

A SUGGESTED APPROACH TOWARD MEASURING SORPTION AND APPLYING SORPTION DATA TO REPOSITORY PERFORMANCE ASSESSMENT

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The prediction of radionuclide migration for the purpose of assessing the safety of a nuclear waste repository will be based on a collective knowledge of hydrologic and geochemical properties of the surrounding rock and groundwater. This knowledge along with assumptions about the interactions of radionuclides with groundwater and minerals form the scientific basis for a model capable of accurately predicting the repository's performance. Because the interaction of radionuclides in geochemical systems is known to be complicated, several fundamental and empirical approaches to measuring the interaction between radionuclides and the geologic barrier have been developed. The approaches applied to the measurement of sorption involve the use of pure minerals, intact, or crushed rock in dynamic and static experiments. Each approach has its advantages and disadvantages. There is no single best method for providing sorption data for performance assessment models which can be applied without invoking information derived from multiple experiments.

Introduction

The containment of radioactive waste in a geologic repository is to be assured through a reliance on multiple barriers. These are the wasteform and canister, the engineered barrier, and the geologic barrier. The geologic barrier is made up of hydrologic and geochemical systems. The transport of radionuclides will ultimately depend on the groundwater flow, groundwater chemistry, mineralogy, and physical properties of the rock. The movement of radio-

nuclides is slowed by the interaction of the dissolved radionuclides with mineral surfaces in the rock, i.e., sorption. The sorption of radionuclides depends on concentration, speciation, mineral composition of the rock, concentration of competing ions, and pH. The large number of parameters affecting sorption suggests that an empirical approach may be favored toward measuring sorption. This was the approach applied to the Yucca Mountain Project by Los Alamos National Laboratory, until recently.

The empirical approach has the drawback of the difficulty in achieving conditions which truly simulate the natural environment. Sorption experiments that will achieve a level of simulation closer to natural conditions will be those performed at the Äspö laboratoriet (the Hard Rock Laboratory)¹ in Sweden. In these experiments sorption on intact rock will be performed in a sonde emplaced in the tunnel wall with groundwater from the surroundings passing through the experimental cell. In this way, the redox potential, carbon dioxide overpressure, and ground water composition are equal to in situ values. Time and money limit the number of chemical elements that can be tested in this approach. The in situ conditions may not be appropriate as a model for all failure scenarios. Altering the conditions to address the effect of these changes will compromise the concept of achieving natural conditions.

The contrasting approach to measuring sorption is to study the basic interaction between a radionuclide and a single mineral. This approach allows the study of many radionuclides over a wide parameter space. The difficulty is in relating the parameters measured for a single mineral to a mixture of minerals in an intact rock matrix. The actual rock is heterogeneous and it may be difficult to analyse the trace mineral composition and/or the availability of minerals to the aqueous phase. The most revealing measurement which can be performed within this approach is the adsorption isotherm. The isotherm can provide useful concentration dependences that can be used to differentiate between a surface adsorption process and precipitation.

Neither of these approaches can completely satisfy the requirements of performance assessment models. The empirical approach is too inflexible to changes in conditions such as, concentration, pH, temperature, and others, as dictated by a particular failure scenario. A fundamental approach may provide an adsorption model which is too complex to be incorporated into an already complicated performance assessment code. This difficulty could be overcome by finding conservative limits to the distribution coefficient which are based on a single mineral (preferably an abundant one). This method of establishing a conservative limit must then be tested by performing validating tests. This form of testing is required for any methodology short of a complete simulation of repository conditions.

Scientific Background

Most performance assessment models rely on some form of the K_d concept. That is that the distribution coefficient can be applied to radionuclide transport by use of a retardation factor (the ratio of tracer velocity to groundwater velocity)²,

$$R_f = 1 + \frac{K_d \rho}{\epsilon} \quad (1)$$

where, K_d is the distribution coefficient, ρ is the dry bulk density, and ϵ is the porosity. The K_d is an experimental quantity determined by measuring the ratio of the solid phase concentration, q , over the aqueous concentration, c . Thus,

$$K_d = \frac{q}{c} \quad (2)$$

The layer of water nearest the mineral surface is affected by the surface charge. The surface charge repels like charged ions or attracts oppositely charged ions. If this effect is included the solid phase concentration for a wet solid can be represented as,

$$q = q_a - q_{ex} \quad (3)$$

where q_a is the concentrations of radionuclide adsorbed on the solid surface and q_{ex} is the concentration of radionuclide excluded from the surrounding water layer. This modification of the definition of solid phase concentration allows for the occurrence of negative K_d s which is consistent with the observation of anion and size exclusion effects. These exclusion effects are manifested as an arrival time earlier than tritiated water, i.e., the retardation factor is less than 1.

The expression in eq. 1 has inherent assumptions about the K_d . These are that: 1) the isotherm is linear, 2) the adsorption reaction is reversible, 3) That the kinetics are rapid enough to allow microscopic equilibrium, 4) the interaction must be adsorption (as opposed to precipitation, for example), and 5) no

significant parameters (i.e., pH, Temperature, RedOx, etc.) vary within the system of interest.

Dynamic experiments to measure R_f must make additional assumptions about the homogeneity of the porous medium. Although there are simple methods of dealing with some types of heterogeneity this is a serious complication. One form of the transport equation³ which includes the statistical distribution of hydrologic properties is,

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

where, λ = the covariance matrix of the velocity field; \bar{u} = mean velocity; j, k = the indices for the axes in the coordinate system; ϵ = porosity; R_f = retardation factor. An example of the agreement between predicted and measured transport using this type of approach is shown later in fig. 9. This example is for the alkaline earth strontium for which the chemistry is simple, the interaction is most likely ion-exchange, the isotherm is linear and the kinetics fast. The challenge will be to predict the transport of less well understood radionuclides, i.e., the actinides.

The details that must be understood in order to predict the transport of radionuclides having complex chemical behavior can be studied using several complementary methods. Assuming that speciation is adequately known the adsorption on pure minerals of radionuclides can be studied using radiochemical and other spectroscopic methods. I will only consider interactions that can normally occur in a laboratory time scale under normal laboratory conditions of temperature and pressure. In other words I am excluding interactions which may occur in conjunction with mineral formation. The chemical interactions responsible for the sorption of radionuclides then are ion exchange, surface complexation, and chemisorption.

Ion Exchange Models

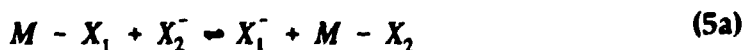
Ion exchange arises from two distinctly different chemical structures on the surfaces of minerals. One is the incorporation of aluminum (valence 3) in a tetrahedrally bonded silicate structure. The other is the amphoteric reaction of metal oxides with acids and bases. The former is a negatively charged surface of a fixed nature with the charge compensated by cations. The latter can be either negatively or positively charged depending on the pH of the aqueous phase. The exchange capacity of the former structure is fixed where the

exchange capacity of the latter depends on pH, Ionic strength, and the concentration of specific inner-sphere complexing ligands. The adsorption of exchangeable ions on an activated metal oxide surface is a form of outer-sphere surface complexation.

The selectivity in aluminosilicates for a given radionuclide over another has been shown to be not a simple binary exchange process, even when the solution is a simple binary aqueous solution. This is because not all positions in aluminosilicate are equivalent with respect to crystallographic structure. For example, there can be differences due to steric crowding. These differences have been studied by deconvolving the ion-exchange isotherm.

The method of deconvolution has been shown effective in studying structural effects on ion selectivities in synthetic zeolites⁴. In that study the shape of the ion exchange isotherm was shown to be due to differences in the crystallographic structure at the ion exchange sites. This interpretation could not be made on the basis of the deconvolution of adsorption isotherms without spectroscopic data. However, the method of deconvolution does allow a quantitative correlation of the ion exchange data with the spectroscopic data.

The method of analysis assumes ion exchange. The thermodynamics of ion exchange have been reviewed by Cremers⁵. The selectivity coefficient K for the hypothetical ion-exchange process in Reaction (5a) is given by Equation (5b), where a_1 and a_2 are the activities in solution of the anion to be exchanged and the entering anion, respectively; q_1 and q_2 are the concentrations of these anions in the solid phase that are expressed as moles of anion per gram of exchanger:



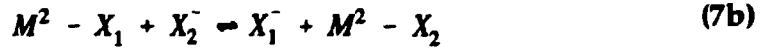
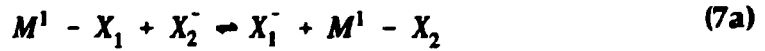
$$K = \frac{q_2 a_1}{q_1 a_2} \quad (5b)$$

As a result of mass balance considerations, Equation (5b) can be rewritten as Equation (6) where Q is the total moles of exchangeable sites per gram of exchanger, C_o is the total concentration of anions in the liquid phase, C_2 is the concentration of the entering anion, and γ_1 and γ_2 are the activity coefficients

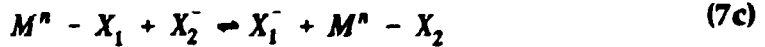
in the solution phase of the anion to be exchanged and the entering anion, respectively.

$$q_2 = \frac{KQ\gamma_2 C_2}{C_0\gamma_1 + (K\gamma_2 - \gamma_1)C_2} \quad (6)$$

Equation (6) represents the dependence of the solid phase concentration on the liquid phase concentration. It has the mathematical form of the Langmuir isotherm. In general, adsorption isotherms do not follow the Langmuir isotherm. Many authors have successfully described cation exchange in terms of multiple sites⁶⁻⁸. The underlying assumption of the deconvolution method is that the nonideality of the adsorption isotherm is due to adsorption at multiple sites. Consequently, one may consider a set of simultaneous equilibria as in Equation (7), where M^1, M^2, \dots, M^n represent different sites in the ion exchanger.



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The solid-phase concentration of the anion X_2^- in site i is given by Equation (8), and the total solid-phase concentration of X_2^- is given by the sum in Equation (9):

$$q_2^i = \frac{K^i Q^i \gamma_2 C_2}{C_0 \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2} \quad (8)$$

$$q_2 = \sum_{i=0}^n q_2^i = \sum_{i=1}^n \frac{K^i Q^i \gamma_2 C_2}{C_0 \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2} \quad (9)$$

This approach is further generalized by replacing the sum in Equation (9) with the integral equation (10), where $f(K)$ is a distribution function for the selectivity coefficient of the exchange:

$$q_2(C_2) = \int q_2(C_2, K) f(K) dK \quad (10)$$

The idea of expressing the heterogeneity of the exchanger in terms of a distribution function has been previously presented⁹⁻¹³. Equation (10) is a Fredholm Integral of the First Kind and the methodology used here to solve for $f(K)$ has been described by the author^{14,15} and others^{16,17} in previous papers. The computer code INVPOS has been written¹⁸ to solve Eq. 10. INVPOS uses the method of Butler, Reeds, and Dawson¹⁶ to find an optimal solution using regularization with a positivity constraint.

Surface Complexation Models

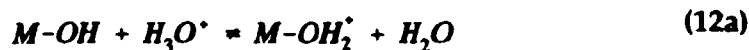
The concept represented by equation 7 could also be applied to mixtures of minerals as well. This would be useful for calculating K_d s of intact rock from mineralogic composition if it were not for surface complexation. Porous minerals such as clays and zeolites have most of their surface area internal to the crystal in pores of diameter on the order of 3 Angstrom units. Nonporous minerals such as metal oxides adsorb radionuclides only on the surface. The sorption of radionuclides on nonporous minerals is therefore much more sensitive to crystal size and shape. In addition, minerals can be sequestered within the intact rock from groundwater by dead end pores.

The models which are used to interpret the results of adsorption experiments on metal oxides are surface complexation models^{19,20}. The most important difference between these models and conventional chemical equilibria is the effect of surface charge on the activity of ions in the triple or double layer. This effect is calculated by multiplying the bulk solution concentration by a Boltzman factor,

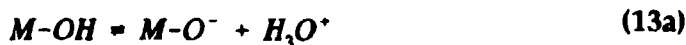
$$[M^*] = [M^*]_{bulk} e^{-\left(\frac{\sigma F}{CRT}\right)} \quad (11)$$

where, R is the gas constant, F is Faradays constant, T is the temperature, C is the capacitance, and σ is the surface charge.

The charge on the metal oxide surface is produced by the amphoteric reaction of the metal oxide surface with acids and bases. The basic charge-producing reactions are with Bronsted acids and bases,

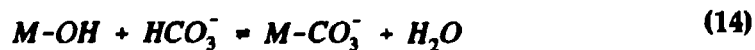


$$K_{a1}^{int} = \frac{[M-OH_2^+]}{[M-OH][H_3O^+]} e^{\left(\frac{\sigma F}{CRT}\right)} \quad (12b)$$



$$K_{a2}^{int} = \frac{[M-O^-][H_3O^+]}{[M-OH]} e^{-\left(\frac{\sigma F}{CRT}\right)} \quad (13b)$$

The surface charge can also be affected by the exchange or adsorption of Lewis acids or bases, (e.g., inner-sphere complexation). For example, we can postulate that bicarbonate oxygen replaces an oxygen on the metal oxide surface. The reaction describing this equilibrium is,



Metal oxides are normally treated as homogenous surfaces with differences only in the mechanism of adsorption. Namely, inner-sphere versus outer-sphere surface complexation. The surface hydroxyl are known to be nonequiva-

lent and have been classified A-type, B-type, and C-type²¹. Nevertheless these surface hydroxyls are considered to behave in some averaged or coupled way. Recent studies²² at Chalmers University of Technology suggest that the Lewis acid sites are affecting the acid/base behavior of goethite. The kinetics of adsorption and desorption of ¹⁴C labeled carbonate suggest steric differences between the carbonate adsorbed on goethite as an inner-sphere complex and as an outer-sphere complex. The carbonate is believed to be adsorbed as an outer-sphere complex by sharing a C-type oxygen in the goethite lattice²³. This site also does not appear to be significant in the adsorption of cations because there is little effect when cation sorption is measured in a nitrogen atmosphere on purged goethite compared with cation sorption measured in air. The point of zero charge appears to be shifted because hydroxyl ions are consumed by the adsorbed carbon dioxide²⁴.

The ion-exchange model and the surface complexation models can be incorporated into chemical equilibrium codes to combine speciation models with sorption. This approach allows the calculation of sorption for geochemical conditions other than those simulated in the laboratory. The ability to model the sorption of radionuclides under differing ionic strength, pH, RedOx conditions, etc. would give confidence that the assumptions made in order to apply eq. 1 to the transport equation are valid. Difficulties in modeling competitive anion exchange on goethite have been observed²⁵. The surface charge for goethite at a pH chosen at a fixed difference from the point of zero charge appears to vary with crystal size²⁶. This variation has been interpreted as being due to differences in sites on the surface of the goethite crystal²⁷. A multisite model has been developed to model the acid base behavior of goethite by Heimstra et al²⁸. The sites in this model are not located in the same position of the crystal and therefore the number of each site depends on the morphology of the crystal. The crystal morphology varies with the chemical conditions during formation²⁹. Therefore the sorption properties of a rock may vary not only with mineral composition but mineral availability and crystal morphology as well.

A multisite model has been proposed for the protonation of alumina by Schulthess³⁰. Schulthess takes the concept farther than Heimstra et al. The use of the Boltzman factor, eq. 11, in the surface complexation model is based on the variation of the equilibrium quotient with surface charge. The logarithm of the equilibrium quotient varies linearly with the surface charge. Schulthess³¹ fits the titration of alumina to a multiple equilibrium model without invoking the Boltzman factor. Heimstra et al. divide the surface into edge and plane sites. The edge sites have a Boltzman factor in the equilibria and the plane sites do not. The fundamental assumptions of the surface complexation model need direct experimental verification.

Empirical Measurements on Rocks

K_d s are more often measured on crushed rock than single minerals. Crushed rock is not necessarily representative of intact rock because the mineral availability, the surface area of minerals, and even the surface chemistry of minerals may have been altered. Exceptions are rocks that have very fine crystal structure (zeolitized tuff for example) for which crushed rock can be representative of the intact rock. The principal advantages of crushed rock are those of expediency. The rock can be homogenized making the sample more representative of a larger volume of rock. The experiments can be carried out in a reasonable time scale for laboratory measurements. The use of crushed rock therefore allows the study of multiple rock samples, concentration dependences, ionic strength dependence, pH dependence, etc^{32,33}.

Dynamic experiments can be performed to measure the retardation factor directly. These experiments, i.e., column experiments, with crushed rock have many of the same disadvantages as the batch measurements. The advantages are 1) that by comparing the results from static and dynamic experiments a failure to meet some of the requirements for eq. 1 would become obvious³⁴ 2) the comparison between static and dynamic experiments are performed on the same material (as opposed to using intact rock to compare with crushed rock) 3) columns constructed from crushed rock can be made hydrologically homogeneous 4) the dynamic experiments are sensitive to slow sorption kinetics³⁵ and 5) accurate determination of anion and size exclusion effects can be made³⁶.

The use of intact rock would appear to be the easiest way to achieve an appropriate K_d to the purpose of modeling transport. Unfortunately this may not be the case. The disadvantages are 1) intact rock is heterogeneous, i.e., a new unknown parameter is the statistical distribution of hydrologic and chemical properties 2) the distribution of hydrologic and mineralogic properties is difficult to characterize 3) the time required to perform experiments is relatively long thereby limiting the number of parameters which can be varied 4) it is difficult to establish a realistic groundwater flow field because the permeability is often low.

Experimental Results

Most of the sorption data available are as K_d s for crushed rock at a single concentrations. A few isotherms have been measured but these are for the most part limited to the few concentrations needed to fit a Freundlich isotherm³⁷. These isotherms are adequate for the purpose of estimating the K_d as a function of concentration over the range of concentration used to fit the

Freundlich isotherm. The Freundlich isotherm is empirical and the parameters derived from the fitting procedure are valid only for the rock and chemical conditions used in the determination. Examples of these experiments are shown in figs. 1 and 2. Fig. 1 shows a cesium data set³⁸ fit to a Freundlich isotherm and fig. 2 shows a strontium data³⁸ fit to a Langmuir isotherm, eq. 6. The cesium isotherm has a curvature that suggests saturation of sites. The data could be better fit with either a modified Freundlich as Fuentes³⁹ et al. have done or a multisite model. There are not sufficient data to warrant applying deconvolution. There are too few points and judging from the spread in points at a given concentration the errors are too large. The stoichiometry of the Langmuir isotherm for strontium is that of a monovalent ion exchange. This implies that either strontium occupies only one charged site displacing a single sodium ion or that strontium only occupies sites which were previously occupied by a divalent ion, i.e., calcium. A general treatment of divalent ion exchange must allow for the additional possibility of a single divalent ion replacing two monovalent ions¹⁵.

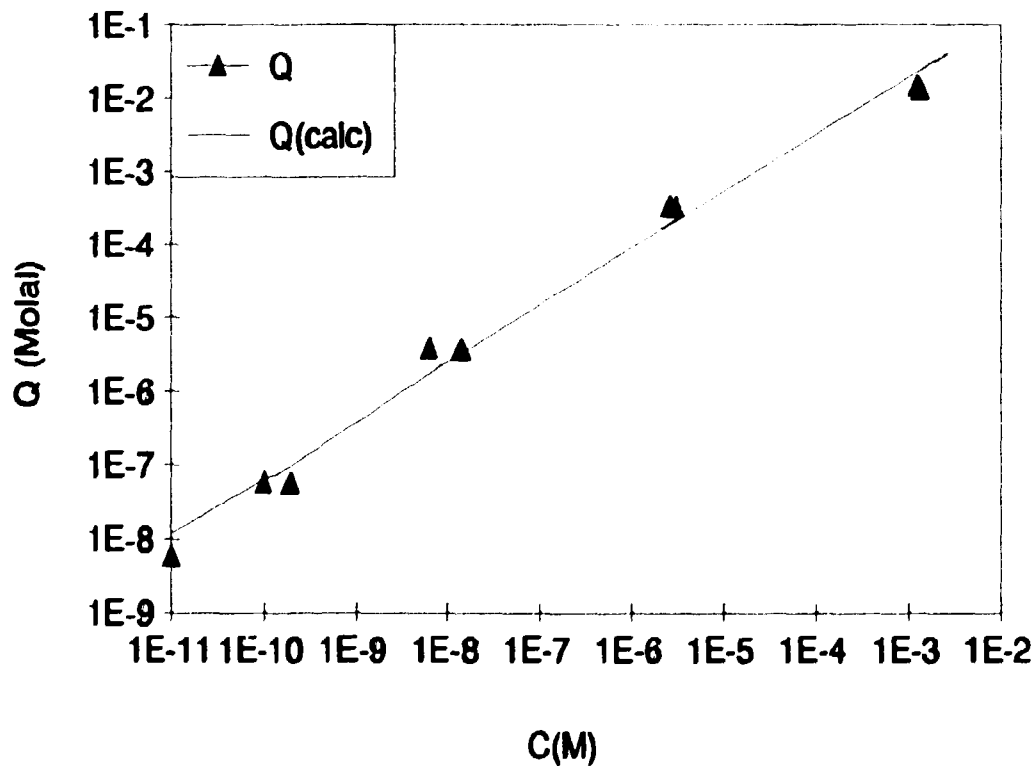


Figure 1 Cesium sorption isotherm for devitrified tuff, YM-22, in J-13 water. The solid curve is a fit to the data (points) using the Freundlich isotherm.

There is a need to put these experiments on a more sound thermodynamic basis using methods such as those described earlier. The best medium for studying the sorption mechanism is pure minerals. Although crushed rock batch sorption experiments could be interpreted in using deconvolution it would be better to use those experiments to test ones ability to provide estimates of the K_d based on mineralogy and groundwater chemistry. An example of single mineral experiments are shown in figs. 3 and 4. Fig. 3 shows the variation of neptunium sorption on Goethite, FeOOH , as a function of pH^{40} . Fig. 4 a ion-exchange isotherm for potassium on a synthetic zeolite, sodium-Y, a Faujasite⁴¹.

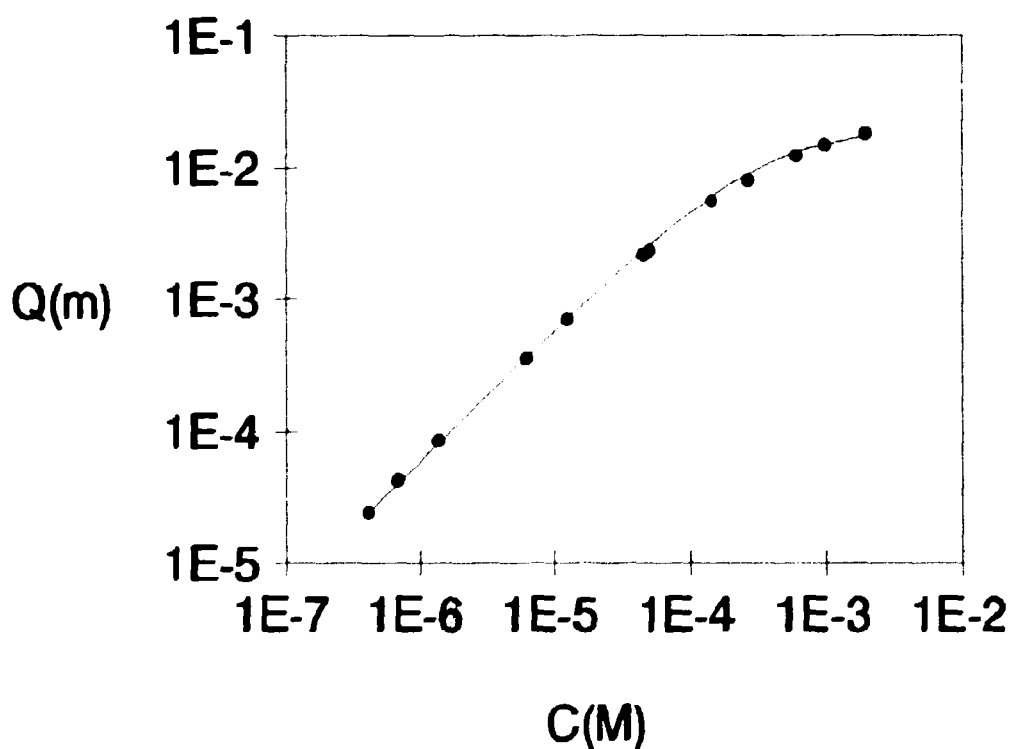


Figure 2 *Strontium isotherm with devitrified tuff, G1-2840, in J-13 water. The solid curve is a fit to the data (points) using a Langmuir isotherm.*

The neptunium isotherm shows that the adsorption of neptunium on goethite is a linear function of hydroxide ion concentration over a range of 6 orders of magnitude in concentration (from pH 3 to about pH 9). That stoichiometry

implies that neptunium (neptunyl ion) is not affecting the surface charge. The surface charge of goethite at pH below the point of zero charge has a logarithmic dependence on hydrogen ion concentration. There are at least two equivalent mechanisms which could be proposed to fit this stoichiometry. The neptunium could be adsorbed as a neutral hydrolyzed neptunyl or the neptunyl ion could displace a hydrogen ion from the goethite surface.

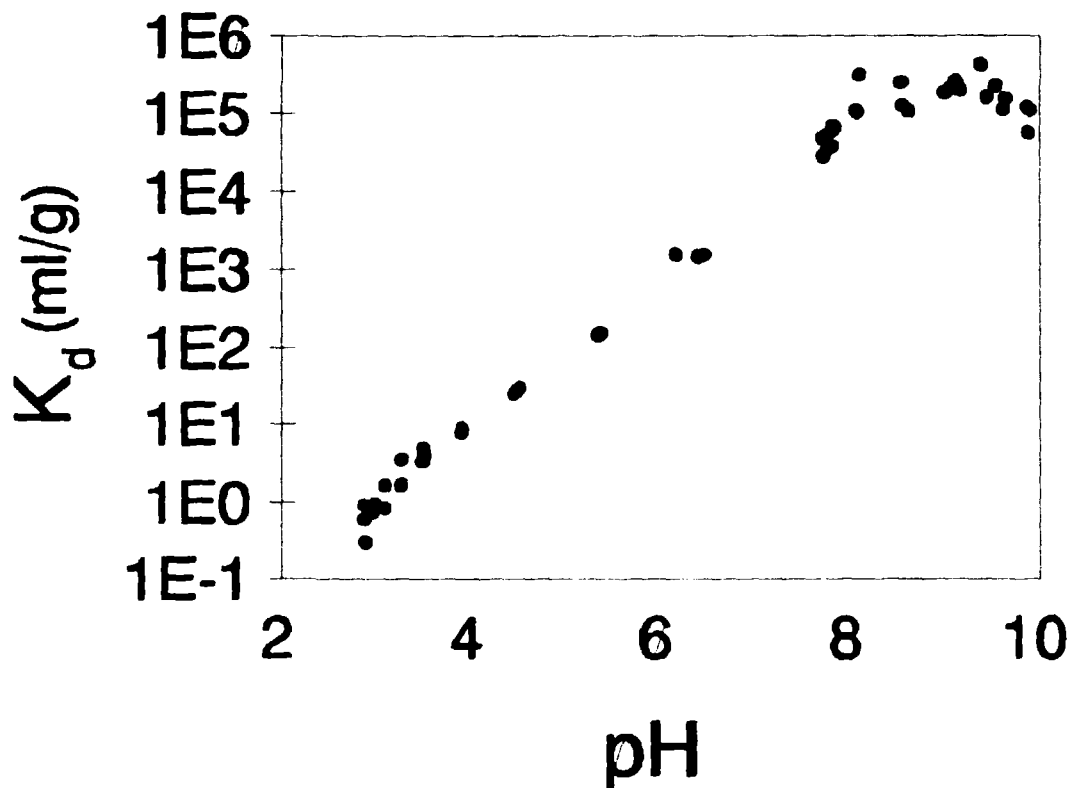


Figure 3 *Neptunium adsorption as a function of pH on goethite at an ionic strength 0.01 M, sodium perchlorate oxidizing conditions.*

The potassium/sodium ion exchange on zeolite Y shown in fig. 4 was fit using the deconvolution procedure. The smooth curve is the sum of sorption in three distinct sites. The three sites were shown to correspond to three crystallographic locations in the zeolite. The most selective site for potassium corresponds to the smallest cage structures in the zeolite. Potassium is favored over sodium because the sodium ion is more hydrated than potassium. In order to fit a sodium in the small cage it must release water of hydration thus

increasing the free energy of the sorbed ion. The largest cage, the supercage, favors the sodium ion. The relative number of charged sites located in the three crystallographic locations depends on the Si/Al ratio.

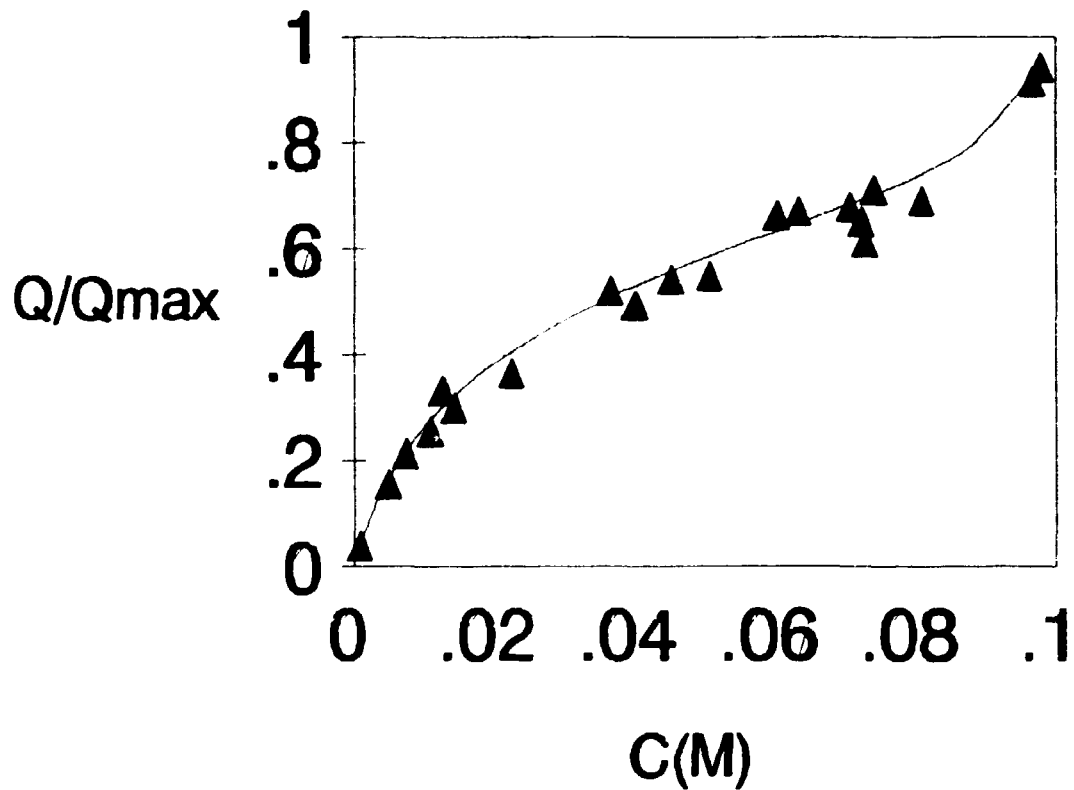


Figure 4 Potassium ion-exchange on faujasite.

Transport experiments using crushed rock columns provide a test of the K_d concept where the mineral availability and hydrodynamic effects (other than those associated with colloid transport) should not be in question. These experiments can be performed in a much shorter time period than intact rock because the permeability and porosity of the crushed rock column are generally greater. Long columns can be constructed to measure anion exclusion as illustrated in figure 5. The unexpectedly early breakthrough of plutonium(V)⁴² in crushed tuff is shown in fig. 6. Similar behavior has been observed for plutonium(VI) and neptunium.

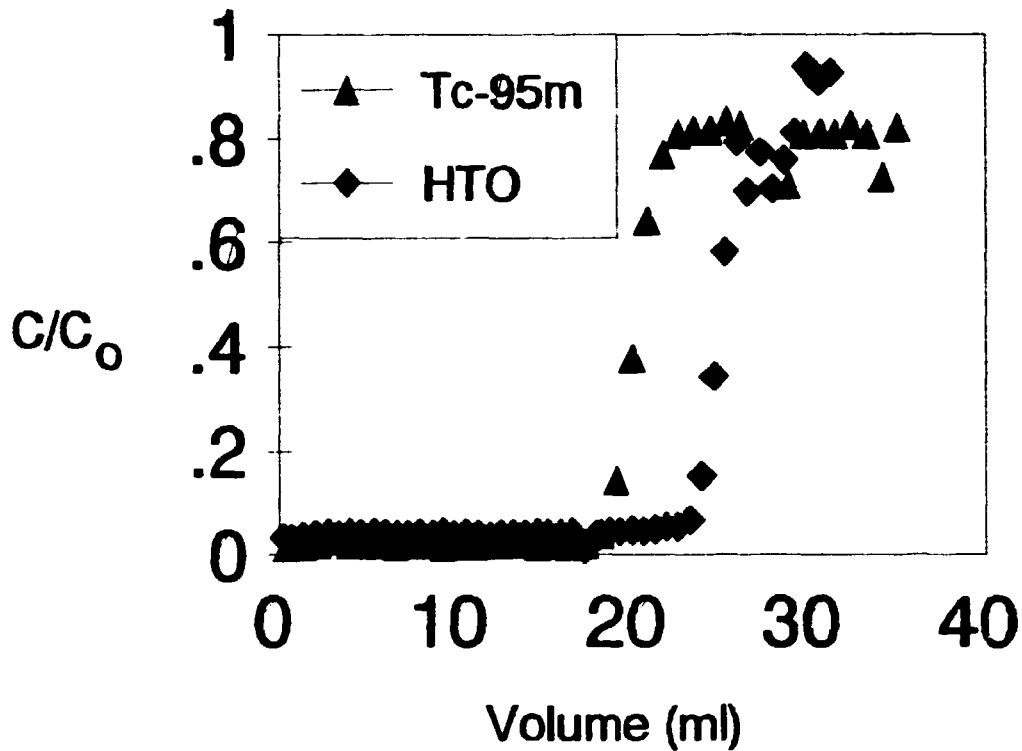


Figure 5 Comparison of tritiated water breakthrough with pertechnetate in zeolitized tuff.

The pertechnetate breakthrough curve leads tritiated water by approximately 4 ml. This effect is due to the exclusion of pertechnetate from the volume of water contained in the cage structure of the zeolites (mostly clinoptilolite). The magnitude of the effect is equal to intracrystalline pore volumes estimated from crystallographic studies of the minerals. The curve does not come up to 100 percent of the initial concentration. About 20 percent of the pertechnetate was adsorbed by the crushed tuff. Most of the missing activity was found to be adsorbed within 15 cm of the inlet. The cause of this effect is yet unexplained. It is possible that the adsorption of pertechnetate was due to an experimental artifact such as bacterial growth. It is also possible that pertechnetate is adsorbed by a trace mineral. The latter explanation is one example of the uncontrolled factors introduced in the use of rock.

The plutonium elution in fig. 6 is nearly unretarded. This elution was done using separated oxidation state plutonium(V). The fraction of the total tracer that is represented by the data is less than 70 percent. Plutonium colloid was found to be 90 percent retained and the 10 percent that does elute significantly leads the tritium elution. This is evidence for the hydrodynamic effect on

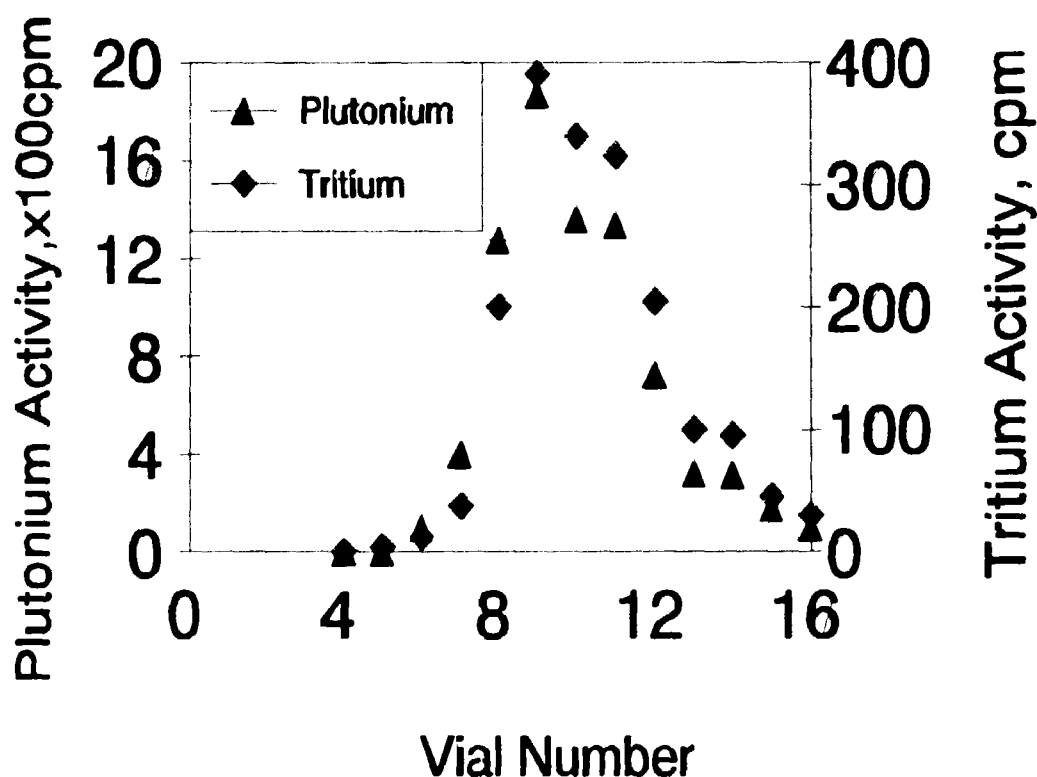


Figure 6 *Plutonium(V) elution through crushed tuff column.*

colloids. Neptunium and Pu(VI) were also found to elute with partial or no retention. Neptunium which is stable in the V state was not retained at all in contradiction with the batch K_d results. It is difficult to resolve these discrepancies without more information on the sorption mechanism and the hydrodynamics of the columns.

Solid rock batch tests are in fact diffusion experiments. Intact rock has the additional complication of mineral accessibility and pore structure, which needs to be considered when calculating retardation based on batch sorption measurements. These experiments usually take a long time to perform so are not suitable for isotherm determinations. An experiment to study the diffusion of neptunium into a slab of intact Stripa granite⁴³ that was undisturbed for 2 years is illustrated in fig. 7.

The neptunium distribution in fig. 7 along was fitted to the diffusion equation. The apparent diffusivity observed was $4.12 \times 10^{-11} \text{ cm}^2/\text{s}$, the intrinsic diffusivity is $1.33 \times 10^{-5} \text{ cm}^2/\text{s}$ (from conductivity data⁴⁴). The retardation factor is on the order of 3 based on a comparison with the effective diffusivity of pertechnetate ($K_d = 0$) in Stripa granite published by Allard et al.⁴⁵ This small retardation

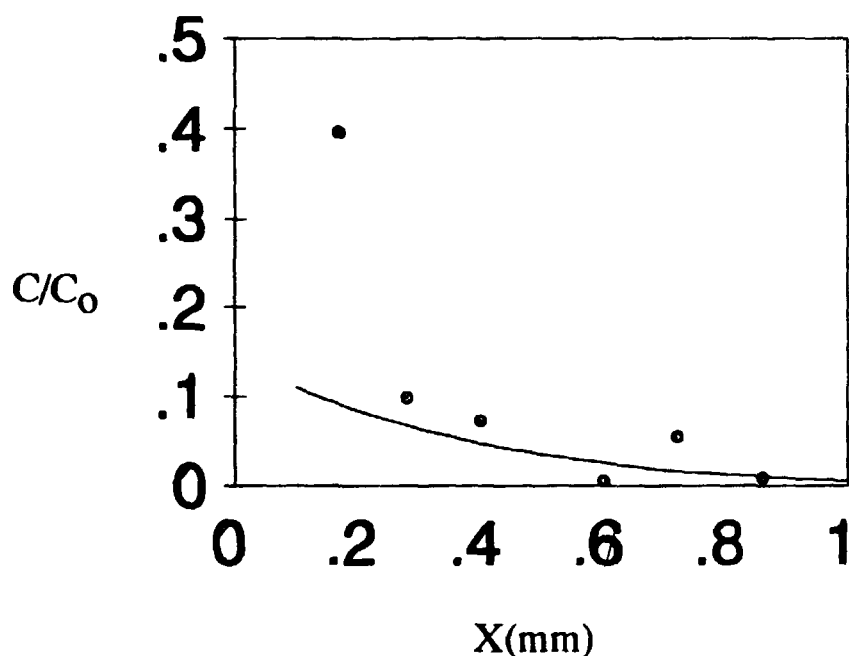


Figure 7 Neptunium penetration into a granite tablet.

factor may be somewhat biased towards the low side by the experimental method. The points used in the fit were the deeper penetrations and the first point was omitted. If one looks at the rock sample as being heterogeneous there is likely to be restricted paths and free paths across the cross section of the rock cylinder. Therefore the deeper points may represent more rapidly diffusing paths. The first point may represent slower paths.

Diffusion of pertechnetate through porous rock can be used to measure low K_d s as illustrated in fig. 8. The pertechnetate diffusion through a zeolitic tuff slab was measured by periodically sampling water from a reservoir on one side the of 1.6 cm slab⁶. The resulting concentration curve was fit to the diffusion equations using the finite difference method. The fit required a retardation factor of 3.7 in order to match the data. The retardation factor is larger than expected on the basis of batch sorption measurements. This is probably due to the anion exclusion effect. If the batch sorption results are corrected for anion exclusion the agreement is good. This also provides evidence that there is a mechanism that could explain the retention of technetium observed in the crushed tuff column experiments. The design of this experiment causes the tracer taking different diffusion paths to mix in the receiving reservoir. The apparent diffusivity observed should therefore be nearly the average of those paths.

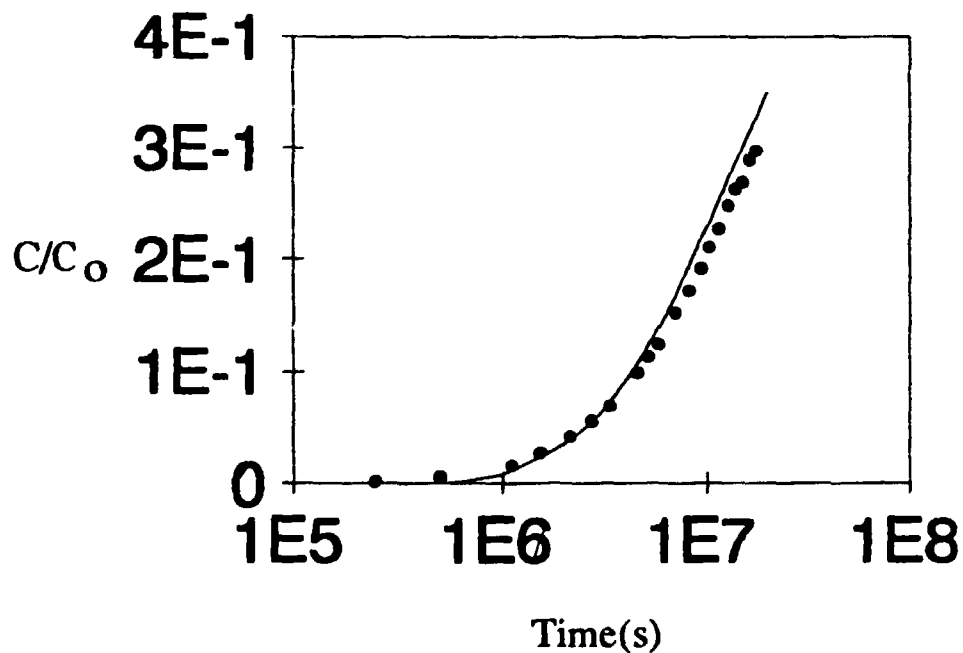


Figure 8 Diffusion of pertechnetate through a zeolitic tuff slab, USW G4-1607a⁴⁶.

The intact tuff columns with densely welded tuff from the Topopah Spring member tuff have exhibited time dependent dispersion⁴⁷. This complicates the interpretation of these experiments in terms of the predictability of retardation calculated from batch sorption, K_d s, measurements and the measured dispersivity (determined from conservative tracer transport). 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 can be orders of magnitude. The results in that study were reconciled by giving the dispersion a time dependence which in the devitrified tuff samples agreed with Gelhar's asymptotic fickian dispersion (see fig. 9). The tritiated water dispersion linearly extrapolated to the times relevant for the strontium elution would provide a conservative value of the dispersion. However, this is probably not universally true.

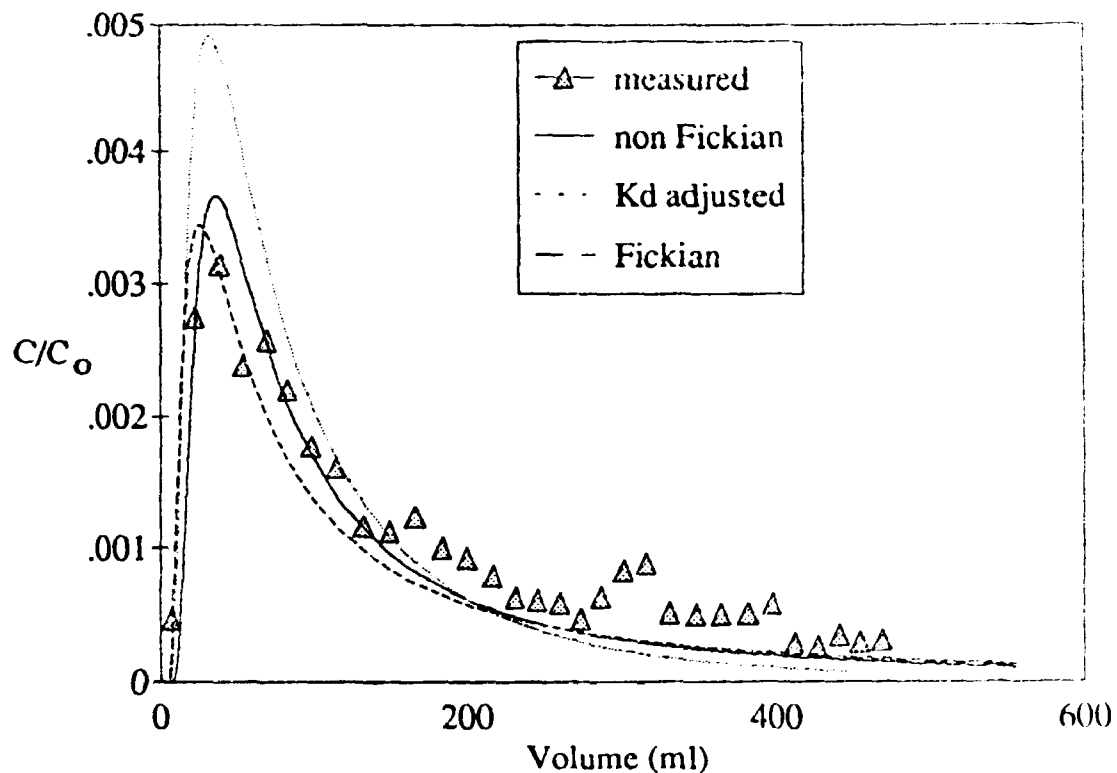


Figure 9 Comparison of strontium elution through intact tuff with calculations.

The analyses of the tracer elutions through intact tuff samples assumed that the distribution of sorption was uniform. The measured distribution of sorbed tracers was found to be nonuniform. Although the experiments with devitrified tuff samples did not exhibit any obvious sensitivity to the distribution of minerals, a general treatment of dispersion should include the spatial covariance of sorbing minerals. The dispersion for a sorbing tracer should depend 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 elutions agreed with the dispersion observed with tritiated water in the Fran Ridge sample. They did not in the zeolitized Calico Hills tuff, USW-G4-1607, see fig. 10. This again suggests that the dispersion depends not only on the hydraulic properties of the rock but on the chemical properties as well. The sorption of pertechnetate observed in the crushed tuff columns and the diffusion cell could be responsible for this phenomenon. It is possible that the mineral that retains pertechnetate is not uniformly distributed across the columns. In that case part of the tracer elutes quicker than tritiated water and part slower than water. The combination of retarded and unretarded flow paths results in a broader than expected elution curve.

These observations point to the need for a more detailed characterization of the hydrologic and geochemical properties of Yucca Mountain tuff. Future experiments will use 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.

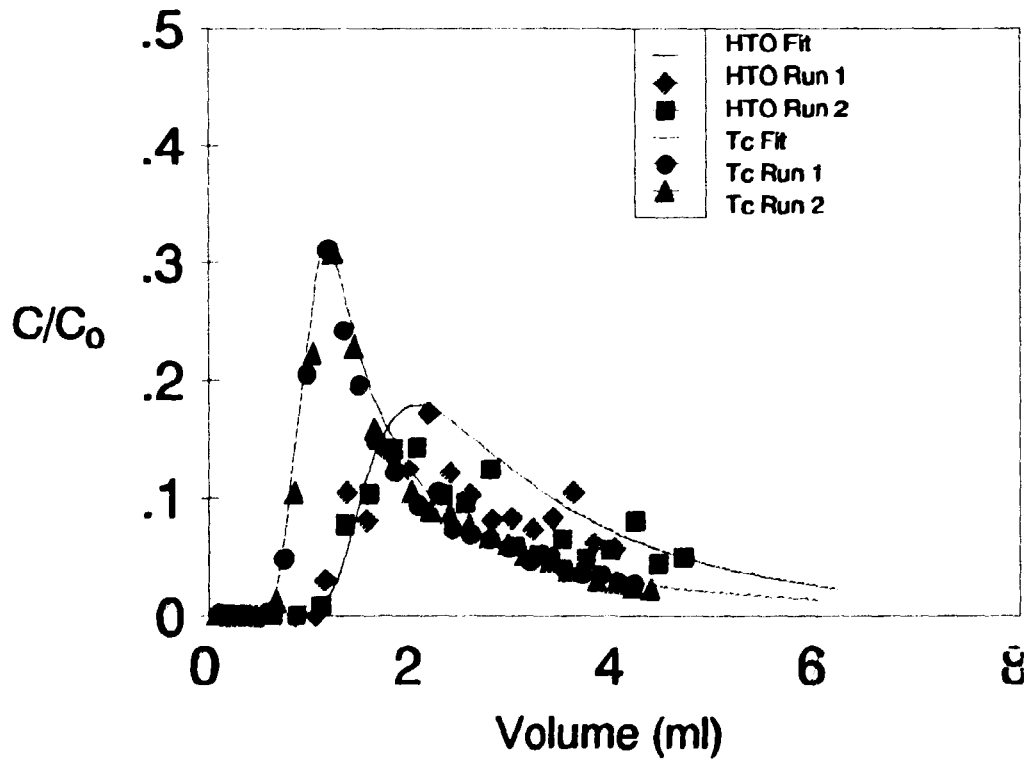


Figure 10 Pertechnetate elution through zeolitic tuff.

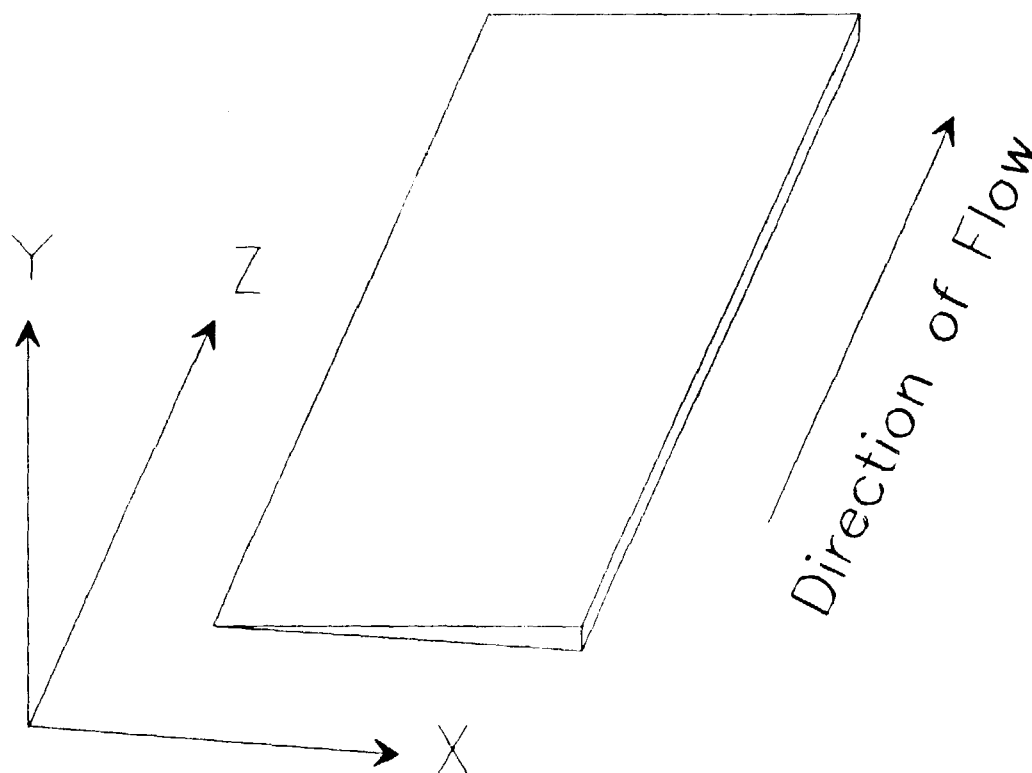


Figure 11 *Drawing of AECL/DOE Large Block experiment.*

There are few dynamic laboratory experiments reported in the literature^{48,49,50}. Most of the experiments use fractured rock columns. Some of these experiments have yielded results which have indicated faster than expected movement of simple cations, such as, cesium. The earlier breakthrough could be due to non Fickian dispersion as observed in intact tuff columns. A large block experiment is being designed in joint Canadian-U.S. experiment which will look at the effect of nonuniform water movement in manufactured granite fractures. Calculations using the transport code TRACRN⁵¹ have shown such effects in the fracture fluid. The preliminary design of one experiment is shown in fig. 11 with simulations calculated using TRACRN and de Marsily's time-dependent dispersion shown in fig. 12. Engineered heterogeneities such as this wedged fracture should give insight into the effect nonuniform fluid flow has on the migration of tracers.

The calculated elution curves show the somewhat subtle effect that nonuniform flow has on the elution of nonsorbing tracers. The points labeled Fickian are a closest fit to the TRACRN and time dependent dispersion model calculations. The Fickian dispersivity was not calculated from the geometry of the fracture.

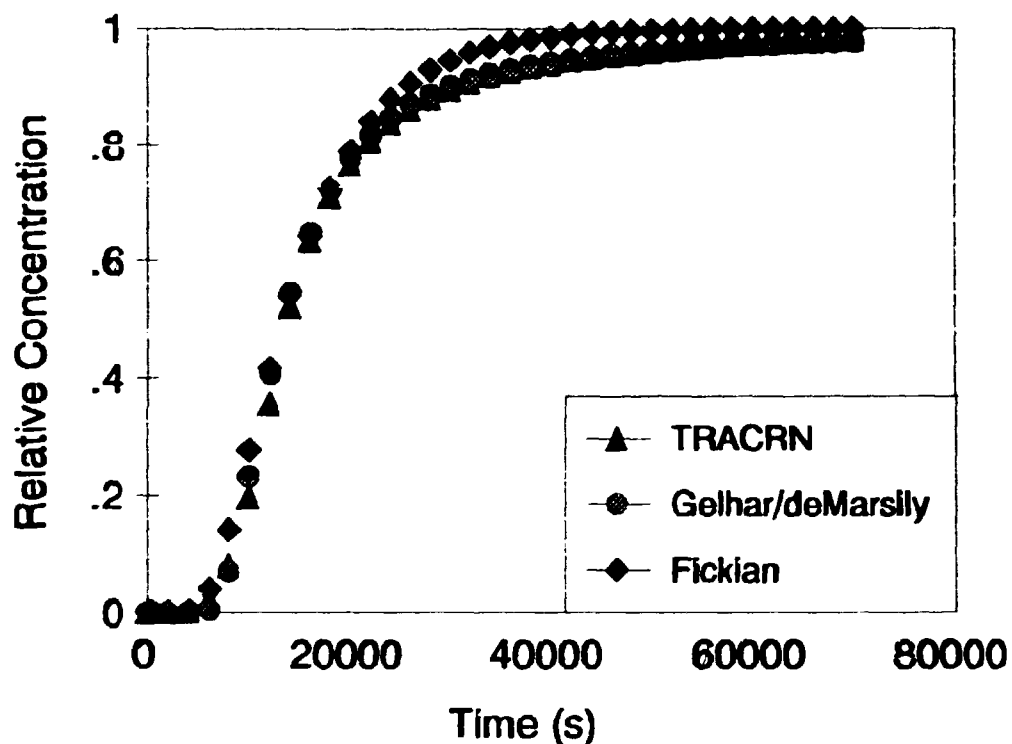


Figure 12 Comparison of tracer migration in simulations using TRACRN and analytical solutions to the geometry illustrated in fig. 11.

The TRACRN and Gelhar⁵² model calculations were based on the permeability distribution across the fracture. The encouraging result is that the TRACRN calculation agrees with the one dimensional approximation using time dependent dispersion. The difference between the Fickian model and the numerical and stochastic models is the tailing which is exhibited as a slow recovery to one hundred percent concentration. The effect is more dramatic for sorbing tracers because the apparent dispersion increases with time. Retarded species elute at much longer times and have much more dispersion than expected on the basis of conservative tracer behavior.

Conclusions

The sorption of radionuclides by rock is an inherently complex process. The data containing the most fundamental chemical information is obtained from single mineral experiments in simple ionic solutions. The stoichiometry observed with respect to tracer concentration and pH has been shown to rule out some possible mechanisms. The theory of adsorption on metal oxides

appears to be in a state of change. The development of new tools for studying surfaces, EXAFS, STM, and AFM will likely enable the resolution of mechanistic questions. If sufficient support is given for basic research in this area it is likely that sorption can be placed on a thermodynamic basis within a decade.

The use of crushed rock columns have shown agreement between batch sorption results and columns results for alkali metals and alkaline earths. The anion exclusion effect has also been studied using crushed rock columns and in the case of tuffs shown to be equal to the intracrystalline volume of porous crystals. The actinides and pertechnetate ion have exhibited migration properties that are difficult to explain. The identification of the sorption mechanisms and sorbing minerals will be important for these element. Progress has already been made for metal oxides. The other side of the actinide problem is the speciation of actinides in groundwater.

Intact rock is a difficult medium to perform experiments in. The challenges presented include the problem of correctly modeling heterogeneity. The chemical aspects which are different from crushed rock and single minerals are: 1) mineralogic characterization for trace minerals; 2) availability of mineral surfaces; 3) chemical composition of mineral surfaces; and 3) crystal morphology. Porous rocks that are composed of porous minerals, such as tuff, have demonstrated that sorption coefficients can be used when the dispersion is modeled correctly and the sorption mechanism is ion exchange.

Recommendations

The sorption coefficients used for performance assessment calculation must be evaluated in terms of their limited applicability. Usually tables are compiled which only report K_d s or ranges of K_d s. There is rarely a notation which would provide a limit to the radionuclide concentration, pH, or ionic strength above or below which these data should not be applied (with perhaps the exception of the ISIRS database). There is no way of telling whether the lowest K_d in the range represents a low due to a choice of unfavorable values for all parameters involved or whether it represents some lower end of the spread of values under average or nominal conditions.

An approach towards the application of sorption in performance assessment models should be developed which uses the body of chemical knowledge available in an efficient manner. It is not necessary or even desirable to use complex sorption models in performance assessments that explicitly incorporate the effects of pH, concentration, temperature, ionic strength, mineral composition and groundwater chemistry. If limits for these parameters can be set for a given calculation it should be possible to establish limits on the

distribution coefficient. This approach can be further simplified by reducing the set of minerals considered to the most common minerals in the rock type being characterized. This approach is currently being attempted at Los Alamos for the Yucca Mountain project⁵³. One considers relying solely on a common but perhaps a poorly adsorbing mineral, such as quartz. By narrowing the number of minerals to be studied a thorough job of examining the dependence of sorption on pH, ionic strength, concentration etc. can be performed. If the mineral set chosen does not provide large enough retardation factors to meet the licensing requirements the set can then be expanded until the requirements are met. This approach has the advantage over the empirical approach of providing a basis for evaluating the sensitivity of sorption to changes in water chemistry, variation in mineralogy, and of being inherently conservative because the minerals not included in the set can to a first order only increase the sorption of radionuclides and thus increase the performance of a site.

The role of whole rock either crushed or intact would be to test the soundness of predictions based on single minerals. This would be a criterion for the acceptance or rejection of the single mineral data set. The observed retardation must be greater than or equal to that predicted on a single mineral basis. If the experiment demonstrates a need for additional research the mineral set and/or parameter space could be enlarged.

To summarize the recommendations towards developing confidence in a quality sorption model. An investigative procedure with the following components should be used. 1. A K_d survey using crushed rock for the purpose of site selection, i.e., does the site offer favorable geochemical conditions. These K_d s should only be used for performance assessment with great reservation. 2. Perform experiments which will lead to a mechanistic approach to sorption. These experiments will rely heavily on single mineral systems. 3. A testing program using columns including intact rock columns to test whether the retardation factors calculated from the body of data collected in steps 1 and 2 are conservative, i.e., underpredict retardation. and 4. Data evaluation using the scientific judgment of researchers having experience in geochemistry, radiochemistry, actinide chemistry, hydrology, and related disciplines. The end result of this data evaluation would be recommended K_d values along with limits of applicability.

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