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TITLE: THE USE OF A HETEROGENEITY-BASED ISOTHERM TO INTERPRET THE TRANSPORT OF REACTIVE RADIONUCLIDES IN VOLCANIC TUFF MEDIA

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THE USE OF A HETEROGENEITY-BASED ISOTHERM TO INTERPRET THE TRANSPORT OF REACTIVE RADIONUCLIDES IN VOLCANIC TUFF MEDIA

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ABSTRACT

The sorption of cesium and strontium has been modeled with a heterogeneity-based isotherm equation for various tuff materials including those within a sequence of geologic stratigraphic units. The theory of the isotherm foresees the relative retardation and the "chemical dispersion" of the studied radionuclides during transport. The concepts of heterogeneity of sites and variability in the maximum number of sites available for sorption are incorporated into the model.

1. INTRODUCTION

Volcanic tuff material is the geologic medium for the shallow land burial of low-level radioactive waste at the Los Alamos National Laboratory in northwestern New Mexico. Also, volcanic tuff material of Yucca Mountain near south-central Nevada is the proposed geologic medium for a repository of high-level radioactive waste [1]. One aspect of the characterization of either disposal area is the sorptive behavior of radionuclides in the tuff materials. This characterization is important in predicting waste migration.

Isotherms have been derived and used to represent sorptive behavior in a variety of disciplines, e.g., soil chemistry, geochemistry, and environmental and chemical engineering [2, 3, 4, 5, 6]. The Langmuir isotherm is based on the simplest of several theories are available to describe the relationship between the amount of a solute adsorbed on a surface and the concentration of the solute in the liquid phase [7]. This isotherm assumes that the energy of adsorption is the same for all active sites on the adsorbent surface. However, in many adsorption cases, the assumption fails because either pure mineral or multi-mineral surfaces interact with solutes with different energies (heterogeneity). These differences among site energies require the identification of those energy distributions that characterize the heterogeneity of a particular adsorbent-solute interaction.

Sips [8] introduced and discussed an isotherm that suggests that a Gaussian-like statistical function could represent the distribution of site-solute interactions. This isotherm, which is based on the assumption of localized adsorption without interaction among sites, was presented as an expansion of the conventional Freundlich isotherm. Sposito [9], following the results obtained by Sips [8] and using a Langmuir isotherm to define site-solute interactions, derived a similar Gaussian-like statistical function that is regarded as a log-normal distribution of a variable that defines the relative affinity of a solute for a solid phase.

The isotherm can be expressed as

$$\frac{S_i}{S_{maxi}} = \frac{K_\zeta^{\beta} C_i^{\beta}}{1 + K_\zeta^{\beta} C_i^{\beta}}, \qquad (1)$$

where

S_i = quantity of solute adsorbed per unit mass of solid phase i,

C_i = concentration of solute in solution in equilibrium with solid phase i,

S_{maxi} = maximum available exchange capacity at solid phase i, and

K_ζ, β = parameters that define the overall solute-solid phase interaction.

If this isotherm applies, then a more comprehensive representation of the heterogeneity of the adsorption is gained from the meaning of K_ζ and β. These two parameters can be found by regressional analysis of a given set of sorption data on the following expression:

$$\log\left(\frac{S_i}{S_{maxi} - S_i}\right) = \beta \log C_i - \log (K_\zeta^{\beta}). \qquad (2)$$

The parameter β has been described by Sposito [9] as a measure of how sharply peaked the statistical function for the distribution of energies at equilibrium is about an average value; the parameter has also been described

by Crickmore and Wojciechoswski [10] as the spread of the statistical function for the distribution of adsorption-desorption rate constants. The parameter K_D has been implicitly related by Sposito [9] to an average distribution coefficient, or an average adsorption energy or affinity; Crickmore and Wojciechoswski [10], on the other hand, define it as the ratio of the reaction rate constants that represent simultaneous β-order adsorption-desorption rates. Both parameters, β and K_D, are temperature and pH dependent.

It is important to notice that Eq. (2) is a general isotherm from which common isotherms can be derived as follows: Linear isotherm (β = [illegible], $K_D^{\beta}C^{\beta}$ [illegible]), the Langmuir isotherm (β = [illegible]), and the Freundlich isotherm ($0 < \beta < 1$, $K_D^{\beta}C^{\beta}$ [illegible]).

The objectives of this paper are (1) to introduce and give chemical meaning to the parameters of the general equation, (2) to verify the validity of the isotherm and to interpret isotherm parameters for sorption of strontium and cesium on Bandelier Tuff with respect to their impact on their transport, and (3) to extend the application of the isotherm to stratigraphic units having materials with different capacities to adsorb radionuclides.

[illegible] MATERIALS AND METHODS

[illegible].1 Experimental

Bandelier Tuff is described geologically as a volcanic ash flow composed mostly of silicic glass with a grain size distribution close to that of a silty sand and a cation exchange capacity (CEC) of 3.3 μmol (p+)/g. Mineralogically the tuff is primarily composed of quartz, tridymite, and alkali feldspars. Detailed procedures and techniques for the batch adsorption experiments are described by Polzer et al. [11]. The description and

procedures of the laboratory column transport studies are given by Fuentes et al. [12].

The tuffs of Yucca Mountain have been described in mineralogic and petrologic studies [13]. The batch sorption procedures followed for the Yucca Mountain tuff media are described by Daniels et al. [14].

The batch sorption studies of the tuffs from Yucca Mountain were not designed to evaluate isotherms, but to evaluate the effect on adsorption of such parameters as contact time, concentration of sorbing elements, particle size, temperature, atmosphere, and lithology. Therefore, the range in concentrations varied from one experiment to another. Only data for a contact time of 14 days, ambient temperature, and air atmosphere were used in the modeling effort. Sorption data include those for samples of all ranges of particle sizes. However, particle sizes varied from one tuff sample to another. Preliminary modeling (15) indicates that available particle sizes had little effect on isotherm parameters.

2.2 Modeling

The data were modeled using the heterogeneity-based isotherm (Modified Freundlich). Data sets were linearly regressed and the results were defined by coefficient of determinations (R^2), confidence level of the regression analysis, coefficient of variation (CV), and the values for the parameters as determined from the slope and from the intercept. The intercept is the dependent variable when the independent variable, concentration in solution, is unity. The error terms associated with the parameter values are also included. These statistics and parameters provide criteria for goodness of isotherm fit and for estimates of the extent of heterogeneity of the adsorption.

3. RESULTS AND DISCUSSION

3.1 Bandelier Tuff Material

The Modified Freundlich isotherm plots for the sorption of strontium and cesium to Bandelier Tuff are presented in Fig. 1. The statistical parameters for the regression analysis and the isotherm parameters are given in Table 1. The R^2 is 0.993 for the cesium regression and 0.999 for strontium regression. The coefficient of variation is 7.3% for cesium and 2.7% for strontium. These statistical data indicate a very good correlation between the fraction of sorbed sites occupied by the tracers [$S/(S_{max} - S)$] and the concentration of tracers (C) in solution. The values for β were 0.842 for strontium and 0.662 for cesium. Based on the theory described, those values suggest that the spread (dispersion) in the breakthrough (or transport) of strontium due to heterogeneity of sorption sites should be less than that of cesium. This spread should be in addition to the spread due to flow. The K_D value for strontium is about one-half of that for cesium (0.172 and 0.308, respectively). Again, based on the above theory, those relative K_D values indicate that the breakthrough or transport of cesium should be retarded by approximately a factor of 2 compared with that of strontium.

The above results and the theory are supported, at least qualitatively by the results of laboratory column breakthrough data shown in Fig. 2. These data are adapted from Fuentes [12]. The relative breakthrough pattern appears to follow that predicted by the isotherm parameters for strontium and cesium. The breakthrough of iodide represents transport of a nonsorbing tracer and the dispersion of iodide should be due to flow conditions. The appearance of the initial and peak breakthroughs of strontium and cesium indicates that cesium is retarded by about a factor of 2 compared with strontium as predicted from the isotherm parameter, K_D. Also, the spread in the breakthrough appears to

be much greater for cesium than for strontium. However, it should be noted that a strict interpretation must include an evaluation of dispersion due to water flow. The spread due to flow dispersion is not the same for the two tracers because of differences in arrival or breakthrough times. The above results and conclusions appear to give validity to the Modified Freundlich isotherm as a means of predicting the relative transport of radionuclides in tuff materials. Work on the coupling of the isotherm equation to a transport model is in progress.

3.2 Yucca Mountain Tuff Materials

The results just discussed above are limited in that the tuff material was collected from a specific area of the Bandelier stratigraphic unit to minimize inhomogenities in characteristics, e.g. maximum sorption capacity (CEC). In order to extend the isotherm model to large environmental areas, a variable maximum sorption capacity needs to be incorporated into the model. For example, within a stratigraphic unit of Yucca Mountain available information indicates that the CEC of the various materials may vary by a factor of 60. This incorporation was accomplished by including a CEC (S_{max}) for each set of sorption data. Thus the dependent variable is composed of two variables, the amount sorbed, S, and the maximum sorption capacity, S_{max}, in the form $S/(S_{max}-S)$. This procedure was used to evaluate the applicability of the isotherm to model sorption for five stratigraphic units of Yucca Mountain located below the candidate repository. The results are presented in Tables 2 and 3. Table 2 gives the number of data sets used in the analysis, the range in maximum sorption capacities (CEC), the coefficient of variation (CV), and the confidence level of the regression analysis. Table 3 presents the parameter estimates for the isotherm based on the regression analysis. Figure 2 provides a "worse" case and "best" case example of sorption according to the

Modified Freundlich isotherm. The "worse" case is the only situation for which the isotherm does not represent the data well. It should be emphasized as mentioned previously that the sorption data were not generated for the purpose of isotherm analysis, which may be a reason for the improper spreading of the experimental values in the worse cases.

The statistics for the regression analysis indicate a coefficient of determination of 0.86 or better for the regression analysis with one exception: R^2 was only 0.55 for the regression of cesium data in the Calico Hills unit. The coefficient of variation of the data about the regression line ranged from about 2 to 11. The higher CV's were only a factor 2 greater than those determined with the Bandelier Tuff. Thus these data suggest that incorporation of S_{max} into the dependent variable does not greatly affect variation of the data about the regression line.

The parameter estimates are plotted as a function of the stratigraphic unit in Fig. 4. Some general trends can be observed within the limits of errors associated with the estimates. The average K_D values for cesium and for strontium follow similar patterns. The log K_D varies from approximately -2.0 to +2.0 with the Calico Hills unit having the highest K_D and the Prow Pass having the lowest K_D. The β values range from approximately 0.03 to 1.15. As mentioned earlier, the β parameter is theoretically expected to be less than 1; the higher value of 1.15 only occurs for strontium in the Calico Hills unit. In this set of observations the data are not uniformly distributed; one observation extends the domain of observations from approximately 1 order of magnitude to about 3.5 orders of magnitude. An influence diagnostic test based on D-Cook-like statistics [16] indicates that the observation unduly influences the regression and the slope (β). If the observation were to be deleted, the slope would decrease, thus maintaining the

β parameter within theoretical predictions. The chemical dispersion, . . . for both strontium and cesium appears to follow a similar pattern of change as that for the K_D, but the pattern is less obvious. Significant differences between the β's for cesium and those for strontium occur in the Tram unit and perhaps in the Bullfrog unit. The similarities in the pattern of change of the K_D values and those of the β values suggest that when the K_D (average) is large, β approaches unity. This relation implies that as the average K_D increases, the spread of individual K_D values about the average is less.

The large error associated with parameter estimates of the cesium tracer in the Calico Hills unit is indicative of the relatively few data available and of their poor distribution over the narrow range of observations (less than 1 order of magnitude). The influence diagnostic test based on D-Cook-like statistics [16] indicates that several sorption observations unduly influence the regression and parameter estimates. Those same observations account for most of the relatively large residual resulting from the regression analysis. Even though the coefficient of determination is relatively poor (0.55), a confidence level of greater than 96% for the regression suggests a definite linearity associated with the regression thus supporting the applicability of the isotherm.

The patterns of change of K_D- and β-values between stratigraphic units become a simplified means to characterize the heterogeneity of the adsorption of strontium and cesium in Yucca Mountain materials. The expected spatial variability for the adsorption process can be scoped from the meaning of K_D and β, namely, retardation intensity (K_D) and variability of retardation (β). This result is an improvement over the use of conventional isotherms that do not recognize the potential heterogeneity of adsorption, e.g., Langmuir. This heterogeneity could be understood as a "chemical dispersion" because it may

cause a difference in radionuclide migration due to differences in retardation. These findings suggest a better approach to handle adsorption in transport modeling of radionuclides in porous media. In recognizing that the data sets used in this study were not collected with this modeling approach in mind, there is a need to improve the data base to further test the response of the model.

ACKNOWLEDGMENT

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Table 1. Statistical and Modified Freundlich isotherm parameters estimated from the regression analysis of the sorption of cesium and strontium on Bandelier tuff[a]

	Sr	Cs
R^2	0.9994	0.9926
CV (%)	2.7	7.3
Confidence Level (0.01%)	0.9999	0.9999
β	0.942 ± 0.010	0.662 ± 0.014
K_D	0.172 ± 0.005	0.308 ± 0.077

[a] K_D and β have units corresponding to S and S_{max} in μmol (p+)/g and C in μmol(p+)/mL in Eq. 2.

Table 2. Experimental parameters for sorption of strontium and cesium on tuff media from stratigraphic units of the Yucca Mountain area and statistical parameters estimated from regression analysis for the Modified Freundlich sorption isotherm[a]

	Topopah Spring		Calico Hills		Prow Pass		Bullfrog		Tram	
	Sr	Cs	Sr	Cs	Sr	Cs	Sr	Cs	Sr	Cs
No. of data sets	16	16	8	8	18	18	21	22	18	17
Range of Initial Concentrations (μmoles/L)	6.0E-11 to 3.0E-03	9.5E-09 to 1.3E-00	8.0E-11 to 4.0E-07	1.0E-09 to 4.0E-09	8.0E-11 to 6.0E-07	1.0E-09 to 4.0E-09	3.0E-09 to 2.0E-05	1.0E-09 to 5.0E-09	5.0E-07 to 1.4E-03	9.5E-09 to 1.3E-00
Range of S (μmole(p+)/g)	44 to 190		603 to 1517		49 to 1300		23 to 1143		38 to 569	
K^2	0.972	0.952	0.991	0.550	0.862	0.947	0.970	0.873	0.970	0.963
CV(%)	10	4.6	1.9	2.2	9.2	2.7	5.4	3.9	11	10
Confidence (0.01%)	0.9999	0.9999	0.9999	0.9649	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999

a) K_D and β have units corresponding to S and S_{max} in μmol(p+)/g and C in μmol(p+)/ml in Eq. 2.

Table 3. Modified Freundlich isotherm parameters estimated from regression analysis for the sorption of strontium and cesium on tuff media from stratigraphic units of the Yucca Mountain area[a]

Stratigraphic Unit	β Sr	β Cs	K Sr	K Cs
Topopah Spring	0.86 ± 0.04	0.82 ± 0.02	0.67 ± 0.34	0.45 ± 0.17
Calico Hills	1.15 ± 0.04	0.83 ± 0.31	58 ± 4	0.35 ± 2.5
Prow Pass	0.68 ± 0.07	0.73 ± 0.04	0.036 ± 0.043	0.01 ± 0.01
Bullfrog	0.82 ± 0.03	0.74 ± 0.06	0.13 ± 0.12	0.07 ± 0.10
Tram	0.87 ± 0.04	0.74 ± 0.04	0.57 ± 0.15	0.26 ± 0.16

[a] K_D and β have units corresponding to S and S_{max} in μmol(p+)/g and C in μmol(p+)/mL in Eq. 2.

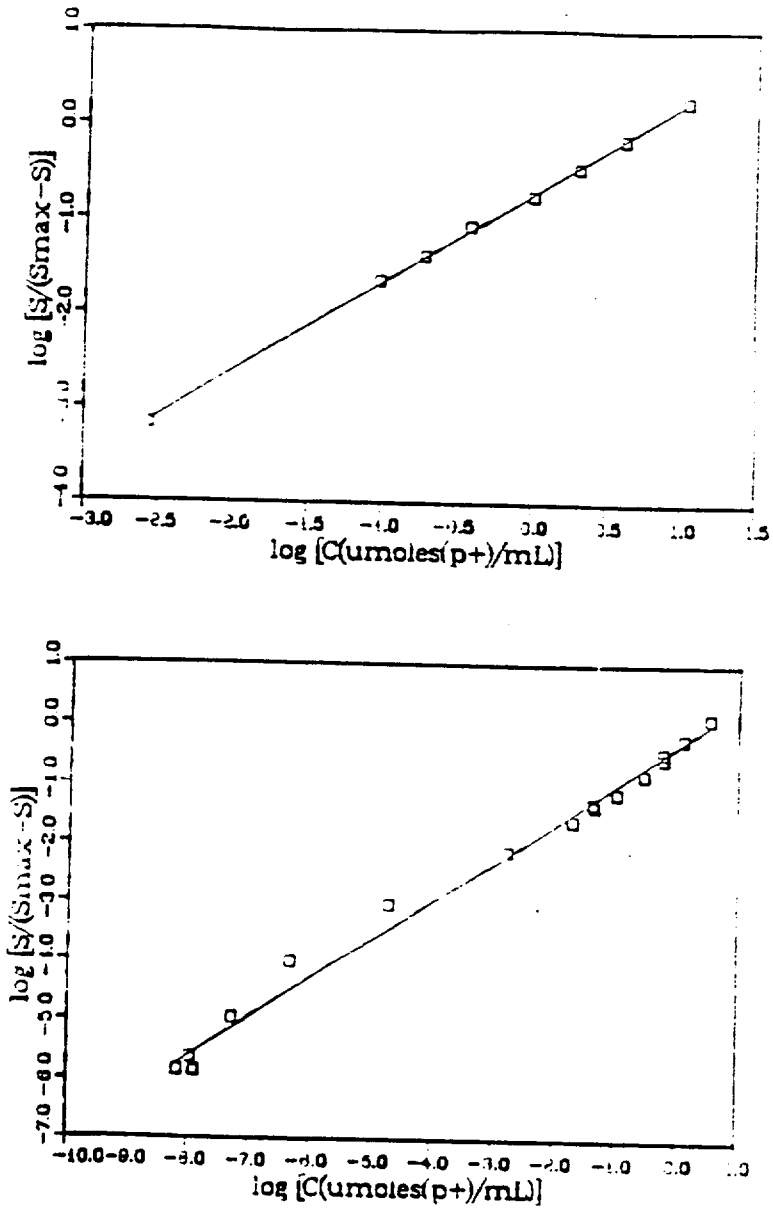

Fig. 1. Modified Freundlich isotherm plots of strontium (upper) and cesium (lower) on Bandelier tuff. Data are for sorption after 48 h of equilibration and at a temperature of 23 ± 3°C.

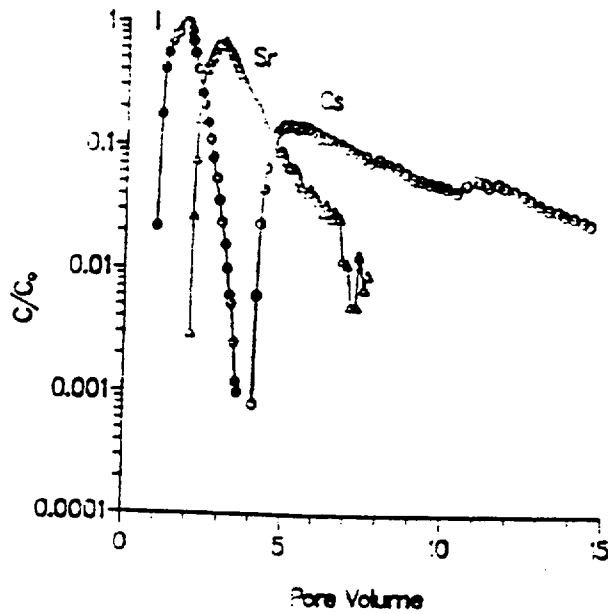

Fig. 2. Breakthrough curves of reactive (strontium and cesium) and nonreactive (iodide) tracers in a laboratory column of Bandelier Tuff at 25°C and under unsaturated flow conditions.

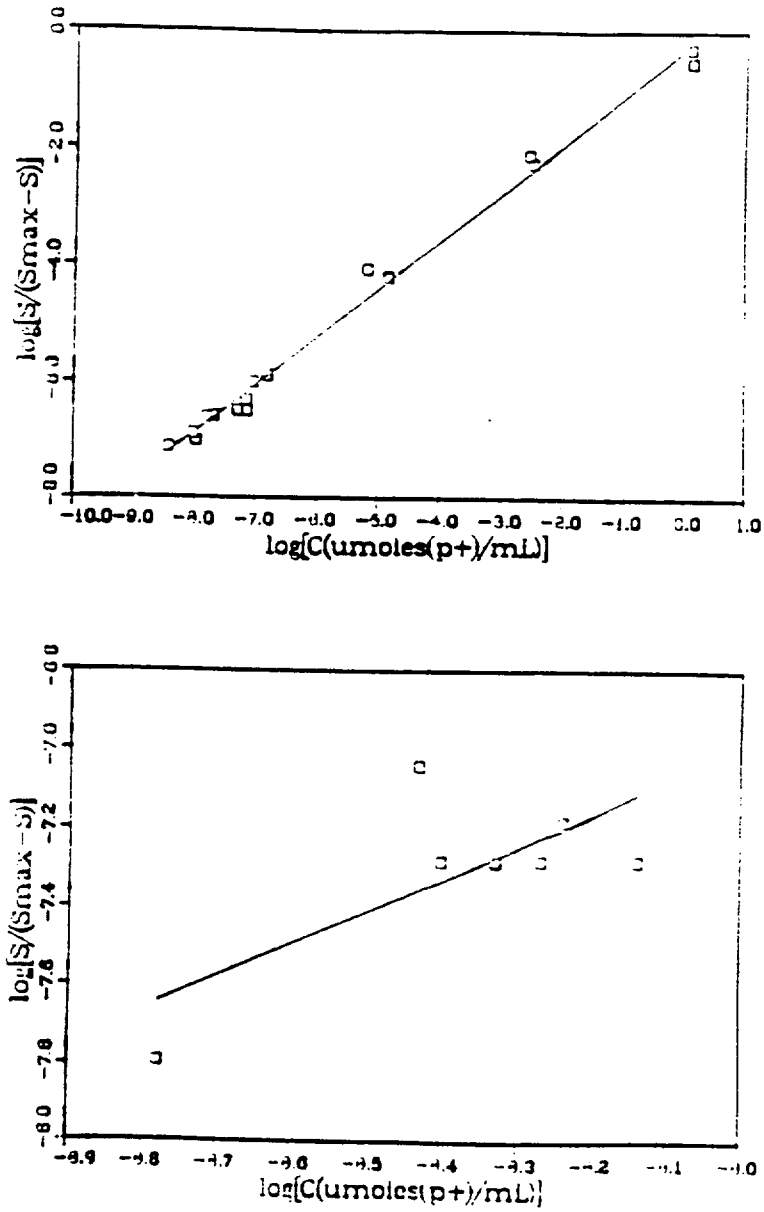

Fig. 3. Modified Freundlich isotherm plots of cesium on Topopah Spring (upper) and Calico Hills (lower) tuff media. The Calico Hills plot represents a "worse" case fit and the Topopah Spring plot represents a "best" case fit.

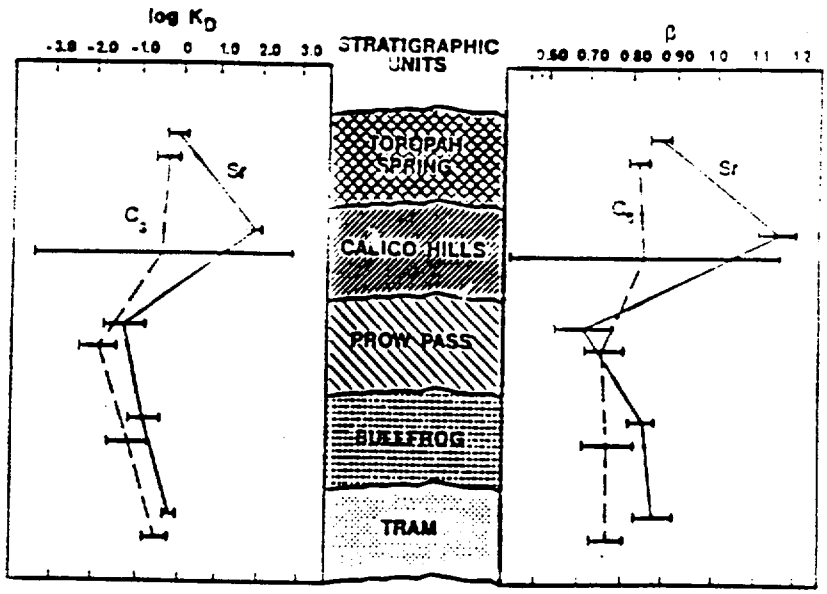

Fig. 4. Modified Freundlich isotherm parameters for strontium and cesium sorption on Yucca Mountain tuff media. The parameter values with their standard errors are plotted relative to stratigraphic units.