

NONEQUILIBRIUM SORPTIVE BEHAVIOR OF COBALT, CESIUM AND STRONTIUM ON BANDELIER TUFF: EXPERIMENTS AND ANALYSIS

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ABSTRACT

Information is presented on the nonequilibrium sorption of cobalt, cesium and strontium on Bandelier Tuff. Both adsorption and desorption were studied in the batch mode at 25°C with constant mixing. The reaction solutions consisted of 20 mg/L of stable cobalt, cesium or strontium with their radioactive tracers ^{60}Co , ^{137}Cs or ^{85}Sr in 0.01N CaCl_2 solution.

Adsorption equilibrium occurs rapidly for strontium, somewhat more slowly for cesium, and very slowly for cobalt. The degree of adsorption is approximately 19% for strontium, 49% for cesium, and 84% for cobalt. Desorption (leaching) initially occurs in a relatively rapid step followed by a much slower rate. The relative adsorption and desorption rates can be explained or predicted by theoretical considerations of the Modified Freundlich isotherm and Hill Plot analyses of equilibrium sorption data. The Modified Freundlich isotherm analysis predicts that soil will exhibit ranges in relative energies of sorption and in reaction rates; the Hill Plot analysis predicts interactions among sorption sites. Nonequilibrium sorption data indicate that the ranges in relative energies and reaction rates are different for specific solutes and are dependent on interactions among sorption sites; the greater the interaction among sorption sites, the greater the range of reaction rates.

The results of this study suggest that equilibrium models may be adequate to describe the movement of strontium in Bandelier Tuff under dynamic flow conditions. However, nonequilibrium models, in all probability, will be needed to describe the movement of cesium and cobalt under those same conditions.

INTRODUCTION

The Los Alamos National Laboratory (Los Alamos) has been conducting field and laboratory studies to assist the Nuclear Regulatory Commission (NRC) in improving leaching and transport information used to assess the performance of low level waste disposal sites.

As part of the laboratory studies, Los Alamos has performed batch experiments leading to the evaluation of nonequilibrium and equilibrium behavior of solutes representative of waste radionuclides on Bandelier Tuff. The purpose of these studies is to improve the understanding of physicochemical processes occurring between radionuclides and soil in laboratory and field studies and to produce recommendations on the modeling and interpretation of the transport of solutes. Present literature suggests that the movement of a solute under nonequilibrium sorption conditions could be significantly different from that under equilibrium sorption conditions.^{1,2,3}

The equilibrium sorption of cobalt, cesium and strontium define three contrasting levels of "chemical dispersion" or, in more conventional terms, three representative degrees of retardation.⁴ The empirical constants of the equilibrium models that support the theoretical presence of such a "chemical dispersion" concept⁵ may also be related to a distribution of sorption rates.⁶ If this connection exists, then it should be expected that solutes showing more equilibrium "chemical dispersion" would also exhibit wider ranges in sorption rates. A wide range in sorption rates may imply that sorption will not be absolutely instantaneous as is usually assumed for ion exchange reactions.

It is also reasonable to expect that interaction among sorption sites should result in a range of reaction rates some of which will not be instantaneous. A Hill Plot analysis of the equilibrium sorption data for the three solutes indicates that at a degree of sorption saturation comparable to that for this nonequilibrium study, solutes should exhibit a negative interaction of sorption sites, i.e. sorption at one site should impede sorption at other sites.⁴ Cobalt should show the greatest amount of interaction; strontium should show only a minimal amount. Thus, if the above relation holds, cobalt should show the greatest range in sorption rates and strontium the least.

This paper presents the preliminary results from the nonequilibrium batch experiments for cobalt, cesium and strontium. The objectives are to compare rates of adsorption and desorption reactions of cobalt, cesium and strontium over various time intervals and to interpret differences in reaction rate behavior of the three solutes from theoretical considerations of equilibrium and nonequilibrium concepts.

The results presented in this paper focus on the general phenomenon of sorption; no commitment is made to any mechanism, i.e. adsorption (a net accumulation at an interface), ion exchange or precipitation. Such a commitment would require additional detailed data on the soil and/or the soil solution chemical composition before and after sorption occurs.

MATERIALS AND METHODS

Soil Aspects

Bandelier Tuff is described geologically as a volcanic ash flow material composed mostly of silicic glass having a grain distribution close to that of a silty sand. After crushing, the tuff was air dried and sieved through a No. 18 Tyler brass screen.

The cation exchange capacity (CEC) for the tuff was estimated at about $3.3 \mu\text{mol}(\text{p}^+)/\text{g}$ within a pH range from 7.0 to 9.0. In order to simplify evaluation of tracer sorption the material used in the experiments was saturated with calcium by contact with a 0.01N (200 mg/L) CaCl_2 solution. More details on the procedures of soil characterization and preparation are described by Polzer et al on equilibrium studies for the same solutes.⁴

Batch Tests

The experiments were conducted in 1000-ml polyethylene bottles in the batch mode at soil-water mixtures of 1:4 (100 g of tuff preconditioned with calcium solution and 400 ml of 0.01N CaCl_2 solution). The calcium solution contained 20 mg/L of the stable solute and a spike of its respective radionuclide (^{60}Co , ^{137}Cs , or ^{85}Sr) as a tracer at an activity level of 1.85 MBq/L in the working solution. This resulting solution remained in equilibrium over 24 hours before soil was added.

Once capped, the bottles were immersed in a water bath shaker at $25 \pm 1^\circ\text{C}$ and pressure defined by ambient room conditions. Mixing conditions were maintained constant throughout the experiments by fixing the shaking rate at 130 strokes per minute in 2.5-cm stroke lengths.

Sample aliquots were drawn from the shaking reaction bottle using a syringe-filter setup. The syringe was a 10-cm³ disposable plastic syringe. Two types of filter holders were used: one was disposable with a 0.45 μm pore diameter filter for sampling at closely spaced time intervals and the other was reusable with 0.45 μm filters for sampling at widely spaced time intervals. A length of 1/4 inch o.d. tygon tubing was attached to the filter and immersed in the soil-water mixture for the purpose of taking a sample. Sampling intervals were spaced as needed to define changes in the second(s), minute(min) and hour(h) ranges.

Each reaction bottle was subjected to two consecutive stages; adsorption and desorption (or leaching). Each was allowed to proceed until equilibrium was reached. At the end of the adsorption stage, the soil-water mixture was vacuum filtered through a 0.45 μm filter to separate the liquid and the solid phases. The immediate addition of fresh 0.01N CaCl_2 solution initiated the desorption stage of the experiment. Each solute was studied in duplicate.

Sample Analysis

The collected samples (in known volumes of about 1 ml) were gamma counted for the tracer of interest. A NaI (Th) crystal detector-photomultiplier system configured with a multi-channel pulse height analyzer was used to quantify the tracer.

As mentioned above solutions from the reaction bottles were separated from the solids by filtration through 0.45 μm filters. Solutes sorbed to colloidal matter of a size less than 0.45 μm , if present in sufficient quantities, could adversely affect the

interpretation given to the results of the nonequilibrium rate studies. Therefore additional separations were performed on solutions extracted from several soil-water mixtures to evaluate the presence of adsorbed solutes in solutions filtered through 0.45 μm filters. Solutions, separated from the mixture at 0.05 μm by centrifugation and at 0.0016 μm by ultrafiltration, were radioassayed to evaluate the presence of colloidal matter containing adsorbed solutes. Those results are given in Table I. Differences between concentrations of tracers in solutions filtered through 0.45 μm filters and in solutions either filtered or centrifuged to remove smaller size colloidal matter were slight and not considered significant.

RESULTS AND DISCUSSION

The results of the nonequilibrium sorption of cobalt, cesium and strontium on Bandelier Tuff are expressed in terms of solute concentration as a function of the contact time between soil and solute. Both the adsorption and desorption experiments are analyzed in three time domains: instantaneous, (0-120 s), short-term (0-240 min) and long term (0- >180 h). This breakdown of time domains grossly relates to the effect of pore water velocities on residence (or contact) time in continuous flow scenarios. It has been demonstrated that, as the pore water velocity increases, residence times of solute decrease and equilibrium behavior (fast rates of reaction) tends to control the sorption process; whereas, as the pore water velocity decreases (longer residence time) nonequilibrium behavior (slow rates of reaction) tends to play a more significant role in controlling the sorption process. Hence, observations from the various time domains should provide an insight into the expected kinetics and extent of sorption for transport and leaching events.

Adsorption data are presented in Figs. 1, 2 and 3. In the instantaneous domain (Fig. 1), a rapid adsorption occurs in the first 10 s (10% cobalt, 22% cesium and 6% strontium) with cesium and strontium adsorption reaching a pseudo-equilibrium plateau soon afterwards, whereas cobalt adsorption continues to increase. A similar pattern occurs in the short-term domain (Fig. 2) with levels of adsorption at the 180th minute of 34% cobalt, 39% cesium and 19% strontium. The long-term domain (Fig. 3) shows that cesium and strontium reach equilibrium at the 40th and 20th hours respectively. Cobalt, on the other hand, continues to be adsorbed at a slow and nearly linear rate. By the 180th hour, cobalt presents the highest level of adsorption (84%) and strontium the lowest (19%) with cesium showing an intermediate value (49%). Solution concentrations and adsorption percentage at representative contact times of the three time domains are compiled in Table II.

The graphed comparison of the nonequilibrium adsorption behavior throughout the entire time domain (Fig. 3) suggests that the gradual adsorption of cobalt, the faster adsorption of cesium and much faster adsorption of strontium correspond to a respective increase in the range of reaction rates.⁶ This observation appears to agree with the theoretical expectation that "chemical dispersion" is least for strontium as predicted by the analysis of equilibrium

TABLE I

The Effectiveness of Colloidal Removal by Filtration
Through 0.45 μm Pore Diameter Filters

Kinetic Adsorption Run				
Solute	Equilibration time (hours)	0.45 μm filter (cts/min/ml) ¹	0.0016 μm ultrafilter (cts/min/ml) ¹	Ratio
⁶⁰ Co	184	273	266	1.03
	191	173	175	0.99
¹³⁷ Cs	189	933	852	1.10
	191	968	937	1.03
⁸⁵ Sr	190	123	122	1.01
	190	120	117	1.03

¹Single samples from duplicate reactors.

Kinetic Desorption Run				
Solute	Equilibration time (hours)	0.45 μm filter (cts/min/ml) ²	0.05 μm centrifuged (cts/min/ml) ²	Ratio
⁶⁰ Co	740	27.9	24.2	1.15
		24.8	23.4	1.06
¹³⁷ Cs	622	268	297	0.90
		263	294	0.89
⁸⁵ Sr	624	29.2	27.3	1.07
		--	28.4	--

²Duplicate samples from single reactor.

TABLE II

Solution Concentration and Percentage of Adsorption of
Cobalt, Cesium, and Strontium at Different Contact Times¹
(Initial Solution Concentration = 20 mg/L; T = 25°C)

Solute	Time Domain		
	Instantaneous (10 s)	Short-term (180 min)	Long-term (180 h)
Cobalt	18.0 mg/L; 10%	12.6 mg/L; 34%	2.2 mg/L; 84%
Cesium	15.6 mg/L; 22%	12.2 mg/L; 39%	10.2 mg/L; 49%
Strontium	18.8 mg/L; 6%	16.3 mg/L; 19%	16.2 mg/L; 19%

¹Percentages were determined with respect to the initial solution concentration.

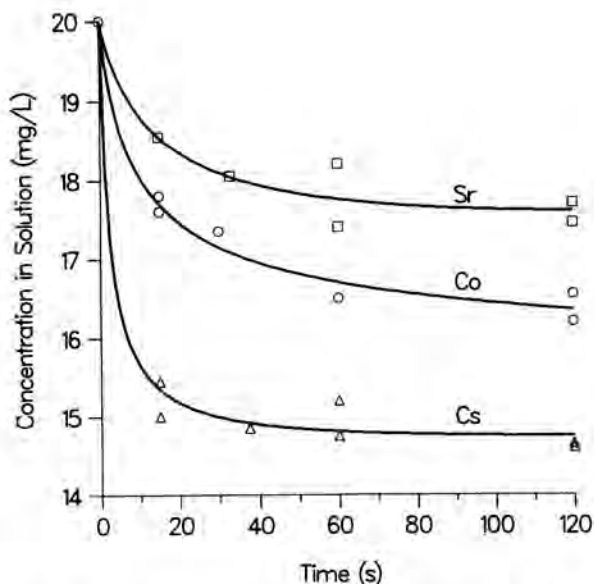


Fig. 1. Adsorption behavior of cobalt, cesium and strontium on Bandelier Tuff in the instantaneous phase at 25°C.

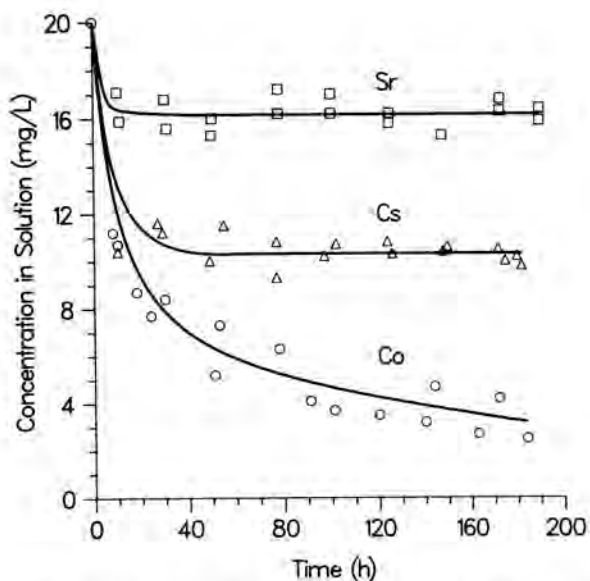


Fig. 3. Adsorption behavior of cobalt, cesium and strontium on Bandelier Tuff in the long-term phase at 25°C.

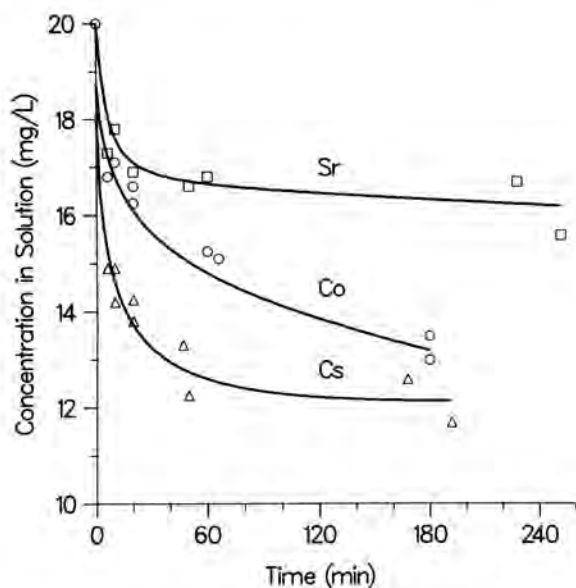


Fig. 2. Adsorption behavior of cobalt, cesium and strontium on Bandelier Tuff in the short-term phase at 25°C.

adsorption data based on the Modified Freundlich isotherm.⁴ Differences between rates of cesium and cobalt adsorption do not, however, fit that interpretation. On the other hand, the above observation does agree with the theoretical expectation based on Hill Plot analysis, i.e. interaction among adsorption sites is least for strontium and greatest for cobalt.⁴ The probable reason for the discrepancy between the theoretical expectation of the Modified Freundlich isotherm and that of the Hill Plot is that the interpretation of the Modified Freundlich isotherm is based on empirical constants averaged over a wide range of concentrations whereas the Hill Plot interpretation is based on a restricted range of concentrations; the

nonequilibrium sorption data is restricted to initial concentrations of about 20 mg/L for each of the solutes.

Although the curves of Figs. 1, 2, and 3 were not fitted to a specific model three regions of reaction rates can be inferred. The first region, within the initial time domain, can be described as a region in which the rates of reaction tend to be independent of concentration, thus little interaction among sorption sites occurs. Reactions in this time domain tend to be instantaneous or very rapid and are usually attributed to ion exchange processes; however, other very rapid chemisorption and diffusion processes cannot be excluded. The second region can be described as the curvilinear region in which rates are dependent on concentration, thus interaction among sorption sites is suggested. The time span of curvilinearity appears to be greatest for cobalt and least for strontium; the number of interactions among sorption sites, therefore, should be greatest for cobalt and least for strontium. The reactions in this region tend to be slower than those in the first region and are usually attributed to chemisorption controlled processes or processes controlled by diffusion. The third region can be described as that region in which no change in concentration is observed because equilibrium has been reached. All three regions can be observed for cesium and strontium. However, the third region is not present for cobalt, i.e., equilibrium had not been achieved during the experiment.⁹ Any additional adsorption will probably be regulated by either internal diffusion or surface chemical kinetics.

The desorption (leaching) of cesium, cobalt and strontium from Bandelier Tuff is presented graphically in Fig. 4 (instantaneous domain), in Fig. 5 (short-term domain) and in Fig. 6 (long-term domain). Solution concentrations and percentage of total desorption for contact times in the three time domains are presented in Table III. In the first 10 s of the instantaneous region 75% cobalt, 50% cesium and 34% strontium desorbed. These percentages were determined with respect to the final equilibrium solution concentrations. The changes in concentration are exponential in nature and reach a temporary pseudo-steady state in approximately 100 s (Fig. 4). A similar pattern occurs in the

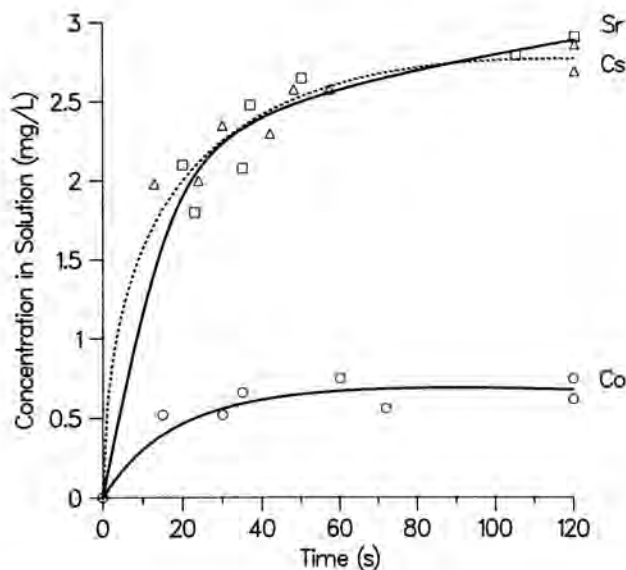


Fig. 4. Desorption behavior of cobalt, cesium and strontium from Bandelier Tuff in the instantaneous phase at 25°C.

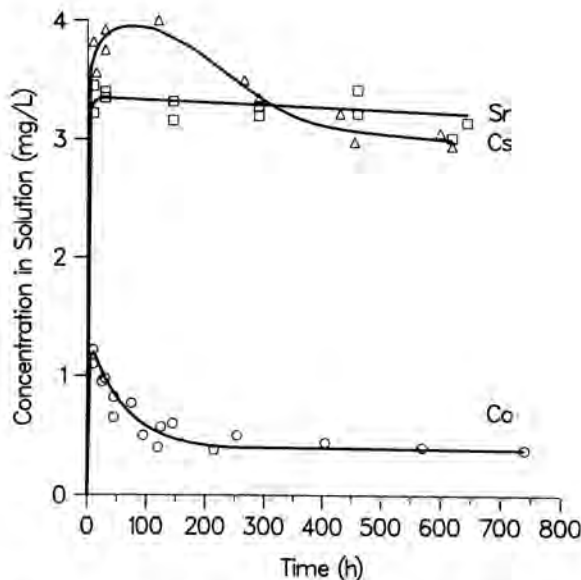


Fig. 6. Desorption behavior of cobalt, cesium and strontium from Bandelier Tuff in the long-term phase at 25°C.

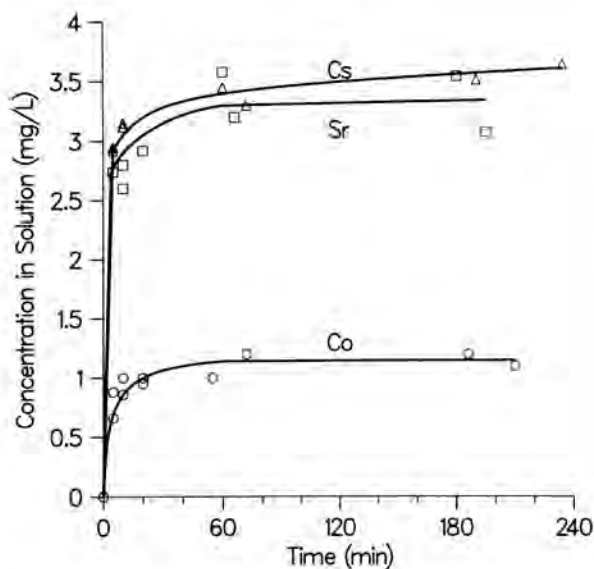


Fig. 5. Desorption behavior of cobalt, cesium and strontium from Bandelier Tuff in the short-term phase at 25°C.

short-term phase (Fig. 5). That behavior has been attributed to surface chemical kinetics because diffusion is minimized in continuously stirred systems.⁸

In the short-term phase desorption percentages of 300% cobalt, 120% cesium and 103% strontium are observed. These values, higher than 100%, indicate an apparent degree of desorption higher than the equilibrium concentrations at longer contact times. This effect corresponds to the pronounced peak for cobalt and cesium depicted by the long-term representation of Fig. 6. The peak does not seem to develop in the case of strontium or, if present, is negligible. This transitional high desorption followed by further adsorption has been observed by other investigators.⁹

One possible explanation of that phenomenon is based on the interpretations of the Modified Freundlich and Hill Plot analyses. Negative interactions among sorption sites exist in the order cobalt > cesium > strontium.

The range in sorption energies and in reaction rates should be in the same order. Although the range in reaction rates is narrow for strontium, those rates are rapid because of low energies of sorption. On the other hand, cobalt and cesium exhibit a wide range in reaction rates, some being rapid and others being slow. In the desorption phase of the experiment, the solutions reach pseudo-equilibrium with respect to the rapid reactions (low energies of sorption). Thus the concentration of solute will exceed that in which equilibrium is reached with respect to the slow reactions (high energies of sorption). Because strontium exhibits primarily fast rates of reactions pseudo-equilibrium is not observed to any extent.

Cobalt appears to reach desorption equilibrium faster than does cesium (Fig. 6). We attribute that to the fact that adsorption equilibrium had not been reached in the cobalt experiment at the time that desorption was initiated. Therefore, the very slow reactions that would have occurred while reaching equilibrium, did not. Thus those very slow reactions were not involved in the desorption phase.

Finally, the distribution coefficient, K_D , at the equilibrium state for both adsorption and desorption were computed and are given in TABLE IV. Because cobalt did not reach equilibrium in the adsorption stage, an estimate was made by extrapolation of the final portion of the curve in Fig. 3. Ratios of the K_D for desorption to the K_D for adsorption yield a value of 5.4 for cobalt, 2.3 for cesium and 0.9 for strontium. Sorption reversibility should yield a ratio of one. However, differences in total concentration of solutes between the adsorption and desorption experiments could account, in part, for the deviation of the ratios from one; a greater K_D is expected at a lower total concentration.⁴ The degree of irreversibility is consistent with the degree of

TABLE III

Solution Concentration and Percentage of Desorption of Cobalt, Cesium, and Strontium at Different Contact Times¹
(Initial Solution Concentration = 0 mg/L; T = 25°C)

Solute	Time Domain		
	Instantaneous (10 s)	Short-term (180 min)	Long-term (600 h)
Cobalt	0.3 mg/L; 75%	1.2 mg/L; 300%	0.4 mg/L; 100%
Cesium	1.5 mg/L; 50%	3.6 mg/L; 120%	3.0 mg/L; 100%
Strontium	1.1 mg/L; 34%	3.3 mg/L; 103%	3.2 mg/L; 100%

¹Percentages were determined with respect to the equilibrium solution concentration.

TABLE IV

Equilibrium Distribution Coefficients, K_D , for Adsorption and Desorption of Cobalt, Cesium, and Strontium

Solute	K_D (L/kg)		$(K_D)_{de}$
	Adsorption	Desorption	$(K_D)_{ad}$
Cobalt ¹	32	174	5.4
Cesium	4	9	2.3
Strontium	0.9	0.8	0.9

¹Determined by extrapolation of the curve in Fig. 3.

interaction among sorption sites, i. e., cobalt > cesium > strontium. Further study is needed to evaluate the cause of the apparent sorption irreversibility of cobalt and cesium.

CONCLUSIONS

The results of the nonequilibrium sorption study indicate differences in the sorptive behavior of strontium, cobalt and cesium on Bandelier Tuff. The degree of sorption is greatest for cobalt and least for strontium. On the other hand, the overall rates of adsorption and desorption are greatest for strontium and least for cobalt. The overall rates can be categorized into two general time domains. In one time domain the rates are rapid and can be described as independent of solute concentration. In the other time domain the rates of sorption are slow and can be described as exponential in nature or concentration dependent. The overall rates of sorption for strontium are comprised mostly of the very rapid rates. The overall rates for cobalt and cesium include a range of slower reactions in addition to rapid rates. Cobalt exhibits a wider range of reaction rates than does cesium.

The differences in rates and degree of sorption for strontium, cesium and cobalt are in agreement with the differences in "chemical dispersion" predicted by the analyses of the adsorption equilibrium data for

those solutes on Bandelier Tuff. The predicted "chemical dispersion" is based on the theory of the Hill Plot and Modified Freundlich isotherm analyses; the more rapid and the narrower the range in sorption rates, the sharper the peaks and the narrower the tailing of solutes in breakthrough curves of dynamic flow systems. The movement through Bandelier tuff should be the most rapid with the least amount of dispersion for strontium and the least rapid with the greatest amount of dispersion for cobalt. The differences in sorption rates also suggest that in a dynamic system the movement of strontium can probably be predicted using equilibrium type models whereas the movement of cesium and cobalt can only be predicted with nonequilibrium type models.

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REFERENCES

1. M. Th. Van Genuchten and R. W. Cleary, "Movement of Solutes in Soil: Computer-Simulated and Laboratory Results," in G. H. Bolt, Soil Chemistry - B: Physico-Chemical Models, Elsevier Scientific, New York, NY (1982).
2. D. E. Elrick, K. T. Erh, and H. K. Krupp, "Applications of Miscible Displacement Techniques to Soils," Water Resour. Res., 2, 717 (1966).
3. D. Schweich and M. Sardin, "Adsorption, Partition, Ion Exchange and Chemical Reaction in Batch Reactors or in Columns-A Review," J. Hydr., 50, 1 (1981).
4. W. L. Polzer, H. R., Fuentes, E. H. Essington, and F. R. Roensch, "Equilibrium Sorption of Cobalt, Cesium and Strontium on Bandelier Tuff: Analysis of Alternative Mathematical Modeling," Waste Management '85, University of Arizona, Tucson, AZ (1985).
5. G. Sposito, "Derivation of the Freundlich Equation for Ion Exchange Reactions in Soils," Soil Sci. Soc. Am.J., 44, 652 (1980).
6. P. J. Crickmore and B. W. Wojciechowski, "Kinetics of Adsorption on Energetically Heterogenous Sites," J. Chem. Soc. Faraday Trans., 173, 1216 (1977).
7. J. G. A. Fiskell, R. S. Mansell, H. M. Selim, and F. G. Martin, "Kinetic Behavior of Phosphate Sorption by Acid, Sandy Soil," J. Environ. Qual., 8, 579 (1979).
8. R. D. Harter and R. G. Lehman, "Use of Kinetics for the Study of Exchange Reactions in Soils," Soil Sci. Soc. Am. J., 47, 666 (1983).
9. D. R. Wiles, "The Radiochemistry of Radium and Thorium in Uranium Mine Tailings," Water, Air, and Soil Poll., 20, 99, (1983).