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# SOME GEOCHEMICAL CONSIDERATIONS FOR A POTENTIAL REPOSITORY SITE IN TUFF AT YUCCA MOUNTAIN, NEVADA*

by

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## ABSTRACT

The Nevada Nuclear Waste Storage Investigations, which is evaluating potential locations for a high-level waste repository at the Nevada Test Site and environs, is currently focusing its investigations on tuff, principally in Yucca Mountain, as a host rock. This paper discusses some of the geochemical investigations. Particular emphasis is placed on definition of some basic elements and necessary technical approaches for the geochemistry data acquisition and modeling program. Some site-specific tuff geochemical information that is important for site selection and repository performance will be identified and the current status of knowledge will then be discussed.

## I. INTRODUCTION

During recent years, deep burial as a means for safe disposal of nuclear reactor waste has gained acceptance because of the concept that the rock surrounding the repository will provide a significant barrier between the radioactive waste and man's environment. Because the rock provides the first natural barrier to radionuclide migration, an understanding of the properties and setting of the host rock is of considerable importance. Such understanding will also be the basis for predicting the performance of a repository and identifying potential deficiencies in the models used for the predictions. Clearly, such an understanding will also be essential in the process of selecting and licensing a repository and in convincing the general public of the ultimate safety of such disposal.

The Nevada Nuclear Waste Storage Investigations (NNWSI), which is evaluating potential locations for a high-level waste repository at the Nevada Test Site (NTS) and environs, is currently focusing its investigations on tuff, principally in Yucca Mountain, as a host rock. As part of the geochemical studies being conducted by Los Alamos National Laboratory, the geochemistry, with particular emphasis on geochemical retardation processes, is being

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*Work performed under the auspices of the US Department of Energy.

extensively investigated. Information gathered through study of these processes will help to predict the rates and concentrations of radionuclides that could be released into the environment and to assess the hazards associated with such potential releases. The experimental program, thus far, has addressed various aspects of sorption by tuff, the physical makeup of tuff, the diffusion process, and various transport processes involved in porous and fracture flow. Some of the principal techniques and results are presented below, with emphasis on those activities that may be of most interest in a general way. Further details are given in Refs. 1 through 9.

## II. GROUNDWATER CHEMISTRY

The main components of fluids used in the drilling of hydrology wells at the NTS are detergent, air, and a natural groundwater reasonably representative of the site. Lithium chloride is also added to serve as a tracer for the water that is used as drilling fluid. To determine the chemistry of the groundwater it is vital to know when the water from a well is formation water (that is, free from any of the drilling fluids). All drilling fluids must be eliminated principally because the oxygen concentration of the groundwater is one of the most important variables in the chemistry of the water--it affects retardation mechanisms and corrosion of the waste package. Winograd and Robertson [10] have suggested that groundwaters in the tuffs of Nevada may always contain dissolved oxygen. It seems logical that the flowing water least influenced by oxygenated recharge water and by air in the unsaturated tuffs or fractured tuffs will be the water in the deepest permeable zone.

A pumping test to sample groundwater from a particular transmissive zone* at 2840 to 2870 ft in Drill Hole UE25b-1h was set up as shown schematically in Fig. 1. An Inflata-Plug was set in the well at 3000-ft depth and a Pip Packer at about 2800-ft depth. Groundwater could then be pumped from between these two packers to the surface for analysis. The pump was set at 2600-ft depth, much deeper than normal for pumping wells. This depth was chosen so that the height of the water column inside the casing at the pump locations would be as great as possible; thus, it would eliminate any possibility of pump cavitation and reduce the diffusion of air down through this column of water to the water being pumped out of the packed-off zone. In addition, nitrogen gas was introduced daily through the access line into the space above the water column to flush out any air.

During the pumping, a portion of the well's total flow was continuously directed through a 1-in. Tygon hose into a mobile laboratory at the well site. This flow could be directed into anaerobic filtration equipment and/or through the electrode cell where measurements of oxygen, pH, Eh, and sulfide could be made without exposing the water flow to the atmosphere.

The anaerobic filtration unit (Fig. 2) consisted of two Nuclepore 1-ℓ stainless steel filtration units, appropriate stainless steel valves and tubing, and 1-ℓ pyrex receiver vessels with pressure stopcocks. Two filtration units are provided in series so that even very dirty water can be filtered in stages, including a final filtering through a 0.05-μm Nuclepore membrane. In this test, only the top filtration unit with a 0.05-μm Nuclepore membrane was used. Samples were anaerobically filtered each day. A 50-cm$^3$ sample of the filtered water was acidified with very pure hydrochloric acid for Fe(II) and Fe(III) determinations. The 1-ℓ pyrex containers were kept full of filtered water (unexposed to air) to be used for reference water and

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*Data supplied by the Nuclear Hydrology Group, US Geological Survey, Denver, Colorado.

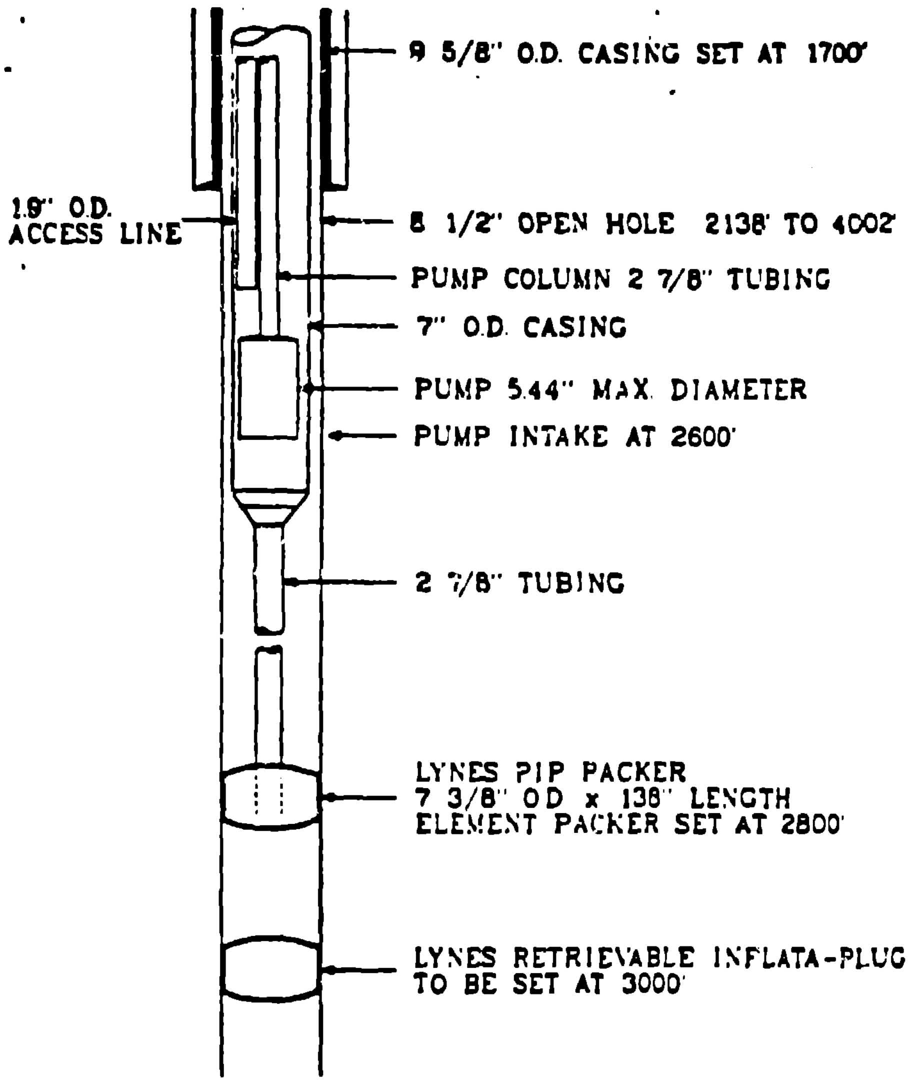

Fig. 1. Schematic of method of pumping between packer and bridge plug.

future analyses for concentration of $^{14}C$, carbon-dioxide, oxygen of <0.1 mg/l, and manganese oxidation states. The anion concentration of the groundwater was usually determined twice a day in a mobile laboratory at the well site, using an ion chromatograph. This instrument proved to be extremely durable and dependable for such a field operation. Samples of anaerobically filtered water, water taken directly from the well, and water exiting the mobile laboratory were all used as samples for anion analysis. Varying sampling procedures did not produce any discernable differences in anion content. Alkalinity was determined by titrating unfiltered samples with hydrochloric acid, using an automatic titrator Titroprocessor. The detergent content of the water was determined spectrophotometrically. Detergent was a good indicator or tracer of drilling fluids in the well. The Eh was measured with a platinum

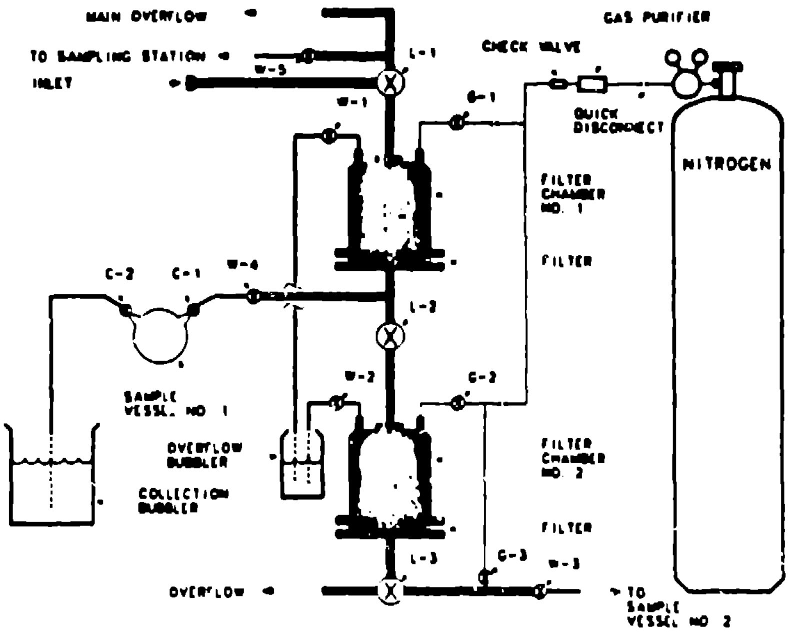

Fig. 2. Field filtration apparatus.

electrode, pH with a combination electrode, sulfide with a sulfide/silver electrode, and oxygen with a dissolved-oxygen meter and electrode.

The detailed results of this pumping test, which lasted 28 days, are given in Ref. 7. Only the major conclusions are briefly described here.

The change in detergent concentration with time is shown in Fig. 3. During the 28-day pumping test, detergent concentration decreased by about 3 orders of magnitude, reaching an undetectable lower limit of 0.007 mg/ℓ near the end of the pumping. This decrease appears to be a very sensitive indication of the clearing of drilling fluids from the water. There is no natural background of detergent in the water, so any detectable amount must have originated from drilling fluids. The length of time required to eliminate detergent from just one permeable area of the entire well illustrates that additives such as detergent should not be used when drilling the well.

In contrast, the air used during drilling was removed rapidly from the packed-off portion of the drill hole. As shown in Fig. 4, the oxygen content dropped to below a detectable amount (0.1 mg/ℓ) in less than 27 hours of pumping. This difference noted between detergent and oxygen is entirely reasonable. Certainly the saturated tuff is more permeable to liquids than to gases and the quantity of each introduced into the tuff at this depth will be directly porportional to this permeability. After about 2 weeks of pumping the oxygen content of the water again became a detectable amount, and it increased to 1.6 mg/ℓ at the end of the test.

The Eh, also shown in Fig. 4, increased with time after the initial drop to a negative value. For the first 11 days the rate of increase was quite slow, but it became more rapid during the last 17 days of the test. It is not known at this time if the break in the curve is real or if it is simply within the limits of accuracy of the determinations.

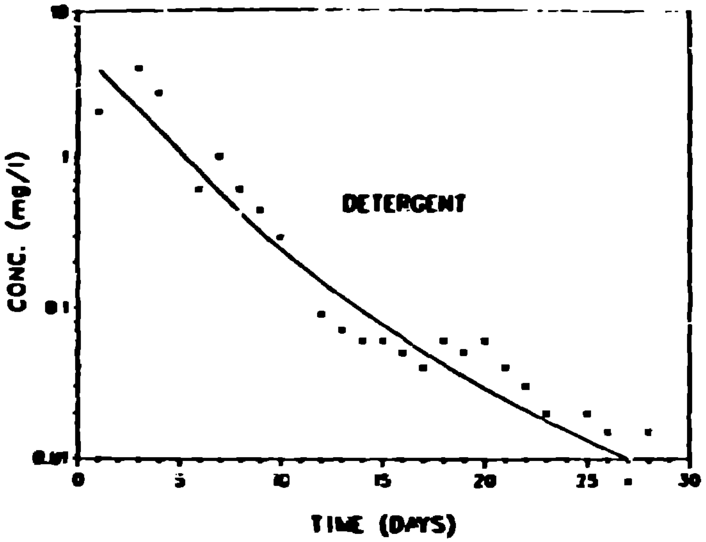

Fig. 3. Well UE25b-1 detergent levels.

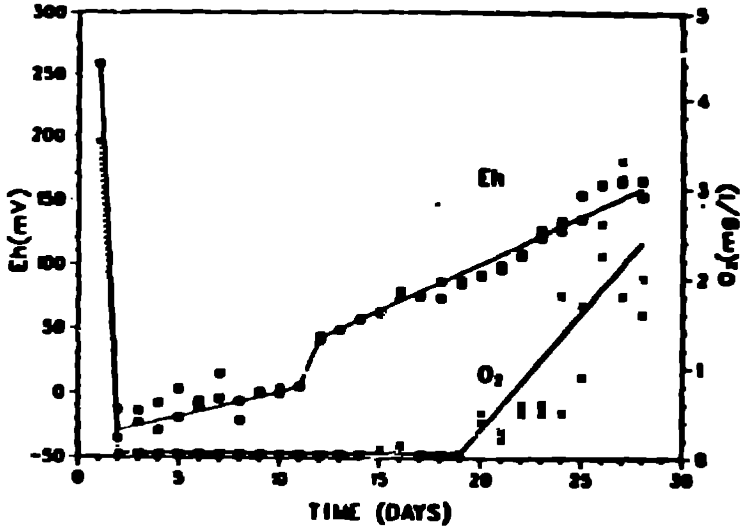

Fig. 4. Well UE25b-1 oxygen and Eh readings.

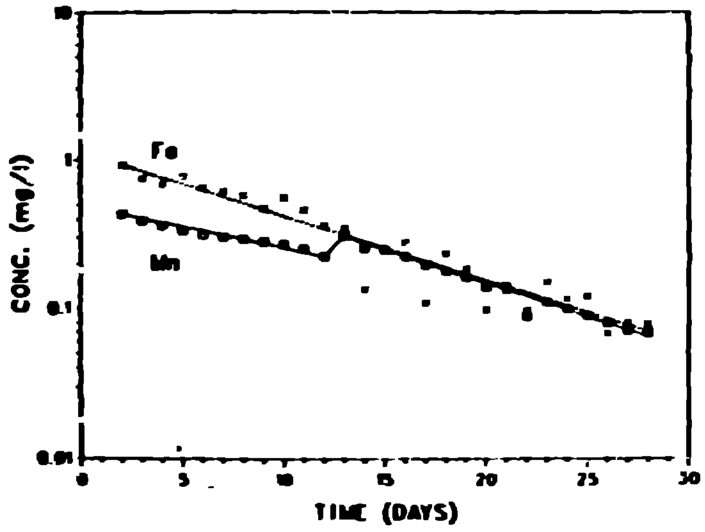

Fig. 5. Well UE25b-1 iron and manganese contents.

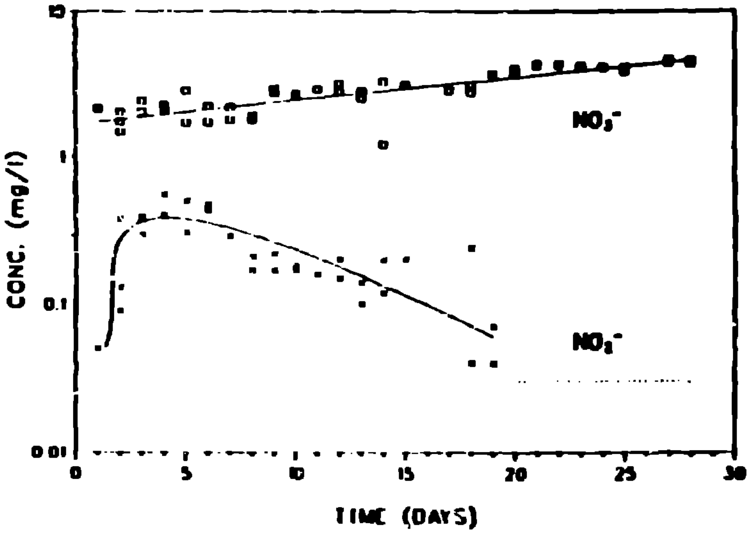

Fig. 6. Well UE25b-1 nitrate-nitrite content.

The Eh is certainly not a direct measure of the water's oxygen concentration, but it is a measure of various oxidized and reduced species in the water. The concentration of these species in various oxidation states, however, is affected by the amount of oxygen in the water. Figures 5 and 6 contain the results of some of these species. Iron and manganese are two elements that can exhibit varying oxidation states. After 2 days of the pumping test, the concentration of these elements is very high compared to most groundwaters in the NTS. Based on solubility limits, these high concentrations must be the result of iron and manganese in the more soluble II oxidation state. With time, the concentration decreased because of oxidation to the more insoluble Fe(III) and Mn(IV) species. Again, it is not known if the break in the curve shown for manganese is within the limits of accuracy of the determination.

An additional oxidation-reduction couple observed in the sampled water is nitrate-nitrite. The concentration of each changes with time (Fig. 6) in a manner similar to that of other oxidizable and reducible species. The nitrite found during the first 2 weeks of pumping becomes detectable as the oxygen increases. The reduction anion nitrite in groundwater of the NTS has not been reported before. Because nitrite is so easily oxidized to nitrate, it is unlikely that nitrite will be detected in any analysis except those done at the well site.

For both chloride and bromide as a function, there is a slow decrease in concentration after an initial increase during the first 3 to 5 days of pumping. The decrease in chloride with time was expected because lithium chloride had been added to all drilling fluids and there might still be evidence in the water of those additions. The lithium decreased with time during the pumping. Alkalinity also decreased slowly with length of pumping.

The overall results suggest that there were three phases to the pump test. At the start of pumping, the groundwater contained a nonequilibrium mixture of products that accumulated because the hole, full of water, was exposed to air to the entire tuff mineralogy for about 0.5 year. In addition to high oxygen and a high Eh, sulfide was detected in the water. However, only a short period of time was needed to pump out these products. This first phase also showed an increase in nitrite and chloride as the second phase developed. In this second phase, which continued as late as through the 10th to 14th day of pumping, the composition of groundwater that may be closest to formation water from this stratigraphic zone was measured; however, detergent and lithium were still detected. The water was devoid of measurable oxygen, exhibited a negative Eh, and contained relatively large quantities of reduced species such as Fe(II), nitrite, and perhaps Mn(II) or Mn(III). It is very interesting to note that, of the observed cations in the water, iron and manganese are the only ones that can exhibit multiple valence states. Because no sulfide is found in the water after the first day of pumping, it is likely that pyrite does not control the Eh of this groundwater. It is not clear at this time what iron- and manganese-containing mineral is controlling the oxidation-reduction potential of the water.

These results observed for oxygen content in this zone of Well UE25b-1 do not necessarily disagree with the conclusions of Winograd and Robertson [10]; rather, the current results extend their work. Because tuff is highly fractured and porous, and contains little surface vegetation or organic material, it is logical that oxygen has not been removed from recharge water; therefore, the upper aquifer is oxygenated. However, the wells investigated in the NTS by Winograd and Robertson produced water almost entirely from the aquifer at the standing water level. Well UE25b-1 is different in this respect; it has several deeper permeable zones separated from the upper oxygenated aquifer by impermeable tuff. The analyzed water from one of these zones contained no detectable amounts of oxygen. This is the first concrete evidence that such waters do exist in Yucca Mountain.

In the third phase of the test the oxygen content increased with time and there was a decrease in the concentration of reduced species. It is not clear why the oxygen content changed during pumping. The packers could have leaked and introduced water from a different zone into the zone being pumped; the zone itself could have changed if nonequilibrium conditions were present; or the zone was pumped at too high a rate, pulling water through fractures from a different zone into the sampled zone. Tests for packer leakage were performed but were not entirely conclusive.

## III. SORPTION MEASUREMENTS

The term sorption has generally been used to describe the group of processes by which elements are removed from solution through their interaction with rock. The processes include ion exchange phenomena, chemisorption, and diffusion into the rock matrix, and then may ultimately end in a variety of precipitation or coprecipitation reactions.

For the purpose of describing the partitioning of a radionuclide between rock and groundwater, we use the term sorption ratio $R_d$, defined by

$$R_d = \frac{\text{activity on solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} \quad .$$

Many investigators refer to this quantity as the distribution coefficient $K_d$. Los Alamos prefers not to use this term except under equilibrium conditions. Los Alamos data indicate that equilibrium is not achieved in many instances, but the sorption ratio is a measurement of an element's distribution between phases under specified conditions, although not necessarily at equilibrium. Sorption of a cation from near-neutral groundwater onto a rock is complicated in the case of tuff; it may involve many competing cations and complexed or hydrated species. Many equilibria must be described before thermodynamic equations can be used to describe sorption of most elements.

A variety of experimental techniques have been used to gain an understanding of these processes, to study the importance of the parameters involved, and to build up a data base that will be used to model the sorption of nuclides by tuffs in the Yucca Mountain area. The details of these techniques are given in Refs. 3 through 9. They include the batch process on crushed rock or tablets of whole rock; flow through columns of crushed material; a system in which the groundwater is circulated through a column of crushed tuff (that is, a recirculating system); and transport of radionuclides through solid samples (cylinders or blocks) of tuff or tuff samples containing real or artificial features.

It is a fundamental conclusion of these studies that quite similar retardation parameters for a given rock type can be obtained, relatively independently of the experimental method, if the proper mathematical interpretation of the measurement is performed and care is taken to follow the detailed requirements of the individual experimental procedures.

For example, Fig. 7 shows the batch sorption data for cesium as a function of depth in Drill Hole USW-G1 for three drill holes. The reproducibility is excellent using our particular batch technique [4]; indeed, the range of values obtained by several different investigators at Los Alamos is about 20%.

The uncertainties associated with averages of sorption data (such as shown in Fig. 7) are the standard deviations of the means $\sigma_m$, defined by

$$\sigma_m = \left(\frac{\Sigma d_i}{n(n-1)}\right)^{\frac{1}{2}} ,$$

where $d_i$ is the deviation from the mean of the ith experimental value and n is the number of values. The standard deviation of the mean is used rather than the standard deviation of the sample or the population; thus, it is possible to avoid including zero in the range of uncertainty when, for example, averaging a large range of individual determinations, all of which indicate a high sorption ratio. The total spread of values averaged in the measurements is often a factor of 5 larger than $\sigma_m$. This is the result of the choice of $\sigma_m$ just discussed, the nonweighted averaging, and the simplifying assumption that the samples belong to the same population when averaging results for different times, particle sizes, etc.

Because we are dealing with a complex sequence [8,9] of silicic volcanic cycles resulting in a layered stratigraphy, it is imperative that we perform detailed mineralogical characterization and that we understand the stability of the phase assemblages under a thermal load. The principal phases that aid in sorption include hydrated volcanic glasses, smectites, and zeolites. The distribution of hydrated glasses is stratigraphically controlled, and the glasses occur in narrow horizons in vitrophyres and as unaltered primary volcanic glass in restricted areas. Glasses are less important sorptive phases than zeolites and smectites, but they are very reactive and can alter to other minerals if heated in the presence of water. Smectite clays are reversibly expandable and are sorptive alteration minerals that are widespread in tuffs, but their beneficial properties can be modified by a prolonged exposure to elevated temperatures. Heating smectites in a dry atmosphere results in water evolution and reversible collapse; prolonged hydrothermal alteration of smectites can produce minerals with decreased volume, expandability, and sorption capacity. The zeolites clinoptilolite-heulandite and mordenite are highly sorptive minerals that occur in high concentrations in silicic tuffs. These zeolites occur mostly as secondary alterations of nonwelded and poorly welded tuffs and their distribution is, therefore, stratigraphically controlled. The distribution of three alteration minerals smectite, illite/muscovite, and clinoptilolite, in addition to unaltered glass are shown in Fig. 8.

Because tuff samples may be composed of more than one sorbing mineral as shown in Fig. 8, Los Alamos is currently researching ways to predict sorption ratios by combining the effects of several minerals. In one approach [5], the combined effect is defined as a weighted sum, the "sorptive mineral content" (SMC), determined by

$$SMC = \Sigma W_i X_i \quad ,$$

where $W_i$ is the weighting factor for each mineral phase and $X_i$ is the abundance (%) of each phase.

The weighting factors are determined relative to clinoptilolite, to which a value of 1.0 is assigned because it is the most strongly sorbing mineral in the group. A set of values for sorption of cesium on other minerals must be obtained from data for the pure minerals or inferred from mixtures. The $K_d$ values for clinoptilolite, mordenite, and montmorillonite are calculated from published thermodynamic data [11-15]. Some simplifying assumptions were made in applying the data to calculate $K_d$ values for the specific tuff-groundwater

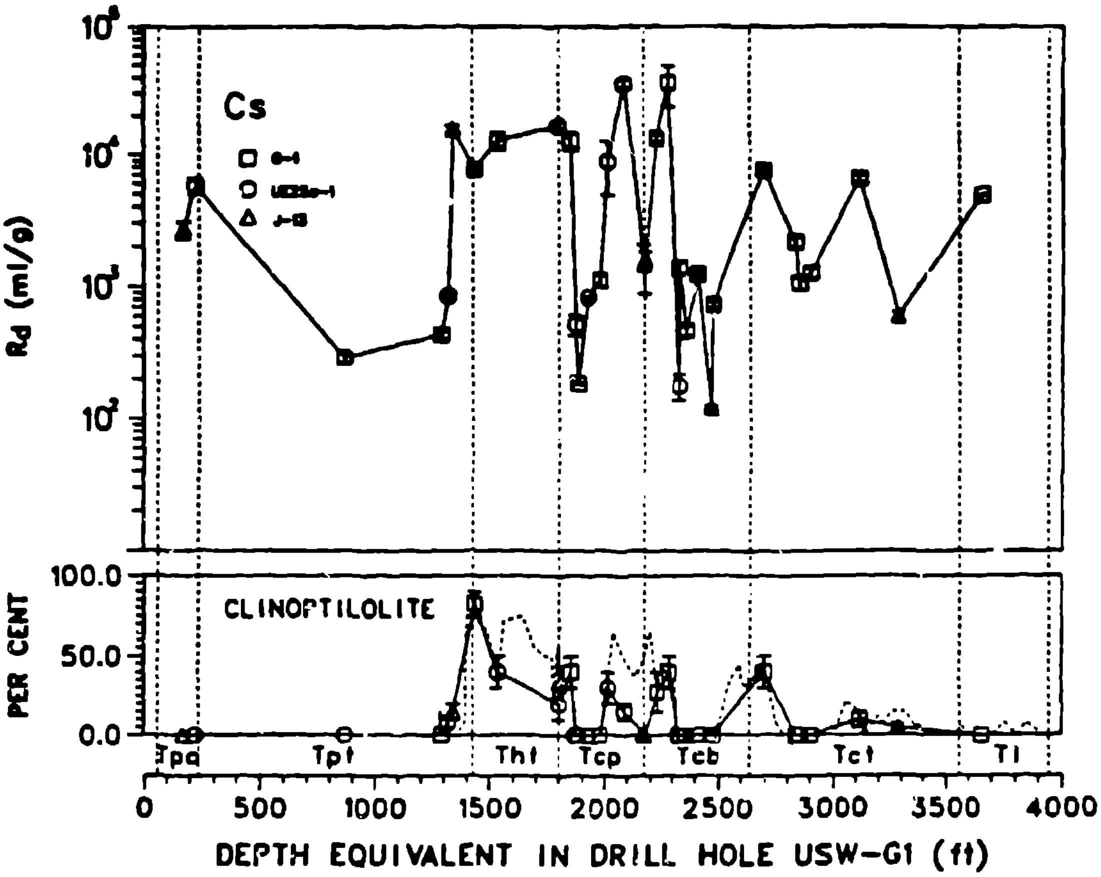

Fig. 7. Sorption ratio variation for cesium as a function of stratigraphic position in USW-G1.

cases. The assumptions are that (1) all mineral phases observed in the x-ray diffraction analyses, which are performed on samples ground to <10 μm, are available for sorption, and the only competition for sorption sites is, in this case, between trace amounts of cesium and sodium; (2) the sodium concentration in the assumed groundwater is 3 mM (the approximate ionic strength of the traced groundwater); and (3) one set of thermodynamic data applies to all samples of each mineral. The last assumption is not strictly true because samples of the same mineral from different localities, when prepared differently, gave different thermodynamic constants [11]. The other weighting factors were determined to be 0.50 (montmorillonite), 0.04 (mordenite), 0.05 (analcime), and 0.016 (glass). The sorption ratios for cesium are plotted as a function of SMC in Fig. 9; Fig. 10 is the same plot for low values of $R_d$. The solid line is the theoretical line based on thermodynamics; the dashed lines represent an error envelope for uncertainties of a factor of 3. As shown, most the experimental values fall within the envelope. This procedure, or a variant, may allow us to predict sorptive properties for the tuffs along pathways to the environment. However, two points must be kept in mind: first, sorption of cesium is probably the simplest test of this concept; second, any such procedure is critically dependent upon accurate determination of the mineral phases available to the groundwater.

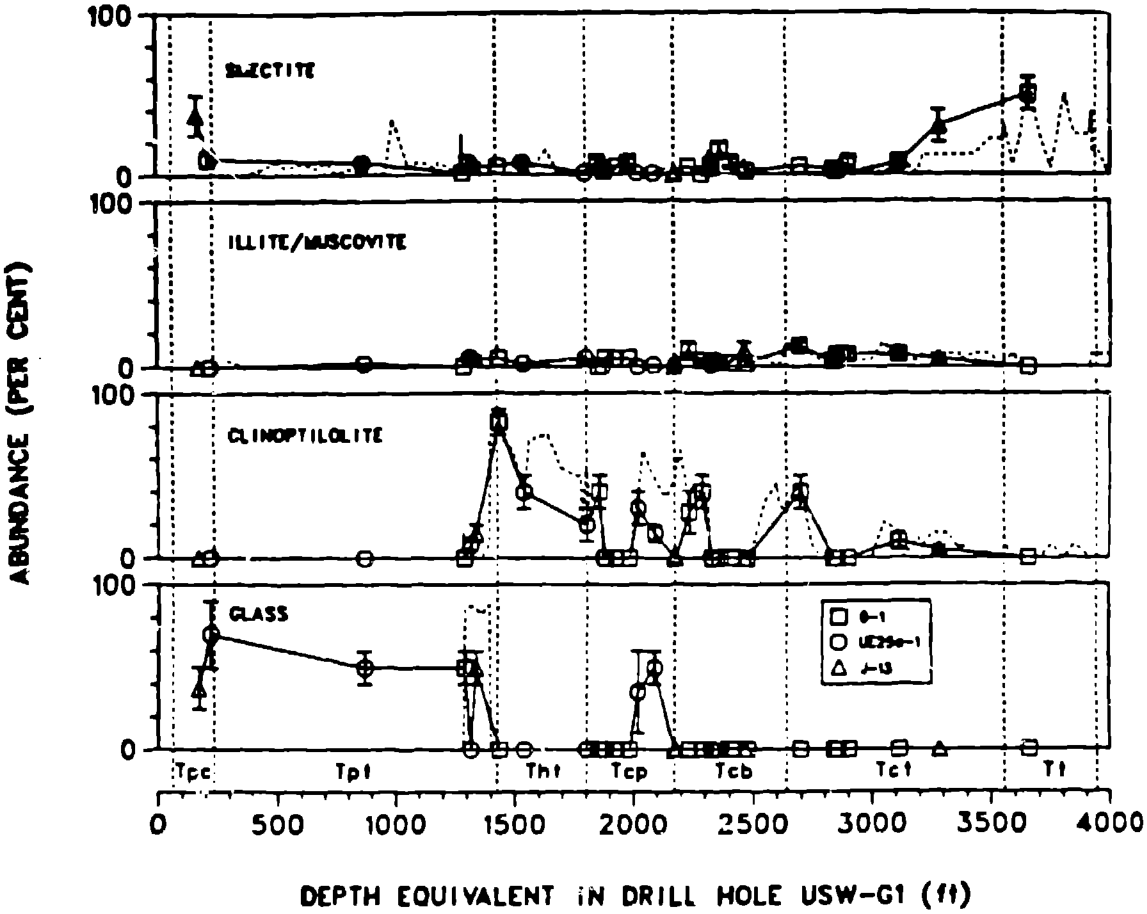

Fig. 8. Variation in mineralogy with depth for unaltered glass and alteration minerals smectite, illite/muscovite, and clinoptilolite.

## IV. SORPTION ISOTHERMS

The study of sorption isotherms is used to (1) determine the influence of groundwater/tuff interactions on the sorptive properties of tuff, (2) accurately model the retardation of waste elements under various source-term and groundwater conditions, (3) detect irreversible sorption processes that could be very positive properties if discovered in tuff, (4) interpret and model diffusion into the tuff matrix as it would occur in fracture flow, and (5) explain the observed dependence of the distribution coefficient on the solution-to-solid ratio and predict real conditions from laboratory measurements.

In most transport codes, sorption is normally treated as a linear isotherm; that is, the distribution coefficient $K_d$ does not depend on the cation concentration. This standard treatment should be valid for ion-exchange equilibrium at tracer-level concentrations with zeolitic tuffs; however, welded, nonzeolitized horizons have been proposed as repository hosts because of their thermomechanical properties.

The Langmuir isotherm is also commonly used. It is appropriate to any sorption mechanism that is first order and has a limited number of sorption sites. The form of the Langmuir isotherm is

$$q = \frac{QKc}{c_o + (K - 1)c} ,$$

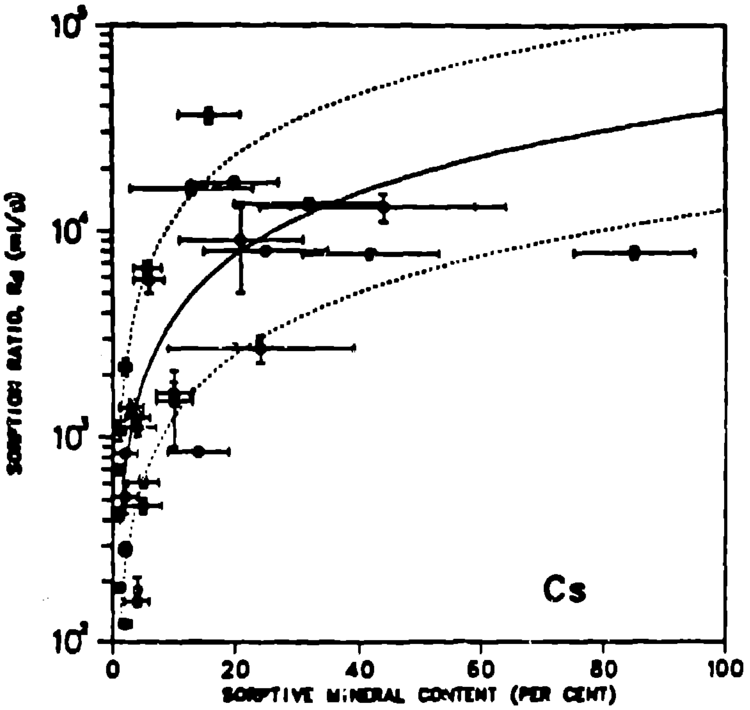

Fig. 9. Sorption ratios for cesium as a function of sorptive mineral content. Solid line is theoretical line based on thermodynamics. Dashed lines give a factor of ±3 uncertainty envelope.

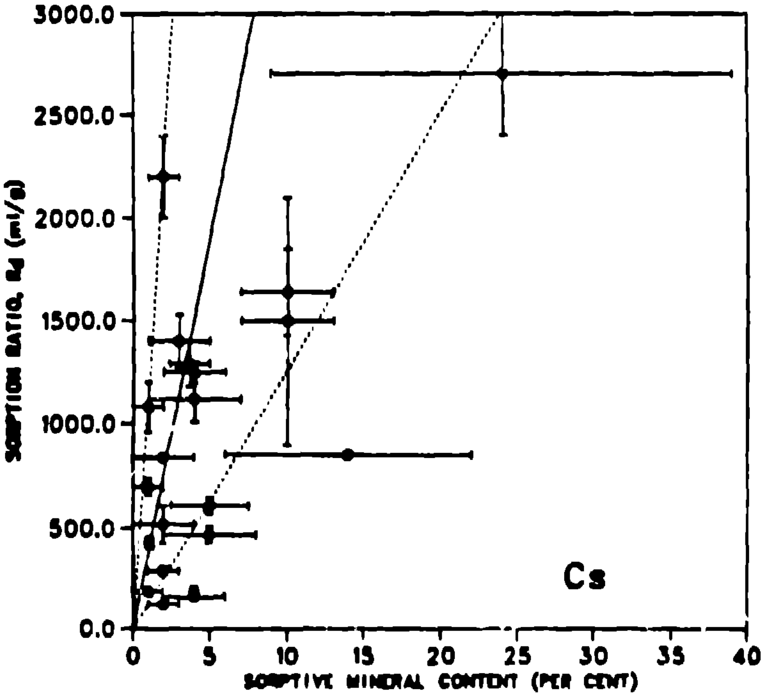

Fig. 10. Early part of Fig. 9 on linear scale.

where q = the solute concentration in the solid phase, c = the solute concentration in the aqueous phase, $c_o$ = the total cation concentration, Q = the cation exchange capacity, and $K^o$= the equilibrium constant. At small solute concentrations where $Kc << c_o$, the Langmuir isotherm becomes linear.

The Freundlich isotherm is also commonly used; it is a purely empirical formula that can be used to summarize a small amount of data. The form of the Freundlich isotherm is

$$q = kc^n \quad ,$$

where k and n are constants. Unfortunately, this isotherm is unbound and does not account for saturation of sites; in addition, it can yield infinite $K_d$ values at zero concentration.

Another approach, which seems most appropriate from a chemical standpoint, is the so-called mass-action equilibrium. This approach seems particularly appropriate for cations that have a charge greater than one. This approach for a given equilibrium takes the form

$$mA + R_mB = mRA + B \quad ,$$

and the equilibrium relation is

$$K_{AB} = \frac{q_A}{c_A}^{m'} \frac{c_B}{q_B} \quad ,$$

where m' lies between m and unity. This approach is more general than the Langmuir isotherm and still has the advantage of incorporating a limited number of sorption sites.

In addition to these sorption isotherms, which imply equilibrium, there is the possibility of an irreversible sorption process. In this case, a certain amount of the waste element would be sorbed independently of the initial concentration.

One of the important tasks of these sorption studies is to identify which of these isotherms is most appropriate to describe sorption on tuff. In addition, it may be possible to extract thermodynamic parameters such as equilibrium constants, thus providing a data base for correlating sorption ratios with mineralogy and groundwater composition.

As an example of our studies, the sorption isotherm for strontium on G1-2840 tuff was determined over a concentration range from 9.6 x 10 [illegible] M to 2.1 x 10 [illegible] M. The best fit appeared to be a simple Langmuir isotherm (Fig. 11). The data was fit to a Langmuir isotherm using a least squares procedure. The resultant equilibrium constant is 22.3 and the cation exchange capacity is 0.79 millimoles/100 g. These results are especially interesting because some sorption data in the literature [15] has assumed a mass action equilibrium with a m' of 2 for strontium sorption. Reviewing the analysis of these literature data show that, in fact, the Langmuir isotherm should have been applied and that the free energies reported are, therefore, incorrect.

An interesting by-product of our studies of the effect of sorption isotherms on retardation is that they can explain the observed dependence of the distribution coefficient $K_d$ on the solution-to-solid ratio and such observations can be directly compared with the results of measurements in which

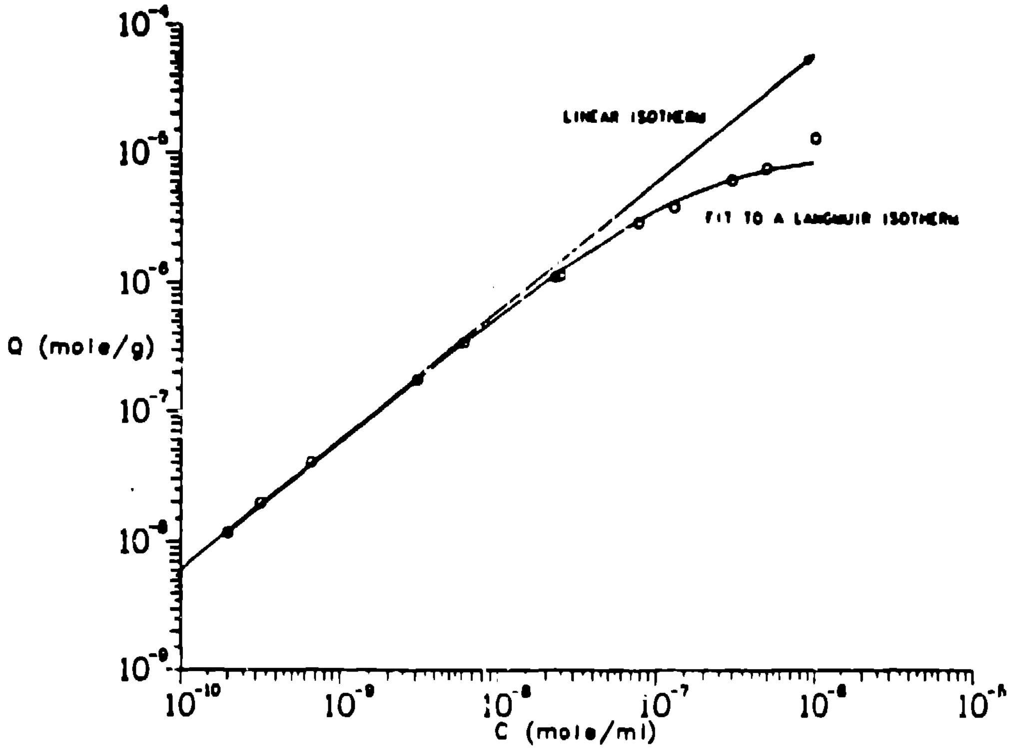

Fig. 11. Strontium sorption isotherm for C1-2840 tuff.

the element concentration was varied (isotherm determinations). The Freundlich isotherm can be expressed as

$$\frac{x}{m} = kc^{n} \quad ,$$

where x = the number of moles of tracer in the solid, m = the mass of the solid, c = the final concentration of tracer in solution, and k and n = constants. Combining

$$K_d = \frac{x/m}{c} = kc^{r-1} \quad ,$$

and

$$c + \frac{m}{V} kc^{n} = c_o \quad ,$$

where $c_o$ = the initial concentration and V = the volume of the solution,

$$K_d = k\left(\frac{c}{1 + \frac{m}{V} K_d}\right)^{n-1} \quad .$$

Therefore,

$$K_d^{1/1-n} = 1 + \frac{m}{V} K_d$$

For $\frac{m}{V} K_d >> 1$ ,

$$K_d = \frac{m}{V}^{\frac{1-n}{n}} \quad .$$

The distribution-coefficient dependence on the solid-to-solid ratio can be expressed in terms of the Freundlich isotherm parameter n. This simple relation seems adequate to explain the observed dependence of $R_d$ value on the solution-to-solid ratio.

## V. PERMEABILITY AND POROSITY

Because moving groundwater provides by far the most probable means of transporting waste elements from the repository, it is necessary to understand water's ability to move through the tuff formation. It is generally assumed that groundwater flow in the tuffs will be primarily through fractures; the permeability of a fracture is certainly much greater than that of the bulk rock. However, fractures must form a continuous connected network to provide an effective pathway for fluid movement. The degree of connectivity of fracture systems can be assessed by comparing laboratory and field measurements of bulk permeability. The issue of fracture intraconnectivity is not only important when characterizing the volume of groundwater flow but is also necessary to assess the volume of rock that will be connected by flowing groundwater. If an appreciable amount of porous flow occurs through the bulk rock, the surface area available for sorption will be appreciably increased.

Laboratory measurements of permeability and storage capacity have been accomplished by means of a transient pressure-pulse method. Porosity has been obtained by measuring the grain density and the wet and dry weights of the samples and by mercury porosimetry. Both permeability and storage capacity are needed to compare with field tests and to predict flow through unfractured tuff in response to a pressure gradient. Such pressure gradients may result from heat caused by the repository. Porosity is a necessary parameter when calculating the effects of diffusion. The combined results of permeability and porosity measurements can be used to gain insights into the pore structure of the tuff, which, in turn, will aid in estimating the diffusion parameters of constrictivity and tortuosity.

Figure 12 indicates several significant differences between two types of tuff, G1-2290, a moderately welded, nonzeolitized tuff, and HF-23, a heavily reworked, nonwelded zeolitized tuff. First, whereas the median pore diameter (determined from the 50% porosity line) for sample G1-2290 is 0.39 μm, the median diameter for sample HF-23 cannot be determined because it is <1.0 μm; a median diameter of 0.025 μm is suggested by the data. Assuming the total porosity calculations are valid, 85% of the total porosity of sample G1-2290 was from pores >0.1 μm, but only 24% of the pores in sample HF-23 are >0.1 μm. Second, the roughly linear trend of the data on a probability plot for sample G1-2290 indicates that pore-size distribution is approximately log-normal. The distribution for sample HF-23 is very nonlinear, although the smallest pores may approach a log-normal distribution. From a large number of such measurements, nearly all of the porosity in tuff is the result of pores 100 μm in diameter. In most of the samples, over 50% of the porosity is attributable to pores <1 μm in diameter. Possibly half of the samples contain a large fraction of their porosity in pores <0.1 μm in diameter.

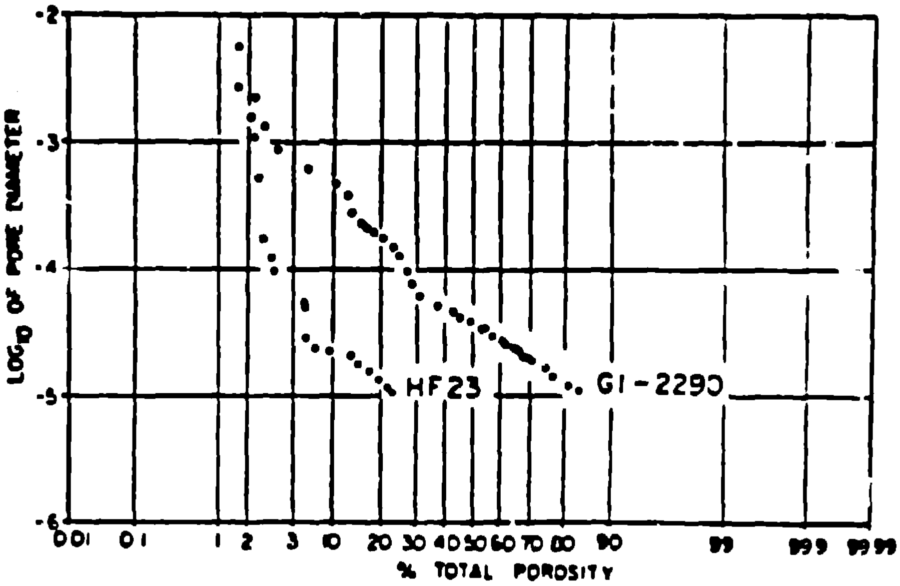

Fig. 12. Log of pore diameter vs per cent of total porosity determined by mercury infusion porosity for samples HF-23 and Gl-2290.

Individual permeability measurements indicate that there is no correlation between permeability and porosity; however, those tuffs with a larger proportion of small pores tend to have lower permeability. Typical permeabilities are (10-20) x $10^{-19}$ $m^2$ for Gl-2290 and (3-30) x $10^{-19}$ $m^2$ for HF-23. This suggests that the constrictivity of tuff may be relatively large.

## VI. SORPTION, DIFFUSION, AND KINETICS

As a consequence of the high porosity characteristic of tuff, diffusion of waste elements into the rock matrix is a very significant retardation process for all radionuclides. Indeed, even troublesome anionic elements such as iodine or technetium will be retarded by this process. However, a mathematical description for this process is not simple and illustrates the types of concerns that must be addressed if an adequate transport model is to be developed.

Kinetic sorption experiments (sorption as a function of time) for several elements have been performed on thin tablets of tuff. An example is given in Fig. 13. Several different models were used to describe this, and similar data, using batch $R_d$ values.

First, these data should fit the solution for diffusion into a plane sheet if any edge effect is ignored. The diffusion equation for this case is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} ,$$

with the initial conditions $C = 0$, $-\ell < x < 1$, and $t = 0$ and with the boundary conditions

$$a \frac{\partial C}{\partial t} = \pm D \frac{\partial C}{\partial x} \quad , x = \pm \ell, \text{ and } t > 0 \quad ,$$

where C = the concentration in solution, D = the apparent diffusion coefficient, a = the corrected depth of solution, ℓ = half the thickness of the tablet (sheet), t = time, and x = the position in the sheet. In other words, the rate of loss of tracer from solution is equal to the rate at which tracer enters the sheet through the surfaces at $x = \pm\ell$.

The general solution to this problem is given by Crank [16] as

$$\frac{M_t}{M} = 1 - \sum_{n=1}^{\infty} \frac{2V(1 + V)}{1 + V + V^2 q_n^2} e^{-Dq_n^2 t/\ell^2} \quad ,$$

where $M_t$ is the amount of solute in the solid phase at time t, values of $q_n$ are the nonzero positive roots of $\tan q_n = -Vq_n$, and $V = a/K\ell$, the solution-to-solid volume ratio divided by the partition factor K. The fractional uptake of activity at equilibrium is given by

$$\frac{M_\infty}{2aC_o} = \frac{1}{1 + V} \quad .$$

If V is small, <0.01, which is the usual case for large $K_d$ values, the following approximate relation may be used for early times:

$$\frac{M_t}{M_\infty} = 1 - e^{T/V^2} \operatorname{erfc} (T/V^2)^{\frac{1}{2}} \quad , \qquad (1)$$

where $T = Dt/\ell^2$.

The formula for the apparent diffusion coefficient is

$$D_{app} = \frac{D^1 \epsilon \, (\alpha/\tau^2)}{K_d \rho} \quad , \qquad (2)$$

where $D^1$ = the ionic diffusion coefficient, $\epsilon$ = the porosity, $\alpha/\tau^2$ = the constrictivity-tortuosity factor, $K_d$ = the distribution coefficient, and $\rho$ = the density.

A plot of Eq. 1, using the batch $R_d$ value for strontium, shows rather poor agreement with experimental data (Fig. 13), indicating that other processes are involved.

In general, the equations that have been used to describe fracture flow with matrix diffusion and simple diffusion into tuffaceous rock treated sorption as linear with concentration [17,18]. This approach clearly has a deficiency because sorption on nonzeolitized tuff has already been show to be

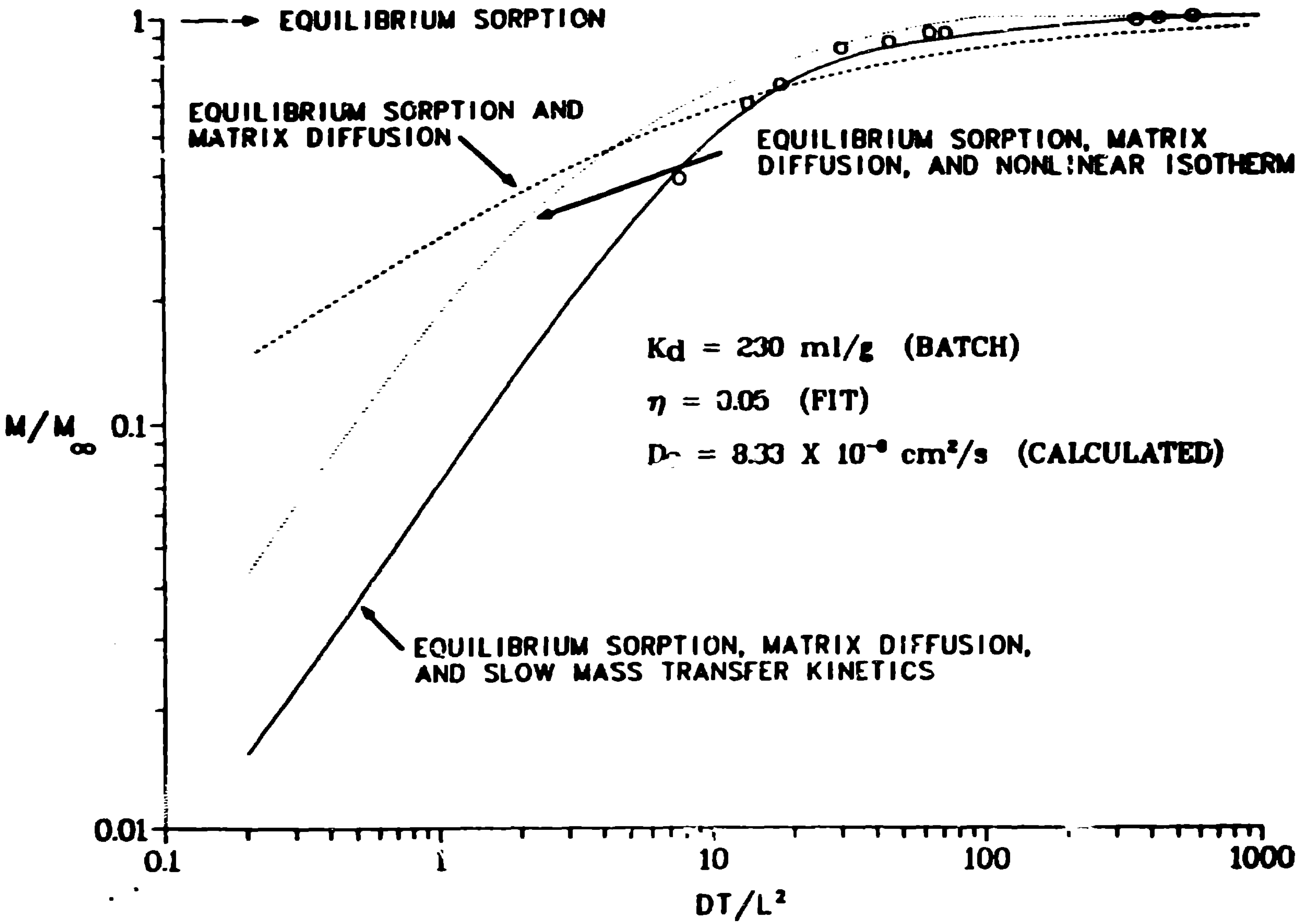

Fig. 13. Sorption of strontium as a function of time for sample G1-1883.

nonlinear. A nonlinear isotherm complicates the equations for matrix diffusion by giving the diffusion coefficient a concentration dependence, rendering the differential equations nonlinear.

Equation 2 shows how the isotherm affects the diffusion coefficient. If the $K_d$ is constant, as in the linear isotherm, the apparent diffusion coefficient remains constant. The Freundlich isotherm presents special problems for the diffusion equations because for a Freundlich isotherm parameter <1, the $K_d$ value is infinity for a concentration of zero and the apparent diffusion coefficient is zero. In a finite-difference analysis of the problem, (1) no diffusion coefficient is zero, and (2) no diffusion can occur unless the initial concentration in the rock is greater than zero. This means that either an arbitrary cutoff must be given to the Freundlich isotherm, below which it becomes linear, or the initial conditions must be altered to arrive at a solution. This problem does not exist for the Langmuir isotherm. Another phenomenon that leads to a nonlinear diffusion equation is fixation, where some fraction of the ions are irreversibly fixed in the matrix. This problem is nearly identical to that presented by Crank [16] for simultaneous diffusion with a bimolecular reaction.

A finite-difference solution of the nonlinear isotherm contribution to the kinetic sorption experiments is also shown in Fig. 13. Although the agreement with experimental data is better, it still does not reflect the early time points. The Freundich isotherm used to calculate the uptake as time had an exponent of 0.6. This is considerably smaller than that observed in batch isotherm measurements, which yielded an exponent of 0.8 for cesium on YM-22. Thus, to attempt to fit the data by adjusting the Freundlich parameters would lead to values that are not consistent with other data.

Therefore, the current treatment attempts to fit the experiment results by allowing for slow (not diffusion limited) sorption kinetics. The sorption of radionuclides on tuff disks can be treated as a reversible reaction with the solid tuff phase. In this case, diffusion is governed by the following equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \quad ,$$

with a simultaneous reaction of the type

$$\frac{\partial S}{\partial t} = \lambda C - \mu S \quad ,$$

where C = the concentration of the solute free to diffuse within the sheet, S = the concentration of the immobilized solute, D = the diffusion constant, $\lambda$ = the rate constant for the forward reaction, and $\mu$ = the rate constant for the backward reaction. The dimensionless rate $\eta = \mu \ell^2/D$, where $\ell$ is the half-thickness of the sheet, appears in the solution and is used as an adjustable parameter in fitting the experimental data.

The analytic solution to these equations for the appropriate boundary conditions is available in Crank [16]. A code was developed to evaluate the analytic solution, and the result of this calculation is also shown in Fig. 12. The agreement between the experimental data and the shapes of the theoretical curves is quite good. The diffusion coefficients and rate constants were determined by fitting the experimental points to the curves. The diffusion coefficients thus determined are reasonably close to the free ionic diffusion coefficients that were determined from ionic conductivities.

It is interesting that both the nonlinear isotherm and kinetic approaches yield similar shapes in the uptake curve but for very different reasons. The nonlinear isotherm (Freundlich n < 1.0) yields a $K_d$ value that increases with time because the solution concentration of radionuclide is decreasing with time as diffusion and sorption proceeds. In the kinetic case, the $K_d$ value effectively increases as the sorption reaction proceeds.

The consequences of these studies may be profound for certain radionuclide release scenarios, in particular, those where the radionuclides are carried by rapidly moving water in fractures. The sorption rate constants determined from these studies will be used in calculations with the nonequilibrium version of our three-dimensional transport code TRACR3D (Ref. 19) to model the results of fractures. Conceptually, the discrepancies observed between theory and experiment are constent with slow kinetics; that is, they exhibit earlier peak arrival with enhanced tail retention.

## VII. CONCLUSIONS

The geochemical considerations presented in this paper are intended to show some of the geochemical factors that must be considered before any "guarantee" can be made that potential releases of radioactive contaminants will not affect the health and safety of present and future generations of mankind. The immediate needs to adequately satisfy such a requirement are to (1) to acquire a basic understanding of the processes by which contaminants can enter into and be transported by groundwater flow systems, (2) find a means to identify and obtain the major parameters that govern contaminant geochemistry, and (3) show that such information is a reliable means of predicting the contamination of groundwater.

Obviously, the results and activities presented are not comprehensive, and are not intended to be so. They do, however, show some facets that must be investigated.

In conclusion, our current knowledge of the geochemistry of the Yucca Mountain site, although far from complete and only partially summarized in this paper, indicates that there are no potentially adverse conditions that would disqualify this site for a nuclear waste repository. Indeed, the studies indicate that the geochemical properties and setting of the Yucca Mountain site will strongly inhibit the movement of radionuclides to the accessible environment.

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