

EQUILIBRIUM SORPTION OF COBALT, CESIUM AND STRONTIUM
ON BANDELIER TUFF: ANALYSIS OF ALTERNATIVE MATHEMATICAL MODELING

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ABSTRACT

Sorption isotherms are derived from batch equilibrium data for cobalt, cesium and strontium on Bandelier Tuff. Experiments were conducted at an average temperature of 23°C and equilibrium was defined at 48 hours. The solute concentrations ranged from 0 to 500 mg/L. The radioactive isotopes ^{60}Co , ^{137}Cs , and ^{85}Sr were used to trace the sorption of the stable solutes. The Linear, Langmuir, Freundlich and a Modified Freundlich isotherm equations are evaluated. The Modified Freundlich isotherm equation is validated as a preferred general mathematical tool for representing the sorption of the three solutes. The empirical constants derived from the Modified Freundlich isotherm equation indicate that under dynamic flow conditions strontium will move most rapidly and cobalt least rapidly. On the other hand, "chemical dispersion" will be greatest for cesium and least for strontium. Hill Plots of the sorption data suggest that in the region of low saturation sorption of all three solutes is impeded by interactions among sorption sites; cobalt exhibits the greatest effect of interactions and strontium shows only a minimal effect. In the saturation region of 50% or more, sorption of cobalt is enhanced slightly by interactions among sorption sites whereas sorption of cesium and strontium appears to be independent of site interactions.

INTRODUCTION

The Los Alamos National Laboratory has been conducting laboratory studies in support of field studies to assist the Nuclear Regulatory Commission (NRC) in improving transport and leaching scenarios used to assess the performance of low level radioactive waste disposal sites. These studies have covered the investigation of chemical processes affecting the transport of reactive solutes in unsaturated Bandelier Tuff. Laboratory studies have included batch studies to evaluate expressions for modeling chemical processes involved in retardation of solute migration.

Chemical processes that may affect reactive solute transport include acid-base equilibria, complex formation, oxidation-reduction, volatilization, biodecay, radioactive decay and sorption. Sorption is a loss of solute from the liquid phase to the solid phase and may be due either to adsorption, ion exchange or precipitation.

Sorption may be modeled as an equilibrium or a nonequilibrium process. Equilibrium models assume "instantaneous" sorption, and nonequilibrium or kinetic models consider a "slower" rate of approach towards equilibrium. This paper concentrates on the equilibrium behavior.

The variety of observed patterns of equilibrium sorption of reactive solutes by soils has incited the development of many mathematical relationships to

describe those patterns.¹ Those expressions range from a simple linear relationship to various formulations of nonlinear relationships. Some expressions are widely used and others have a better theoretical explanation. In all cases the expressions are only empirical. The selection of the isotherm that fits best to the experimental data should reflect more objective predictions when applied to transport models. However, a current practice among transport phenomena modelers is to adopt the simplest expressions, e.g. Linear, as the norm because of easier analytical and numerical solutions. This approach obviously diminishes the success of a model to predict. It also diminishes the possibility of better understanding the influence of other processes, e.g. physical dispersion, as well as the possibility of better understanding the complexities resulting from competition among various solutes. Competition among solutes represents the actual situation in the environment.

In this paper several equilibrium isotherm equations are examined and evaluated relative to their limitations in modeling the sorption of reactive solutes by soil. A common set of experimental data is used to illustrate the applicability or limitation of the various equations to modeling. The equations include three of the most commonly used equilibrium isotherms (Linear, Langmuir and Freundlich) and a Modified Freundlich whose predictive power is based on theoretical considerations. In an attempt to find additional information on interactions among sorption sites, the value of the Hill Plot approach is also examined.

The results presented in this paper focus on the general phenomenon of sorption; no specific sorption mechanism is implied, i.e. adsorption (a net accumulation at an interface), ion exchange or precipitation. In order to specify a mechanism additional data would be required on the chemical composition of the soil and/or of the soil solution before and after sorption occurs.

SORPTION MODELS

Linear Isotherm

The simplest and most widely used of the equilibrium sorption isotherms is that given by the linear relationship.

$$S = K_D C \quad (1)$$

where

S = mass of solute sorbed by the soil
 C = concentration of solute in the soil solution
 K_D = distribution coefficient.

This expression has been frequently used in transport models to describe the sorption of radioactive and nonradioactive solutes by soils. One limitation is that it does not imply a maximum quantity of adsorption.

The distribution coefficient, K_D , is a measure of the retention of solute by the soil and is assumed to be independent of concentration. This is not necessarily the case and thus conclusions from analyses based on assumptions of linear behavior may not be valid.

Throughout this paper, each variable is defined once when introduced for the first time and thus it has the same meaning in subsequent equations.

Freundlich Isotherm

The Freundlich isotherm has the form

$$S = K C^N \quad (2)$$

where

K, N = empirical constants.

Estimation of the constants is possible by the simple transformation to the expression

$$\log S = N \log C + \log K. \quad (3)$$

This expression is also very popular in the literature. One reason is that log-log equations are easy to use and are relatively insensitive, lending themselves to imprecise data. However, the Freundlich is limited in that it only shows linearity over a relatively narrow range of concentrations.

Langmuir Isotherm

Langmuir developed a quantitative model that has also been widely applied to describe experimental data.² The Langmuir equation was derived for the sorption of gases on a solid surface. Nevertheless, it has been extended to include the sorption of solutes to soils. The basic expression takes the form

$$S = \frac{k b C}{1 + k b C} \quad (4)$$

where

k, b = empirical constants.

Various transformations allow evaluation of both constants. A standard and more precise form is

$$C/S = (1/b)C + 1/kb. \quad (5)$$

In this expression, k is a measure of the strength of the sorption bond and b is the maximum amount of the solute that can be sorbed by the soil.

This isotherm is based on the theoretical assumption that the sorption sites are homogeneously distributed relative to energy potentials.² This assumption does not apply to most sorbent surfaces, e.g. soil and geologic material.

Modified Freundlich Isotherm

Solute exchange on soil adsorption sites is known to be heterogeneous, that is, not monoenergetic. Sips³ derived the general Langmuir equation to accommodate sorption to surfaces exhibiting heterogeneous sorption surfaces. Sposito, using statistical mechanics, derived rigorously the following equation with the assumptions that the exchanger surface is heterogeneous, and that each class of exchange sites adsorbs individually according to the Langmuir isotherm.⁴

$$S_1 = \frac{S_{\max} \alpha (a_1/a_2)^\beta}{1 + \alpha (a_1/a_2)^\beta} \quad (6)$$

where

α = $A a_2^b / S_{\max}$
 a_1 = activity of solute 1 in solution
 a_2 = activity of solute 2 in solution
 S_1 = amount of solute 1 sorbed
 S_{\max} = maximum available exchange sites or cation exchange capacity
 A, β = empirical constants.

Equation (6) becomes the Freundlich isotherm equation when $(a_1/a_2)^b \ll 1$, i.e. when the adsorbing solute (solute 1) is in trace quantities. However, without limiting the sorbing solute to trace quantities, Eq. (6) is a modified form of the Freundlich isotherm as shown by transforming it as follows:

$$\log \frac{S_1}{S_{\max} - S_1} = \beta \log C_1 + \log \frac{A}{S_{\max}} \quad (7)$$

where the activities have been replaced by concentrations (a_1, a_2 for C_1, C_2 respectively). The empirical constants A and β are determined through linear regression analysis. The parameter α , as defined in Eq. (6), can also be estimated.

The values of A, β, α then can be used to compute the site distribution function $m(q)$ as follows:

$$m_{\max} = \frac{S_{\max}}{2\pi} \tan\left(\frac{\pi\beta}{2}\right) \quad (8)$$

$$q_m = \left(\frac{1}{\beta}\right) \ln \alpha \quad (9)$$

$$m(q) = m_{\max} \times \quad (10)$$

$$\frac{2 \cos(\pi\beta) \exp[\beta(q_m - q)] + 2 \exp[\beta(q_m - q)]}{1 + 2 \cos(\pi\beta) \exp[\beta(q_m - q)] + \exp[2\beta(q_m - q)]}$$

where

m_{\max} = value of $m(q)$ at its maximum
 q_m = value of q at m_{\max}
 q = relative affinity parameter that defines the class of adsorption sites ($-\infty$ to $+\infty$).

The parameter β has been described by Sposito as a measure of how sharply peaked $m(q)$ is about the value $q = q_m$.⁴

Crickmore and Wojciechowski derived rate models for adsorption and desorption from a Langmuir type isotherm by allowing the adsorption energy to vary with the amount of solute adsorbed.⁵ Their derived equations, as given by Murali and Aylmore⁶ but in our notation, are as follows

$$\frac{\delta S}{\delta t} = k_a C_1 S_{\max} \left(1 - \frac{S}{S_{\max}}\right)^{1/\beta} - k_d S_{\max} \frac{S}{S_{\max}} \quad (11)$$

and under equilibrium conditions

$$S = \frac{S_{\max} K_D \beta C_1^\beta}{1 + K_D \beta C_1^\beta} \quad (12)$$

where

k_a = adsorption rate coefficient
 K_D = desorption rate coefficient
 $K_D = \frac{k_a}{k_d}$ = equilibrium distribution coefficient
 t = time.

Crickmore and Wojciechowski have described the two experimental parameters k_a and k_d as weighted average rate constants and a third experimental parameter β as a measure of the coefficient of variation of the rate constant distribution.⁵

Under those conditions the parameter A given by Sposito⁴ can be equated to the parameter K_D , as

$$A = S_{\max} K_D \beta \quad (13)$$

Thus the parameter A is a measure of a weighted average distribution coefficient for which the parameter β describes the spread (coefficient of variation) of many distribution coefficients about the average distribution coefficient (K_D).

Hill Plot

All the afore reviewed models require regression analysis to estimate their constants. On the other hand, the Hill Plot yields information on the binding process without the need for statistical curve fitting. The equation as originally given by Hill⁷ may be expressed as

$$\frac{S}{S_{\max}} = y = \frac{K^* C^a}{1 + K^* C^a} \quad (14)$$

where

y = fraction of the total number of sites occupied by C

K^*, a = empirical constants.

These empirical constants are respectively related to the stability constants of the process and the number of binding sites.

The equation can be rearranged to the linear form

$$\log \frac{S_1}{S_{\max} - S_1} = \log \frac{y}{1 - y} = a \log C_1 + \log K^* \quad (15)$$

and the resulting plot of $\log (S_1 / (S_{\max} - S_1))$ or $\log (y / (1 - y))$ against $\log C_1$ is known as the Hill Plot. The plot is obtained by drawing a smooth curve through the points. Notice the similarity of Eq. (7) and Eq. (15).

The value of the Hill Plot approach stems from its clues on the interactions of sorption sites.⁸ Three kinds of interactions can be evaluated: zero, positive and negative co-operativities. Zero co-operativity indicates that sorption at one site is independent of sorption at other sites. Positive co-operativity indicates that sorption at one site is enhanced by sorption at other sites; and negative co-operativity indicates that sorption at one site is impeded by sorption at other sites.

MATERIALS AND METHODS

Soil Analysis

The Bandelier Tuff (the soil material used in these experiments) is described geologically as a volcanic ash flow composed mostly of silicic glass having a grain size distribution close to that of a silty sand. It was originally collected from a local quarry using front end loaders to mine and crush it before screening to a 12.7 mm size. The screened material was then delivered to the field experimental site. For the laboratory work this material was air dried and sieved through a No. 18, Tyler equivalent, 16 mesh, 1 mm opening brass screen.

The cation exchange capacity (CEC) for the tuff is listed in TABLE I. The concern that the low observed CEC at pH 7.0 might not reflect the true CEC at the pH of the natural soil system was investigated by measuring the CEC at pH 8.0 and pH 9.0 where hydrous oxides could contribute significantly to the CEC. Values of CEC at pH 8.0 and 9.0 were not different from those at pH 7.0. An average of all analyses, 3.3 $\mu\text{mol } (p^+)/\text{g}$, was used as S_{\max} .

TABLE I
Cation Exchange Capacity of Bandelier Tuff Determined at pH 7, 8, and 9.

pH	Number of samples	CEC (Mean \pm SD ^a) [$\mu\text{mol } (p^+)/100 \text{ g}$]
7	4	0.31 \pm 0.05
8	2	0.38 \pm 0.01
9	2	0.30 \pm 0.01
	8	0.33 \pm 0.05 ^b

^aSD is the standard deviation
^bmean of all determinations

In order to simplify evaluation of tracer sorption the crushed tuff was preconditioned with calcium. To condition the tuff a lucite tube (3.81cm id) was fitted with a rubber stopper and delivery tube containing a wad of pyrex glass wool and was filled with the dry sieved tuff. A solution of 0.01N (200 mg/L) calcium was slowly passed through the column until the effluent calcium concentration equaled that of the influent. The calcium solution for all tests was prepared by dissolving 0.735 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter of distilled water. The calcium levels were determined by titration and adjustments made as required to insure a 200 ± 10 mg/L concentration. Contaminant levels in this calcium chloride lot were determined to be: 0.02 mg/L for cesium, and 0.01 mg/L each for cobalt, cesium and strontium.

Batch Tests

Tests were performed to determine the sorption of strontium, cesium and cobalt. All of the tests used calcium treated tuff, a solid to solution ratio of 1 to 4 by weight, and continuous mixing for 48 hours at a temperature of $23 \pm 3^\circ\text{C}$. Each condition was replicated three times. The 48-hour mixing time was based on past experience with sorption studies of strontium and cesium and was sufficient for strontium and cesium to equilibrate with the tuff. However, in the case of cobalt equilibration was only 70% complete in 48 hours as evidenced in the nonequilibrium studies. Reacted solutions were separated from the tuff by centrifuging under conditions effecting a $0.05 \mu\text{m}$ pore diameter separation. Each test received a spike of a radioactive tracer corresponding to the stable solute in study, i.e. ^{60}Co , ^{137}Cs and ^{85}Sr .

The experiments covered various levels of initial concentrations as follows:

1. Cobalt experiment: stable cobalt at 3×10^{-6} , 1×10^{-5} , 1×10^{-4} , 1×10^{-3} , 1×10^{-2} , 1×10^{-1} , 1.0, 5, 10, 20, 50, 100, 200, and 500 mg/L; calcium at 200 mg/L; and ^{60}Co tracer at 74 MBq/L.
2. Cesium experiment: stable cesium at 2×10^{-4} , 1×10^{-3} , 1×10^{-2} , 1×10^{-1} , 1.0, 5, 10, 20, 50, 100, 200, and 500 mg/L; calcium at 200 mg/L; and ^{137}Cs tracer at 370 MBq/L.
3. Strontium experiment: stable strontium at 0.1, 5, 10, 20, 50, 100, 200, and 500 mg/L; calcium at 200 mg/L; and ^{85}Sr tracer at 74 Bq/L.

The data for the above concentrations of cobalt and cesium were derived from two different experimental runs. The concentrations for the first run were the same as those of strontium. Lower concentrations were used in the second run in order to better evaluate the sorption isotherms of cobalt and cesium. Concentrations of 10 and 100 mg/L were common to both runs.

Radioanalysis

Samples of solution from the batch studies were analyzed by radioactivity measurements of the tracers applied (^{60}Co , ^{137}Cs and ^{85}Sr). A NaI (Th) crystal detector photomultiplier system configured with a multi-channel pulse-height analyzer was used for integrating peak areas representative of the radionuclide of concern.

Raw data at equilibrium conditions, and for each initial concentration, were organized as defined by the Linear, Langmuir, Freundlich and Modified Freundlich equations in TABLE II. Linear regression analysis yielded the empirical parameters and correlation coefficients for those equations (TABLE II). The correlation coefficients for all the models are reasonably good with the highest value being associated with the Modified Freundlich equation.

The basic data and solutions to those derived equations are log transformed and presented for comparison in Fig. 1. For cobalt the Modified Freundlich equation provides the best fit over the entire range of concentrations; the Freundlich equation fits reasonably well at the lower concentrations while the Langmuir fits well at the higher concentrations. For cesium the Freundlich and Modified Freundlich equations fit the data reasonably well over the entire range of concentrations; the Linear and Langmuir equations provide poor fits. For strontium all but the Linear equation fit the data reasonably well. Based on the comparisons in Fig. 1 and the correlation coefficients presented in TABLE II the Modified Freundlich equation appears to provide the best fit for all the solutes. It should be noted that modeling by the Linear expression is poor even though a reasonably high degree of correlation (R^2) is indicated.

Boyd et al modified the Langmuir equation to account for two-solute competitive adsorption. This equation was evaluated for cobalt, cesium or strontium and calcium with poor results.⁹ This analysis is not included on behalf of brevity.

Figure 2 represents the data for each solute as modeled by the Modified Freundlich equation according to Eq. (7) which provides a means for evaluating the empirical constants A and β .

The strong linearity presented by the Modified Freundlich isotherm equation over the whole range of concentrations demonstrates its powerful ability to represent sorption at tracer quantities of solutes as well as high concentrations (~ 0 -500 mg/L). Moreover, its empirical constants provide a means for visualizing the general sorption process relative to the distribution of sorptive energies imparted by the exchange surface.

The definition of $m(q)$ and q were used with the corresponding empirical constants to produce the distributions shown in Fig. 3. These distributions indicate that the tuff has the greatest distribution of affinities for cesium and the least for strontium. The empirical constant A is also a measure of a weighted average K_D and the empirical constant β is also a measure of the spread (coefficient of variation) of the individual K_D 's about the average value. The data in TABLE II indicate that the average K_D value is greatest for cobalt. This suggests that in a dynamic system in which sorption equilibrium exists, on the average, cobalt would move the slowest and strontium the fastest. On the other hand, cesium would show the greatest "chemical dispersion" and strontium the least. Historically, solute dispersion has been attributed to physical dispersion processes. However, the above results suggest that "chemical dispersion" could be an important factor in the modeling of solute transport through porous media.

The raw data were also arranged in accordance with Eq. (15); $\log(S/(S_{\text{max}}-S))$ is plotted against $\log C_1$ within the 10-90% saturation region (Fig. 4).

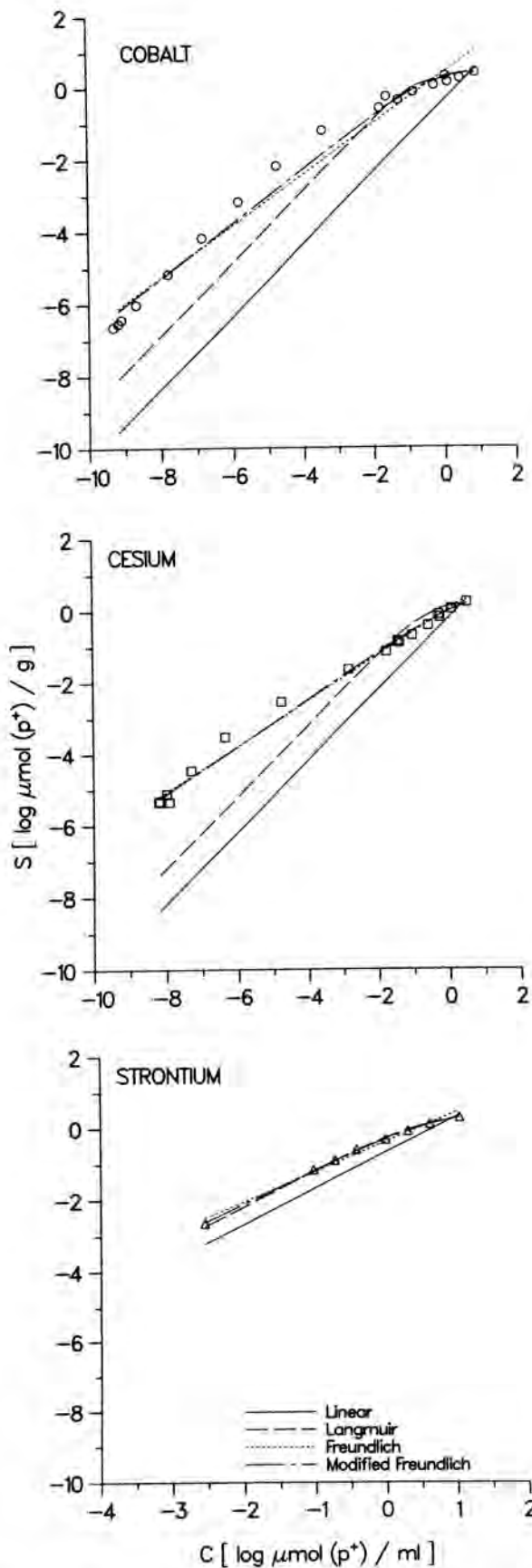


Fig. 1. Modeling of sorption equilibrium data for cobalt, cesium, and strontium by the Linear, Langmuir, Freundlich, and Modified Freundlich equations.

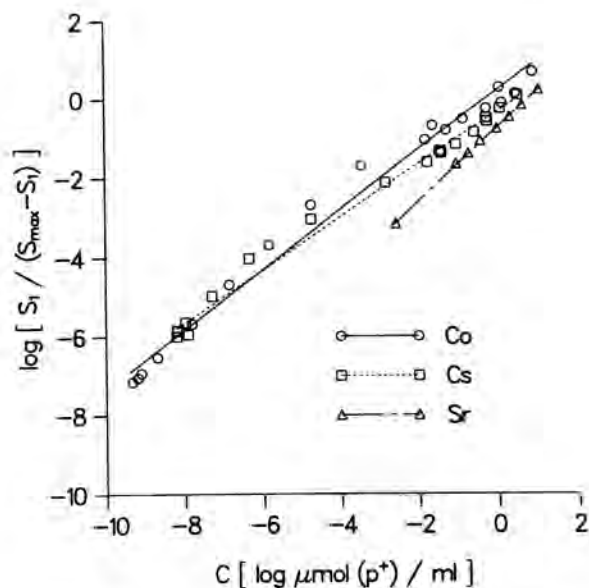


Fig. 2. Modeling of sorption equilibrium data for cobalt, cesium, and strontium by the Modified Freundlich equation.

Reliability of data is usually much better around the region of 50% saturation (15% to 85%) than in regions above and below.⁷ An analysis of the region of low saturation in Fig. 4 yields a slope less than one for all the solutes. A slope less than one indicates that sorption at one site is impeded by sorption at other sites (negative co-operativity). The intensity or degree of negative co-operativity is different for each of the solutes; e.g. cobalt has the greatest negative co-operativity and strontium the least. Analysis of the region of higher saturation yields a

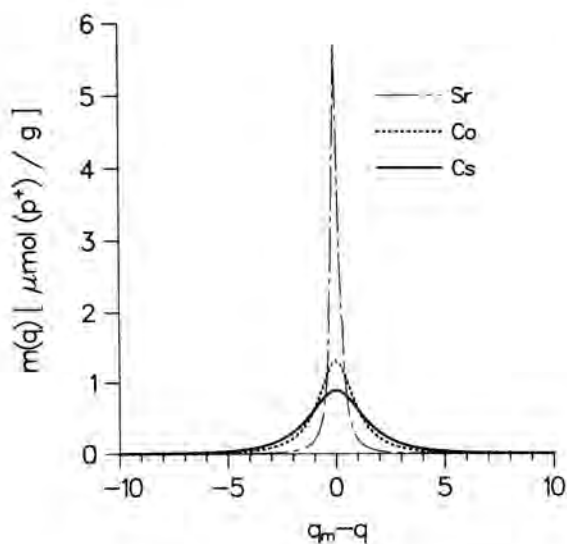


Fig. 3. Frequency distribution of the relative affinities of cobalt, cesium, and strontium for sorption sites as derived from the constants of the Modified Freundlich equations.

TABLE II
Statistical and Empirical Data Estimated from Isotherm Equations for Sorption of Cobalt, Cesium, and Strontium on Bandelier Tuff

	Isotherm			
	Linear	Langmuir	Freundlich	Modified Freundlich
Equation	$S = K_D C$	$S = \frac{k b C}{1 + k C}$	$S = K C^N$	$\frac{S_1}{S_{\max} - S_1} = \frac{A}{S_{\max}} C_1^\beta$ $A = S_{\max} K_D^\beta$
Regression	S vs C	C/S vs C	log S vs log C	$\log \frac{S_1}{S_{\max} - S_1}$ vs $\log C_1$
Correlation Coefficient (R^2)				
Co	0.685	0.961	0.972	0.984
Cs	0.888	0.831	0.991	0.991
Sr	0.946	0.981	0.984	0.999
Empirical Constant	K_D	b k	K N	A β K_D
Co	0.446	2.65 5.07	2.68 0.711	5.38 0.752 1.91
Cs	0.661	1.82 3.47	1.16 0.643	1.54 0.665 0.319
Sr	0.224	2.86 0.245	0.440 0.835	0.627 0.941 0.171

Units: K_D in ml/g; b in $\mu\text{mol (p}^+)/\text{g}$; k in ml/ $\mu\text{mol (p}^+)$; k, N, A and β have units corresponding to S in $\mu\text{mol (p}^+)/\text{g}$ and C in $\mu\text{mol (p}^+)/\text{ml}$.

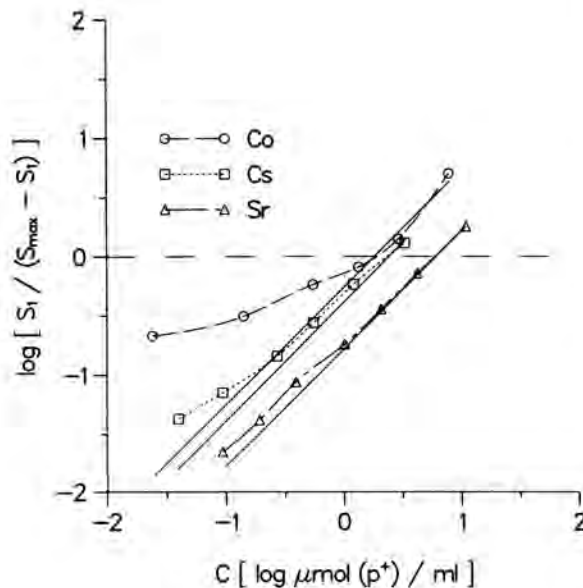


Fig. 4. Hill Plots for cobalt, cesium, and strontium about the 50% saturation zone. The solid lines have slopes equal to one.

slope slightly greater than one for cobalt and a slope of about one for cesium and strontium. Therefore, the sorption of cobalt at one site tends to be enhanced by sorption at other sites (positive co-operativity); on the other hand, sorption of cesium and strontium tends to be independent of sorption at other sites (zero co-operativity).

The results of the Hill Plot analysis suggest that the degree of sorption and of "chemical dispersion" should be greatest for cobalt and least for strontium. Those results differ from those of the Modified Freundlich analysis in that the latter suggests that "chemical dispersion" should be greatest for cesium. That difference between the two analyses may be attributed to the fact that the Modified Freundlich analysis is based on the whole range of data and the Hill Plot analysis is based on a restricted range of data.

CONCLUSIONS

From the evaluation and comparison of the Linear, Langmuir, Freundlich and Modified Freundlich isotherm equations, it is concluded that the latter model fits best the equilibrium behavior for cobalt, cesium, and strontium in the range of solute concentrations between ~ 0 and 500 mg/L.

The empirical parameters estimated from the Modified Freundlich isotherm equation indicate that in a dynamic system of water moving through Bandelier Tuff in which sorption equilibrium exists, strontium will move the fastest and cobalt the slowest; but cesium will exhibit the greatest "chemical dispersion" and strontium the least.

Finally the analysis of the Hill Plots for cobalt, cesium and strontium indicates that at a relatively low degree of saturation, sorption at one site impedes

sorption at other sites (negative co-operativity). The sorption of cobalt exhibits the greatest amount of impedance; sorption of strontium only exhibits a minimal amount. On the other hand, sorption at 50% saturation or above differs from that at the lower saturation. Strontium and cesium exhibits zero co-operativity and cobalt exhibits positive co-operativity.

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