hydrodynamic dispersion. One would expect dispersion to increase as saturation decreases because it seems natural that the tortuousity of connected flow paths should increase. Future experiments examining migration in unsaturated tuff columns will test this hypothesis and demonstrate the importance of time dependent dispersion in the unsaturated zone relative to the saturated tuff.

Acknowledgements

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