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*Preliminary Report on the
Statistical Evaluation of Sorption Data:
Sorption as a Function of Mineralogy,
Temperature, Time, and Particle Size*

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PRELIMINARY REPORT ON THE STATISTICAL EVALUATION OF SORPTION DATA:

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R. Beckman, K. Thomas, and B. Crowe

ABSTRACT

The Yucca Mountain area of Nevada is a candidate of the US Department of Energy as a permanent geologic repository for the isolation of high-level wastes. To determine the site's suitability as a repository, studies are being done of the transport of radionuclides from a repository to the environment by dissolution of the stored solid-waste form and subsequent transport in water. The sorption process may retard this movement of radionuclides from the repository to the accessible environment. A measure of this retardation process is the sorption ratio, R_D , where

$$R_D = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}}$$

In this study, predictions of the R_D values for the elements barium, cerium, cesium, europium, and strontium are developed from linear regression techniques. An R_D value was obtained for numerous drill core samples. Additional data include the particle size of the rock, temperature condition during the experiment, concentration of the sorbing element, and length of the sorption experiment. Preliminary regression results based on these data show that the temperature and length of the experiment are the most significant factors influencing the R_D values. Particle size has a slight effect, and based on a small amount of data, it appears that concentration had no effect.

The x-ray diffraction data are used to classify the samples by mineralogy, and regression techniques are used to develop estimates of the R_D values. Zeolite abundance of 10% or more with some addition of clay increases the sorption values significantly.

Two intervals are given to assess the uncertainty in the estimate. In the first interval, only random variability is considered. The second type considers variability caused by geologic processes. From these data, predictions were made within one-half order of magnitude.

I. INTRODUCTION

Yucca Mountain, Nevada, has been recommended by the US Department of Energy in its Environmental Assessment¹ as a candidate for site characterization; this characterization, by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project, will determine the site's suitability as a permanent geologic repository for isolation of high-level nuclear waste. Yucca Mountain (Fig. 1) is located on the southwestern edge of the Nevada Test Site (NTS), on adjacent land controlled by the US Air Force, and on US Bureau of Land Management land (see Fig. 1).¹ The repository would be sited in the Topopah Spring Member in the unsaturated zone of Yucca Mountain at an average depth of 300 m below the mountain surface. The Topopah Spring Member is an ash-flow tuff and contains a thick interval of densely welded, devitrified tuff. It is underlain by several other tuff units, including the tuffaceous beds of Calico Hills, the Prow Pass and Bullfrog Members of the Crater Flat Tuff, and the Tram and Lithic Ridge Formations. The tuffaceous beds of Calico Hills and the Prow Pass Member locally are above the groundwater table and are strongly zeolitized.

The most likely mechanism for transport of radionuclides from a waste repository to the accessible environment is by dissolution of the stored solid-waste form and subsequent transport in water. The altered tuffs of Yucca Mountain and vicinity, with their high content of zeolites and clays, have great capacity for sorption of radionuclides. As water containing dissolved radionuclides moves away from the repository, it will contact these altered tuffs. Sorption can delay or retard the movement of radionuclides relative to the water flow. Thus, sorption processes can affect whether the Yucca Mountain environment can meet the release limits specified by the Environmental Protection Agency (40 CFR Part 191) (Ref. 2) and the Nuclear Regulatory Commission (NRC) (10 CFR Part 60) (Ref. 3).

The purpose of the sorption studies is to evaluate the contribution of sorption processes retarding the transport of radionuclides from the repository to the accessible environment. Movement of water in the unsaturated zone is such a slow process, however, that it is not possible to make direct measurements of radionuclide travel under repository conditions. Therefore, to perform the required performance-assessment calculations of possible releases of radionuclides from a repository, it is necessary to understand the mechanisms of radionuclide transport and retardation in tuff and to have a data base of sorptive behavior by element and rock type. Specifically, the investigations in this task will be used to assess the NRC's licensing requirements as specified in 10 CFR Part 60 (Ref. 3) with specific application to sections 60.122 (b) (1), 60.122 (b) (3), and 60.122 (c) (8) and as outlined in the NRC technical position paper on sorption.⁴ Within the NNWSI Project, the results of these studies will be applied to the NNWSI Issues Hierarchy⁵ and to specific tasks such as Dynamic Transport (WBS 1.2.3.4.1.6.A, Los Alamos), Retardation Sensitivity Analysis (WBS 1.2.3.4.1.7.A, Los Alamos),

Fig. 1. Yucca Mountain site in southern Nevada.

Performance Assessment Calculations (Sandia National Laboratories), the Site Characterization Plan, and the Environmental Impact Statement for Yucca Mountain.

The sorption ratio, R_D , as used in these studies, provides a measure of sorption as a function of many parameters. It is defined as

$$R_D = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}}$$

and is expressed in units of milliliters per gram. This ratio is often referred to as the distribution coefficient, K_D . Los Alamos prefers not to use this term, which implies equilibrium, because reversible equilibrium is usually not attained. If equilibrium is attained, the $K_D = R_D$ and is related to a retardation factor, R_F , in a uniform flowing system by

$$R_F = K_D(\rho/\epsilon) + 1 \quad ,$$

where ρ is the bulk density and ϵ is the porosity of the rock. (See Thomas⁶ for a more extensive discussion of sorption measurements.)

Sorption studies were undertaken in support of the NNWSI and were performed at the Los Alamos National Laboratory. The work has been partly generic in nature (to understand the sorptive behavior of tuff as a function of many variables) and partly site specific (to obtain data for a possible repository site in Yucca Mountain tuff). Partly because of the Project's emphasis on research directly tied to Yucca Mountain, a decision was made to follow an empirical approach to studying sorption. It was felt that this method would generate the greatest amount of usable site-specific data in the (what at the time was considered) very limited time available for these studies. In retrospect, given the program delays, a more systematic approach geared toward generating data useful to a modeling scheme might have been a better approach. Nevertheless, sorption has been investigated as a function of mineralogy, temperature, particle size, waste-element concentration, water composition, sorption time, and other variables. The major radionuclides studied to date include americium, cesium, neptunium, plutonium, thorium, uranium, strontium, technetium, tin, barium, radium, cerium, europium, and selenium. A complete discussion of sorption measurements, techniques, parameters, and data for all sorption measurements made by Los Alamos through 1985 is found in Thomas.⁶ The present work discusses statistical analyses of the effect of temperature, particle size, waste-element concentration, and sorption time on measured sorption coefficients of barium, cerium, cesium, europium, and strontium. These elements and variables were chosen for the initial analysis because they had the greatest number of data points available and because, as discussed in Thomas, they exhibited the simplest and most easily understood patterns of sorption behavior.

II. DATA BASE

Sorption data obtained for the NNWSI Project are entered into the DATATRIEVE data base management system on a VAX 11/780. To date, over 1700 data entries have been filed in the data base system from published data sources (see Thomas⁶ for a summary of sorption measurements and data references). The data fields described below are used for storage and retrieval of the sorption data.

Sample/ID: sample number of the rock used for the sorption measurement. All samples of drill core are obtained from exploratory drill holes. The sample number is divided into two parts: (1) an alphanumeric prefix that indicates the drill hole from which the core was obtained and (2) a second number that is the drill hole depth (in feet) from which the sample was obtained. For example, the prefix JA- indicates the sample was collected from drill hole J-13; the prefix YM- refers to exploratory drill hole UE25a#1. The prefix G followed by a number refers to a sequence of exploratory geologic drill holes that were drilled within and surrounding the exploratory block at Yucca Mountain. The numeric labels after the YM- and JA- prefixes do not refer to the drill hole depth but are keyed to the sample labels used in the mineralogy and petrology report by, respectively, Sykes *et al.* (1979)⁷ and Heiken and Bevier (1979).⁸

Particle Size: range of particle sizes used for the sorption measurements. The parameter is divided into two values for entry into the data base: a minimum particle size (PMIN) and a maximum particle size (PMAX); both are in microns.

Temperature: temperature conditions during the batch sorption measurements. The majority of experiments were run under ambient conditions; a limited number of experiments were run at 70 and 85°C.

Atmosphere: most of the experiments were run under atmospheric (data entry as AIR), and therefore oxidizing, conditions. A select number of experiments were performed in a glove box with either a controlled CO₂ concentration (data entry as CO₂) or a nitrogen atmosphere.

pH: pH of the batch experiments at the completion of the experiment. Over time, the pH of the waters used in the experiments rose to ~8.5 except under conditions of controlled CO₂ atmosphere.

Comment: general comments on experimental conditions not included in the data fields.

Element: element analyzed in the batch sorption experiment. In this report, the elements are restricted to barium, cesium, strontium, cerium, and europium.

Concentration: absolute concentration (in molarity) of the sorbing element in the spiked solution. The version of DATATRIEVE used when the sorption data base was developed did not accept entries in exponential notation; therefore, the CONCENTRATION was entered in two fields, SIGNIFICANT/DIGITS/CONC and DECIMAL/EXPONENT/CONC.

Sorption/Time/Days: length of the batch sorption experiment in days.

Sorption/Rd1 and Sorption/Rd2: batch sorption ratio expressed in units of milliliters per gram. The Rd1 and Rd2 represent duplicate measurements for the same sample.

Desorption/Time/Days: length of the batch desorption experiment in days.

Desorption/Rd1 and Desorption/Rd2: batch desorption ratio expressed in units of milliliters per gram. The Rd1 and Rd2 represent duplicate measurements for the same sample.

References: published references for the batch sorption information.

The sorption data set was evaluated and edited to provide the highest quality data before statistical analysis. The data editing was accomplished using procedure KDALL2 in DATATRIEVE on a VAX 11/780 (this procedure is listed in Appendix 1). The data set used for this study can be reproduced at any time by running the procedure DKALL2. The sorption data base was refined to remove three sources of data variance: (1) sorption measurements made while experimental techniques were being developed, (2) particle-size effects, and (3) semi-quantitative measurements of the mineralogical composition of rock samples made by x-ray diffraction techniques.

Development of Experimental Procedures. A number of batch sorption measurements were made before experimental techniques were standardized. Preliminary analyses of sorption data showed that aberrant data points on plots of sorption by element vs time could be traced to data published from the earlier experiments in the sorption program.⁹ When these data were removed from the working data set, the number of samples was reduced from 1744 to 1531.

Particle-Size Effects. One source of potential data bias in batch sorption studies is the use of crushed-rock samples. Crushing the rock samples potentially increases the surface area of sorption sites and may produce a higher content of fines that have a higher abundance of sorptive clay minerals. To minimize this source of bias, we established a particle-size cutoff of 106 μm . Only batch sorption samples with particle sizes of 106 μm or greater were used in the data set. This criterium further reduced the sample set to 620 samples.

The X-Ray Diffraction Mineralogical Analysis. In the early stages of the NNWSI program, x-ray diffraction mineralogical analyses of core samples was completed before analytical techniques were refined [drill hole J-13 (Ref. 7), drill hole UE25a-1 (Ref. 7), and drill hole USW-G1 (Ref. 10)]. To evaluate this source of data variance, the sorption data set was examined using both the x-ray diffraction mineralogical data and major rock groups selected from examination of the x-ray diffraction data. These major rock groups, summarized in Table I, include subgroups of devitrified welded tuff, zeolitized primary and reworked tuff, vitric (glass-bearing) tuff, and tuff in which secondary clays are more abundant than secondary zeolite minerals. (The classification of the tuff samples is discussed in Sec. IV.)

III. Regression Techniques

Regression techniques were the primary tools used to investigate factors that significantly influence sorption ratio estimates. This section is an introduction to these techniques and the methods used to produce confidence intervals on the sorption ratio estimates for various rock types.

Least squares or regression techniques require a set of independent variables $X_1, X_2 \dots X_m$. These variables may represent continuous measured variables such as sorption time, concentration, or pH, or the variables may be categorical variables such as classes of particle sizes, temperature conditions (ambient and 70°C), or sample IDs. In addition, regression requires a dependent variable y . This variable is the variable of interest (in this case, the sorption ratios). It is assumed that this dependent variable is related to the independent variables by the linear function

$$y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \dots + \alpha_m X_m + \epsilon = f(X_1, X_2 \dots X_m) + \epsilon \quad (1)$$

where $\alpha_0, \alpha_1, \dots \alpha_m$ represent unknown parameters and ϵ represents a random error term.

Let y_i denote the i^{th} out of n observed dependent variables and $X_{i1}, X_{i2}, \dots X_{im}$ the corresponding independent variables. Then the unknown parameters α in Eq. (1) are estimated by minimization of the sum of squares

$$\sum_{i=1}^n [y_i - f(X_{i1}, X_{i2}, \dots X_{im})]^2 \quad (2)$$

In this study, the Statistical Analysis System (SAS) was used to minimize Eq. (2). The SAS is a collection of statistical analysis routines interfaced with a data base manager. Included are routines that perform most classical statistical analyses. In particular, two of the routines, GLM and REG, do analyses of variance and regression. These two routines were used extensively to obtain the statistical results of this study.

TABLE I
CLASSIFICATION OF TUFF SAMPLES

FOUR MAJOR ROCK GROUPS

1. DEVITRIFIED

composed primarily of quartz and alkali feldspar

2. ZEOLITIZED

dominated by an alteration assemblage of zeolites

3. GLASS

high percentage of original glass in sample (not devitrified or altered to zeolites)

4. CLAYS

clays are the major alteration assemblage

SUBGROUPS

1. DEVITRIFIED – <10% clays, <10% zeolites

DEVIT1– >10% clays, <10% zeolites

DEVIT2– <10% clays, >10% zeolites

2. ZEOLITIZED – >20% zeolites, <10% clays, <10% glass

ZEOLIT1– >20% zeolites, >10% clays, <10% glass

ZEOLIT2– >20% zeolites, <10% clays, >10% glass

3. GLASS – >40% glass, <10% clays, <10% zeolites

GLASS1– >40% glass, >10% clays, <10% zeolites

GLASS2– >40% glass, <10% clays, >10% zeolites

4. CLAYS– >40% clays

For categorical or class variables, the independent variables take on the values 1 or 0; if there are k levels of the categorical variables, such as k different particle-size classes, then k independent variables may be used to represent these variables. In this scheme, the i^{th} independent variable for the class being 1 denotes the presence of the i^{th} category of that variable. For example, consider six samples that comprise three particle sizes, say PS-1, PS-2, and PS-3. If the first two samples correspond to the first particle size, the next two to the second size, and the last two to the third size, then Eq. (1) becomes

$$\begin{array}{llll}
 y_2 & = & \alpha_o + \alpha_1 & + \epsilon_1 \quad \text{PS-1 sample} \\
 y_2 & = & \alpha_o + \alpha_1 & + \epsilon_2 \quad \text{PS-1 sample} \\
 y_3 & = & \alpha_o & + \alpha_2 + \epsilon_3 \quad \text{PS-2 sample} \\
 y_4 & = & \alpha_o & + \alpha_2 + \epsilon_4 \quad \text{PS-2 sample} \\
 y_5 & = & \alpha_o & + \alpha_3 + \epsilon_5 \quad \text{PS-3 sample} \\
 y_6 & = & \alpha_o & + \alpha_3 + \epsilon_6 \quad \text{PS-3 sample}
 \end{array}$$

This may be represented with the three independent variables X_{i1} , X_{i2} , and X_{i3} as

$$y_i = \alpha_o + \alpha_1 X_{i1} + \alpha_2 X_{i2} + \alpha_3 X_{i3} + \epsilon_i ,$$

where $X_{ij} = 1$ if the i^{th} sample is from PS-j, and $X_{ij} = 0$ otherwise.

Unfortunately, because of the nonidentifiability of the parameters α_o , and α_j in the terms $\alpha_o + \alpha_j$, the least squares estimates of $\alpha_o, \alpha_1 \dots \alpha_m$ under this type of parameterization are not unique. That is, the estimates for each of the x_j can be reduced by a constant amount, whereas the estimate of α_o is increased by that amount and the sum of squares in Eq. (2) will remain the same. Therefore, in these cases the model in Eq. (1) must be reparameterized, which results in the individual parameter estimates becoming biased estimates. However, linear functions of these estimators are unbiased, and it is these linear functions, such as $\alpha_o + \alpha_1$, that we wish to estimate. There are many methods of reparameterization; the one employed here and by the SAS package used in this study makes the last level of an effect zero. In the example above, then, $\alpha_3 = 0$.

To make inferences about the statistical significance of any of the parameters, a probabilistic distribution must be assumed for the error term ϵ in Eq. (1). Preliminary investigations of the measured sorption ratios show that they are skewed toward the higher values. Therefore, logarithms of the sorption values were used as the dependent variables y_i . It is assumed throughout this report that the logarithms of the sorption ratios follow a normal or Gaussian distribution.

Under the assumption of normality, significant effects are determined by the size of the effect's P-value. The P-value is the probability of a value of the dependent variable (for example, sorption ratio) as discrepant as that observed in the study when the factor in question (for example, particle size) does not in fact affect the dependent variable. Hence, small P-values denote significant effects or factors; it is unlikely that factors that do not affect the dependent variable would produce such small P-values by chance. Usually P-values are deemed small if they are less than 0.05 or 0.01; here we use 0.01.

Standard deviations of the parameter estimates are available after the least squares fit. Using the assumption of normally distributed error terms, we can compute confidence intervals on both the predicted lines (such as $\hat{\alpha}_0 + \hat{\alpha}_1$ in the above example) and the values of future experimental observations at a particular combination of factors (for instance, a confidence interval on future observed y values from PS-1 in the above example). Both types of intervals are given in this paper. The first of these intervals (intervals on predicted lines) demonstrates the degree of confidence we have in the function $f(X_1, X_2, \dots, X_m)$ as predicted by the least squares estimates $\alpha_1, \alpha_2, \dots, \alpha_m$. If the majority of the error in the measured sorption values is due to experimental error, then these intervals measure the error in the predicted sorption ratios. On the other hand, if the majority of the error is in the geological sampling (that is, there are variabilities in the sorption ratios for similar mineralogical rock types that are not due to the experimental error), then the second type of interval is more appropriate for estimating the range of possible values for the sorption estimates.

Further discussions on least squares and regression techniques can be found in the books by Weisberg¹¹ and Draper and Smith.¹²

IV. Preliminary Analysis of the Drill Data Sets

The majority of the data for the drill hole data sets is concentrated in the three samples JA-18, JA-32, and JA-37. For each of the five elements barium, cerium, cesium, europium, and strontium and each of these three samples, a model in the sense of $f(x)$ in Sec. III is developed. This model is then fit to data for all drill core samples.

The purpose of this preliminary fit is to determine which, if any, of the factors (temperature, particle size, concentration, or sorption time) is significant. Sorption as a function of temperature, particle size, and sorption time is shown in Fig. 2 for the barium data in data set JA-18. In this figure, the circles represent 70°C data and the squares represent sorption values obtained at ambient temperatures. Open symbols are for particle sizes of 355 to 500 μm , and closed are for particle sizes of 106 to 150 μm . All these data were at the same concentration of barium (1×10^{-6} M). This plot is representative of data for the remaining four elements in the three samples JA-18, JA-32, and JA-37.

Fig. 2. Barium sorption ratios for JA-18 as a function of sorption time; responses are shown for different temperatures.

From this figure it is evident that the sorption ratio increases as the sorption time increases. This increase seems to be asymptotic as the sorption time increases past 80 days. As a first approximation, this increase in sorption is taken to be linear with time.

For most data sets, the concentration either is constant or it is confounded with the other effects, particle size or temperature. For example, for strontium in the JA-18 data set, all concentrations were at 1×10^{-6} M. The strontium data from hole JA-37 has a concentration of 3×10^{-6} M for those data at ambient temperatures and 2×10^{-6} M at 70°C . Only barium for data set JA-37 allows one to test for significance of concentration. In this data set, 355- to $500\text{-}\mu\text{m}$ particle sizes at 70°C were subjected to a concentration of barium of 1×10^{-6} M. The remaining samples of 106- to $150\text{-}\mu\text{m}$ data at both ambient and 70°C and the ambient 106- to $150\text{-}\mu\text{m}$ data were all run at a barium concentration of 2×10^{-6} M.

The complete data set contains data in five particle-size ranges: size 1 = 160 to $150\text{ }\mu\text{m}$, size 2 = 250 to $355\text{ }\mu\text{m}$, size 3 = 106 to $500\text{ }\mu\text{m}$, size 4 = 250 to $500\text{ }\mu\text{m}$, and size 5 = 355 to $500\text{ }\mu\text{m}$. As these particle sizes are not continuous, this variable is considered a categorical variable with five levels.

There are two temperatures: ambient and 70°C. This is also considered a categorical variable with two levels.

The model for each of the data sets and elements is

$$Y_{ijk} = \mu + T_i + S_j + C_k + \beta_i(Time) + \epsilon$$

where Y_{ijk} is the $\log_{10}$ sorption value,

μ represents the overall mean,

T_i represents ambient temperature for $i = 1$ and 70°C for $i = 2$,

S_j $j = 1, 2, \dots, 5$, represents the five particle sizes,

C_k $k = 1, 2$, represents the two concentrations for barium JA-37 data only
(otherwise this term is not in the model),

β_i $i = 1, 2$, is the slope with sorption time

(one slope is estimated for each of the two temperatures),

$Time$ is the sorption time in days, and

ϵ is the error term.

TABLE II
P-VALUES

	JA-18			JA-32			JA-37		
	Size	Temp	Conc	Size	Temp	Conc	Size	Temp	Conc
Ba	0.62	0.0001	NA	0.24	0.0002	NA	0.62	0.004	0.98
Ce	0.11	0.0023	NA	0.04	0.61	NA	NA	NA	NA
Cs	0.75	0.0059	NA	0.14	0.0014	NA	0.50	0.0001	NA
Eu	0.0079	0.0001	NA	0.64	0.0068	NA	0.54	0.85	NA
Sr	0.21	0.0032	NA	0.71	0.0001	NA	0.15	0.0001	NA

The P-values for fits to this model are found in Table II. From this table, the P-value for concentration in the barium JA-37 fit is 0.98. Hence, there is no concentration effect in this fit. This is the only data set that allows for a test of significance for concentration. Based on the result of this test, no concentration effect appears to exist.

The P-values for the size effect are for the most part greater than 0.01. The only exception to this trend is europium in the JA-18 data, where the P-value is 0.0079. The particle-size classes 106 to 150 μm and 355 to 500 μm were the only ones present in these data sets. Any

effect of intermediate-size particulates is completely confounded with the sample IDs, other than JA-18, JA-32, and JA-37, and cannot be deduced. If there is a particle-size effect, it would be most visible in data with particle sizes at the extremes.

The temperature effect is significant except in a few cases. The sorption values are estimated to be 0.1 to 1 order of magnitude higher at 70°C than at ambient temperatures for all data that exhibited a significant temperature effect. Any differences that result from other factors such as particle size or concentration are completely overwhelmed and are minor compared to the effect of temperature.

To produce reasonable confidence intervals on the estimated sorption values and to investigate the possibility of using mineralogy to describe these values, the following model was fit to the entire data set for each element.

$$y = \mu + ID_i + T_j + \beta_{ij}(time) + \epsilon$$

In this model,

- μ represents the overall mean,
- ID_i represents the effect of the i^{th} drill hole depth,
- T_j represents the effect of the two temperatures,
- β_{ij} is the slope with sorption time (one slope is estimated for each temperature, hole-depth combination), and
- $Time$ is the sorption time in days.

When the results from the fit to this model were used, we obtained 95% confidence intervals on the estimated sorption values at ambient temperatures for both 21 and 42 days. These intervals are given in Tables III and IV. Because there are no data at 42 days, it was not possible to predict the sorption values for many of the IDs for this time. The ID values in these tables are ordered by their mineralogy, which was determined by a rough look at x-ray diffraction data, in which those samples denoted as devitrified assemblages are characterized by less than 10% zeolite and no glass. Zeolites are samples that contain more than 20% zeolites. Greater than 40% glass characterizes the glass samples, and clays contain more than 40% clay.

The estimated sorption values are smallest for devitrified samples, and the 21-day estimate ranges from 100 to 2000 ml/g. Glass assemblages are estimated to be in the range of 3000 to 50 000 ml/g, whereas zeolites are estimated to have sorption between 6000 and 125 000 ml/g. The highest sorption values were estimated for clays with values in the range of 86 000 to 211 000 ml/g.

The sorption estimate for YM-48 is about 0.5 order of magnitude less than the estimates for the remaining zeolite samples G1-2289 and YM-38. This may be because the sample

YM-48 could have been classified as a glass because it contains 50% glass; the other two zeolite samples are devoid of glass.

The results presented in Tables III and IV show that it is possible to predict sorption values by using the mineralogy of the sample. It is encouraging that the samples, when classified according to mineralogy, may be estimated within an order of magnitude of each other. It should be remembered, however, that the estimates in Tables III and IV are dependent upon the slopes β_{ij} , which are allowed to change for each sample ID. This accuracy will not be possible when mineralogy rather than sample ID is used to predict the sorption values, resulting in fits that are more variable.

V. Estimates of Sorption Using Mineralogy

The mineralogy of each of the samples listed in Tables III and IV was determined by x-ray diffraction. Because the uncertainties in the resulting estimates are broad, the categorical classifications from Table I are used to describe the samples.

In these samples, glass either was not present or was abundant (greater than 50%). Therefore, only two categories of glass were used, one representing no glass in the sample and the second representing 50% or more. Zeolites and clays were classified according to the five categories in weight per cent: 0: <1%, 1: 1 to 10%, 2: 10 to 20%, 3: 20 to 50%, and 4: greater than 50%.

Weight per cent classifications for zeolites and clays were determined from the x-ray diffraction data. These data were given in terms of the maximum and minimum weight per cent of smectite, illite, clinoptilolite, mordenite, and analcime. The minimum weight per cent zeolite was obtained by adding the minimum weight per cent clinoptilolite, mordenite, and analcime. The sum of the maximum abundance of these three minerals was used as the overall maximum. The overall minimum and maximum abundances were then averaged to produce the weight per cent zeolite that was used in this study. The weight per cent clay was obtained in the same way using the weight per cent smectite and illite.

For each element the following model was fit:

$$y = \mu + C_i + Z_j + G_k + S_l + T_m + \beta_m Time \quad , \quad (3)$$

TABLE III

SORPTION ESTIMATES WITH 95% LOWER AND UPPER CONFIDENCE BOUNDS
PROJECTED TO 21 DAYS AND AMBIENT TEMPERATURE

TYPE ^a /ID	Ba			Ce			Cs			Eu			Sr		
	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper
D G1-1883	102	160	251		NA		125	185	275	100	160	254	15	22	31
D G1-1982	413	780	1,474		NA		687	1,200	2,097	570	1,100	2,124	40	66	109
D G1-2363	140	220	345		NA		266	395	586	442	673	1,071	42	60	85
D JA-32	244	302	375	51	61	74	84	101	123	60	75	94	41	48	57
D JA-37	494	619	774		NA		524	639	780	2,719	3,435	4,339	230	274	328
D YM-22	561	880	1,379	890	1,296	1,887	212	314	466	784	1,249	1,989	34	48	69
D YM-45	635	1,200	2,267	588	1,000	1,702	275	480	839	1,088	2,100	4,055	103	170	281
D YM-54	167	241	348	106	180	306	116	161	222	342	500	731	39	52	69
G JA-18	3,607	4,434	5,450	26	32	39	10,585	13,018	16,009	18	23	29	8,982	10,823	13,042
G YM-49	17,810	27,982	43,795	360	524	763	22,073	32,756	48,608	688	1,095	1,745	1,856	2,650	3,782
Z G1-2289	50,616	79,372	124,465		NA		19,807	29,393	43,618	512	815	1,298	5,671	8,094	11,553
Z YM-38	52,632	75,994	109,725	529	900	1,530	9,635	13,299	18,356	1,175	1,718	2,512	13,208	17,660	23,614
Z YM-48	6,351	12,000	22,672	511	870	1,480	8,584	15,000	26,212	880	1,700	3,282	9,069	15,000	24,810
C G1-3658	86,030	134,906	211,549		NA		33,355	49,497	73,450	3,319	5,285	8,416	91,078	130,000	185,552

^a D = devitrified; G = glass; Z = zeolitized; and C = clays.

TABLE IV

SORPTION ESTIMATES WITH 95% LOWER AND UPPER CONFIDENCE BOUNDS
PROJECTED TO 42 DAYS AND AMBIENT TEMPERATURE

TYPE ^a /ID	Ba			Ce			Cs			Eu			Sr		
	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper	Lower	Estimate	Upper
D G1-1883		NA			NA			NA			NA			NA	
D G1-1982	47	1,127	27,125		NA		73	1,200	19,566	86	2,302	61,800	12	143	1,700
D G1-2363		NA			NA			NA			NA			NA	
D JA-32	323	423	555	75	94	117	103	130	165	81	107	142	49	61	75
D JA-37	593	749	947		NA		528	648	796	4,466	5,689	7,248	240	288	347
D YM-22	519	980	1,852	764	1,300	2,212	155	270	472	880	1,700	3,283	33	55	91
D YM-45	741	1,400	2,645	417	710	1,208	183	320	559	829	1,600	3,090	103	170	281
D YM-54	312	590	1,115	64	110	187	114	200	350	192	370	714	48	80	132
G JA-18	4,110	5,068	6,250	36	43	52	12,615	15,315	18,592	24	30	37	10,508	12,516	14,906
G YM-49	31,228	59,000	111,470	476	810	1,378	20,600	36,000	62,910	777	1,500	2,897	2,297	3,800	6,285
Z G1-2289		NA			NA			NA			Na			NA	
Z YM-38	42,872	81,000	153,034	364	619	1,054	4,692	8,200	14,329	777	1,550	2,897	6,046	10,000	16,540
Z YM-48	12,173	23,000	43,454	1,117	1,900	3,233	12,589	22,000	38,445	1,389	2,700	5,214	1,512	2,500	4,135
C G1-3658		NA			NA			NA			NA			NA	

^a D = devitrified; G = glass; Z = zeolitized; and C = clays.

where

- y is the logarithm base 10 of the sorption ratio,
 μ is the overall mean,
 C_i is the i^{th} clay category $i = 0,1,2,3,4$,
 Z_j is the j^{th} zeolite category $j = 0,1,2,3,4$,
 G_k is the k^{th} glass category, $k = 0,1$,
 S_ℓ is the ℓ^{th} size category $\ell = 1,2,3,4,5$
(size categories as described in Sec. IV),
 T_m is the m^{th} temperature effect $m = 1,2$,
 β_m is the slope caused by sorption time in each temperature, and
 $Time$ is the sorption time in hours.

Tests for significant particle sizes produce P-values: 0.37 for barium, 0.57 for cerium, 0.0001 for cesium, 0.32 for europium, and 0.68 for strontium. The significant particle-size effect in the cesium data is interesting; it is caused by only two size-4 (250- to 500- μm) data points in the data set. When these two data points are removed from the data set, the P-value for particle size becomes 0.98.

Figure 3 shows the residuals plotted against the sorption time for a fit to the function form in Eq. (3), excluding the term for particle size. The different particle sizes are highlighted on this figure. The two residuals corresponding to particle-size 4 are denoted by * and are to the extreme right. These two points are both samples from G1-1982, a devitrified sample with 1 to 10% clay. There is no apparent reason for aberrant behavior of the two data points for this sample.

Based on these results, the final model for fitting sorption values was given by Eq. (3) without the particle-size term. The parameter estimates for this fit are given in Table V along with the estimated standard deviations of these parameters, which are given in parentheses. These estimates reflect the reparameterization scheme discussed in Sec. III. Each of the categorical variables, temperature, glass, zeolites, and clay, has one estimate fixed at 0. Predictions based on these estimates are within 0.5 order of magnitude of the observed values.

Although predicted sorption values using these parameter estimates are excellent, one should be cautioned against direct interpretation of parameter results. There are not enough data, and the parameter estimates are too highly correlated to allow one to make the statement that, for example, barium sorption increases with zeolite concentration. The correlation between the barium parameter estimates of zeolite at 1 to 10% and clay at 20 to 50% is -0.73 .

RESIDUALS AS A FUNCTION OF SIZE

Fig. 3. Residuals from the fitted model for cesium as a function of particle sizes and sorption times.

TABLE V
PARAMETER ESTIMATES

Effect	Ba	Ce	Cs	Eu	Sr
Mean	8.1350 (0.39)	3.0219 (0.19)	7.4184 (0.37)	5.3631 (0.37)	8.1131 (0.39)
Temp					
Ambient	-0.6015 (0.10)	-0.0929 (0.14)	-0.1104 (0.10)	-0.2887 (0.10)	-0.4334 (0.10)
70°C	0	0	0	0	0
Glass					
None	0.1913 (0.23)	-1.1551 (0.24)	-0.4384 (0.21)	-0.7850 (0.21)	-0.0555 (0.23)
50%	0	0	0	0	0
Zeolite					
<1%	-2.6956 (0.20)	-0.0809 (0.18)	-2.2012 (0.19)	-0.7079 (0.19)	-2.5658 (0.20)
1%-10%	-1.1961 (0.37)	-1.5386 (0.17)	-0.4838 (0.35)	-1.9571 (0.34)	-0.4469 (0.36)
10%-20%	-0.6889 (0.39)	-1.2262 (0.23)	-0.6434 (0.37)	-1.3680 (0.37)	-0.9745 (0.38)
20%-50%	-0.5383 (0.23)	0	-0.6605 (0.21)	-0.4360 (0.21)	-0.2044 (0.23)
>50%	0	no data	0	0	0
Clay					
<1%	-2.9259 (0.20)	0	-2.4276 (0.19)	-1.5197 (0.19)	-3.7715 (0.20)
1%-10%	-2.4247 (0.15)	0.9193 (0.11)	-2.1706 (0.14)	-0.8100 (0.14)	-3.3039 (0.15)
10%-20%	-2.7449 (0.15)	0	-2.7240 (0.14)	-1.8317 (0.14)	-3.3920 (0.15)
20%-50%	-3.8275 (0.28)	no data	-3.5249 (0.27)	1.0108 (0.27)	-4.6922 (0.28)
>50%	0	no data	0	0	0
Slopes					
Ambient	0.0048(0.0017)	0.0057 (0.0023)	0.0012 (0.0016)	0.0067 (0.0016)	0.0026 (0.0017)
70°C	0.0093 (0.0022)	0.0039 (0.0029)	0.0016 (0.0021)	0.0061 (0.0021)	-0.0019 (0.0022)

Therefore, a positive change in the parameter estimate for zeolite in abundance 1 to 10% will result in a negative change in the parameter estimate for 10 to 50% clay. Hence, the parameter estimates for any element must be examined in total.

Predicted sorption values for zeolites, clays, and glasses in differing abundance are given in Table VI. These predictions, denoted by "estimate" in the table, are based on ambient temperatures and 42 days of sorption time. The two types of confidence intervals discussed in Sec. III are also given in this table. The first interval, the 95% prediction interval, should be used if it is believed that all the error in the estimates is due to measurement error. The second interval, the 95% interval on a future value, measures the uncertainty in the estimates if the major source of variability is the geology rather than measurement error. These intervals are broader than the first intervals and present the practitioner with conservative intervals even though measurement error may be the dominant source of variability. As such, these second intervals should be considered the appropriate intervals for the estimation of sorption values.

It is interesting to note from Table VI that 10% or more zeolite abundance with some addition of clay increases the sorption values significantly. Because of this tendency, sorption estimates for each element except cerium increase from the tens and hundreds to the thousands and ten thousands. This is particularly true for barium where the DEVIT estimate is 202.8 ml/g compared to the ZEOLITE1 estimate of 43796 ml/g. Sorption estimates for cerium do not follow this trend, as glass appears to be the dominant factor in their determination. However, cerium sorption estimates are based on a limited amount of data and are probably the least reliable of all the estimates.

VI. Conclusions and Summary

Regression techniques were used to model sorption values as a function of sorption time, particle size, and the mineralogy of the samples under investigation. From a study of three large sample sets, JA-18, JA-32, and JA-37, it was evident that particle size has no effect on the sorption values. When combined data were used, particle size significantly affected the sorption estimates only for cerium. This effect, however, was entirely due to two data points; when these points were removed, the effect vanished.

Because of a lack of data, it was only possible to test for a significant concentration effect for barium in the JA-37 data set. No significant concentration effect was noted. This does not rule out concentration effects for other elements in other data sets. However, the P-value for concentration in the barium JA-37 data was 0.98, which is extremely large.

Samples were available at ambient temperatures and 70°C. The temperature effect was significant in determining the sorption value because sorption increased significantly with temperature.

TABLE VI
SORPTION ESTIMATES FOR AMBIENT TEMPERATURE AT 42 DAYS

Classification	Mineralogy			Element	Estimate	Prediction		Future Value	
	Zeolite	Glass	Clay			95% Lower	95% Upper	95% Lower	95% Upper
	(%)	(%)	(%)						
DEVIT	0-1	None	0-1	Ba	202.8	103.7	392.7	65.2	624.8
DEVIT 1	0-1	None	10-20	Ba	306.2	232.0	403.1	118.0	794.6
DEVIT 2	10-20	None	0-1	Ba	20493.0	3762.0	111634.0	2988.5	140539.0
ZEOLITE	20-50	None	0-1	Ba	28983.0	12454.0	67450.0	8355.5	100539.0
ZEOLITE 1	20-50	None	10-20	Ba	43796.0	24399.0	79259.0	14836.0	130349.0
ZEOLITE 2	20-50	20-50	0-1	Ba	18659.0	9734.0	35767.0	6080.0	57253.0
GLASS	0-1	20-50	0-1	Ba	129.9	56.4	299.5	37.7	447.8
GLASS 1	0-1	20-50	10-20	Ba	197.1	66.7	582.8	47.8	813.4
GLASS 2	10-20	20-50	0-1	Ba	13193.0	5458.0	31889.0	3705.0	46972.0
CLAY	0-1	None	>50	Ba	107173.0	87449.0	331150.0	54972.0	526787.0
DEVIT 1	0-1	None	10-20	Ce	85.7	61.8	119.0	29.7	247.8
ZEOLITE 1	20-50	None	10-20	Ce	103.3	43.2	246.8	27.2	391.8
ZEOLITE 2	20-50	20-50	0-1	Ce	1476.0	716.9	3039.0	426.7	5107.0
GLASS	0-1	20-50	0-1	Ce	1225.0	413.0	3632.0	278.0	5399.0
DEVIT	0-1	None	0-1	Cs	196.4	105.2	366.7	68.2	566.1
DEVIT 1	0-1	None	10-20	Cs	99.3	76.7	128.4	40.7	242.4
DEVIT 2	10-20	None	0-1	Cs	7095.0	1451.0	34710.0	1169.0	43057.0
ZEOLITE	20-50	None	0-1	Cs	6822.0	3092.0	15053.0	2128.0	21869.0
ZEOLITE 1	20-50	None	10-20	Cs	3447.0	1986.0	5985.0	1246.0	9535.0
ZEOLITE 2	20-50	20-50	0-1	Cs	18721.0	10178.0	34436.0	6552.0	53489.0
GLASS	0-1	20-50	0-1	Cs	539.0	246.6	1178.0	169.2	1717.0
GLASS 1	0-1	20-50	10-20	Cs	272.4	98.7	751.8	72.3	1027.0
GLASS 2	10-20	20-50	0-1	Cs	19472.0	8518.0	44510.0	5928.0	63953.0
CLAY	0-1	None	>50	Cs	52573.0	28163.0	98138.0	18243.0	151506.0
DEVIT	0-1	None	0-1	Eu	221.2	118.6	412.7	76.8	636.8
DEVIT 1	0-1	None	10-20	Eu	107.8	83.4	139.5	44.2	263.1
DEVIT 2	10-20	None	0-1	Eu	48.4	9.9	236.3	8.0	293.1
ZEOLITE	20-50	None	0-1	Eu	413.7	187.6	912.1	129.2	1324.0
ZEOLITE 1	20-50	None	10-20	Eu	201.7	116.2	349.9	73.0	557.3

TABLE VI (Cont)

Classification	Mineralogy			Element	Estimate	Prediction		Future Value	
	Zeolite	Glass	Clay			95% Lower	95% Upper	95% Lower	95% Upper
	%	%	%						
ZEOLITE 2	20-50	20-50	0-1	Eu	2521.0	1371.0	4635.0	838.4	7197.0
GLASS	0-1	20-50	0-1	Eu	1348.0	617.3	2944.0	423.8	4289.0
GLASS 1	0-1	20-50	10-20	Eu	657.4	238.4	1812.0	174.0	2475.0
GLASS 2	10-20	20-50	0-1	Eu	294.9	129.1	673.6	89.9	967.5
CLAY	0-1	None	>50	Eu	7320.0	3923.0	13657.0	2542.0	21075.0
DEVIT	0-1	None	0-1	Sr	25.0	12.4	43.3	8.2	76.4
DEVIT 1	0-1	None	10-20	Sr	59.9	45.6	78.6	23.3	153.5
DEVIT 2	10-20	None	0-1	Sr	975.6	182.8	5207.0	145.6	6536.0
ZEOLITE	20-50	None	0-1	Sr	5744.0	2492.0	13239.0	1681.0	19632.0
ZEOLITE 1	20-50	None	10-20	Sr	13756.0	7687.0	24615.0	4703.0	40232.0
ZEOLITE 2	20-50	20-50	0-1	Sr	6528.0	3432.0	12416.0	2156.0	19758.0
GLASS	0-1	20-50	0-1	Sr	28.4	12.5	64.8	8.4	96.4
GLASS 1	0-1	20-50	10-20	Sr	68.0	23.3	198.5	16.8	275.9
GLASS 2	10-20	20-50	0-1	Sr	1109.0	463.4	2651.0	316.2	3887.0
CLAY	0-1	None	>50	Sr	147730.0	76470.0	285393.0	48366.0	451229.0

Sorption also increased with experimental sorption time. This rate of increase seemed to be different for the two temperatures. Therefore, two parameters, each representing the rate of increase in sorption at one of the temperatures, were added to the model. In most cases, these slopes were significantly different from zero.

Mineralogy of the sample was characterized by five categories of both zeolite and clay abundance and two classes of glass. Using these factors, temperature, and a slope to account for the increase in sorption with sorption time, it was possible to predict all the individual sorption data values within 0.5 order of magnitude. Parameters to determine sorption estimates were given. In general, sorption increased significantly as the amount of zeolite or clay increased.

For various rock types, two intervals were given that measure the uncertainty in the sorption estimates at ambient temperatures and 42-day sorption time. Most of these intervals have widths of less than an order of magnitude.

This investigation has shown that mineralogy as determined by x-ray diffraction can be

used successfully to predict sorption. These predictions were based on a relatively small amount of data and semi-quantitative x-ray diffraction classifications. Further work will refine these predictions by using mineralogical data obtained from more x-ray diffraction analyses.* In addition, water composition data for batch sorption experiments will be factored into the regression analysis. With refined data, a more quantitative study of those factors that most affect sorption will be undertaken.

* Information received from David L. Bish, Group ESS-1, Los Alamos National Laboratory, 1987.

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APPENDIX
THE DATA EDITING PROCEDURE KDALL2

```

REDEFINE PROCEDURE KDALL2.
! **** Sort the data base by particle.
! **** Size. Eliminate the fines using a 106-micron cutoff.
! **** Remove early experiments where experimental techniques
! **** were under development by dropping all entries where
! **** Reference = 1. This refers to the tuff 1 report,
! **** the first report completed in the sorption experiment
! **** series.
FIND SORPTION WITH PMIN GE 106 AND
PMAX GE 106 AND REFERENCES NE 1.
! **** Sort the data base to include the elements with the
! **** greatest number of data points and the simplest
! **** and most easily understood patterns of sorption
! **** behavior.
FIND CURRENT WITH ELEMENT = "CS" OR ELEMENT = "BA" OR
ELEMENT = "SR" OR ELEMENT = "EU" OR ELEMENT = "CE."
! **** Sort the final data base by element and sample for
! **** ease in working with the data and for consistent
! **** formatting.
SORT BY ELEMENT, SAMPLE.
! **** Use DATATRIEVE command to allow output of data file
! **** to variable devices (disk file, printer etc).
REPORT ON *. "REPORT SPECIFICATION."
! **** Use DATATRIEVE command for maximum column width.
SET COLUMNS.PAGE = 132.
! **** Set lines per page to value that exceeds the number of
! **** samples so there are no page breaks in the data listing.
SET LINES.PAGE = 2000.
! **** Set title of report which is printed at the top of page.
SET REPORT_NAME = "Kd DATA SORTED BY ELEMENT/SAMPLE."
! **** The samples were entered in the data base by the drill core
! **** label. Multiple batch experiments were run on the same drill
! **** core samples. Therefore a unique sample id does not exist in
! **** in the data base for individual samples. To assign a unique
! **** label to each sample, the variable "running count" is assigned
! **** sequentially as the samples are pulled into the sorted
! **** data file. The next command establishes this variable and
! **** pulls selected experimental parameters into the data file.
PRINT RUNNING COUNT ("COUNT"), SAMPLE, ELEMENT,
SRD1 ("SORPT 1"), SRD2 ("SORPT 2"),
STIM ("SORPT TIME"), DTIM ("DESORPT TIME"), TEMP,
SIG ("DIGS CONC"), EXP ("EXP CONC"),
PMIN ("MIN SIZE"), PMAX ("MAX SIZE").
END_REPORT.
END_PROCEDURE.

```