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AUTHOR(S): H. R. Fuentes
W. L. Polzer
E. H. Essington

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# Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

# EFFECTS OF SORPTION AND TEMPERATURE
## ON SOLUTE TRANSPORT IN
## UNSATURATED STEADY FLOW

H. R. Fuentes, W. L. Polzer, and E. H. Essington
Environmental Science Group, HSE-12
Los Alamos National Laboratory
Los Alamos, NM 87545

## ABSTRACT

It is known that temperature affects physical and chemical processes and that these processes may alter the transport of solutes in the environment. Laboratory column studies were performed in unsaturated flow conditions with a composite pulse containing iodide, cobalt, cesium and strontium each at $10^{-3}$ M. The experiments were performed with Bandelier Tuff and produced breakthrough curves that indicate significant changes in transport due to a temperature change from 25°C to 5°for nonconservative solutes. Also the interpretation of the temperature and sorption data suggest that the differences in transport between 5°C and 25°C for nonconservative solutes may be predicted in a qualitative manner from batch equilibrium and nonequilibrium sorption data and the theory of sorption used in deriving the modified Freundlich isotherm equation. These effects should be of concern in modeling and management of spills and waste disposal within this range of environmental temperatures.

## INTRODUCTION

The Environmental Science Group at the Los Alamos National Laboratory has conducted field caisson experiments to evaluate concepts and strategies for low level radioactive waste land disposal in arid environments. Flow and contaminant transport problems in surface and subsurface systems have been studied. Laboratory batch and column studies have been conducted in support of those field experiments. In recognizing the effect of temperature on chemical processes, e.g. on sorption, as well as on physical processes, e.g. on hydraulic conductivity, a set of laboratory column experiments were designed to evaluate the overall effect of environmental temperature changes on solute transport in the unsaturated zone. It is also recognized that sorption will retard the movement of solutes. In this paper the effects of sorption and temperature on solute transport will be evaluated and interpreted on the basis of the theory of sorption of solutes according to the modified Freundlich isotherm. The results of this study should aid in the interpretation of the effectiveness of current modeling efforts which include codes that assume isothermal and linear sorption behavior.

## THEORY

In previous work[1,2] batch equilibrium and nonequilibrium sorption experiments were conducted and interpreted on the basis of the theory used to derive the modified Freundlich equation. Those results indicated that heterogeneity is involved in the sorption of nonconservative (sorbing) solutes. As a result of that heterogeneity, sorption can be expressed in terms of a mean $K_D$ (indicator of sorption energy) and the distribution of individual $K_D$'s (sorption energies) about the mean. That theory also suggests that the rates of sorption of a solute are related to their sorption energies, e.g., rates can be expressed in terms of a mean and the distribution of individual rates about the mean. Therefore under dynamic flow and sorption equilibrium conditions, dispersion of solutes should occur due to sorption processes (chemical dispersion over and above the physical dispersion due to flow dynamics). This chemical dispersion could affect the transport of solutes. Competition among solutes may also affect (reduce) the rates of sorption[3], thus affecting chemical dispersion.

In the case of sorption of solutes on Bandelier Tuff at 25°C, chemical dispersion is predicted to be the greatest for cesium and least for strontium. On the other hand, transport is predicted to be the greatest for strontium and the least for cobalt.

Under dynamic flow conditions transport may be predicted in terms of equilibrium sorption, if sorption occurs rapidly. On the other hand, transport may best be predicted in terms of nonequilibrium sorption, if sorption occurs slowly.

Temperature should also affect rates of sorption according to the Arrhenius theory[4]. If the energy of activation is large, then temperature changes will have a considerable effect on rates. If the energy of activation is small, then temperature changes will have very little effect on rates of sorption. The previous work[2] indicates that strontium has the fastest average rate of sorption and cobalt the slowest average rate of sorption on Bandelier Tuff. Therefore changes in temperature should affect the transport of cobalt to the greatest extent and the transport of strontium to the least extent.

## EXPERIMENTAL FEATURES

Bandelier tuff was the soil matrix used in the experiments. This material is a silicic glass with a size distribution typical of a silty sand. Its cation exchange capacity is about 3.3 μmol (p+)/g. Tuff samples are obtained from a local quarry and crushed. Only sizes less than 1mm (Tyler No. 18) were used for laboratory work. Previous batch experiments[1] showed that cobalt, cesium and strontium should adsorb on the tuff to different extents. Thus a representative composite of iodide, cobalt, cesium and strontium was chosen to be simultaneously applied to the columns. Iodide was included to define the flow pattern through the columns and to reference the movement of the other solutes. These stable solutes were added as KI,

$CoCl_2 \cdot 6H_2O$, CsCl, and $SrCl_2 \cdot 6H_2O$, each at a concentration of 0.001 N. All these substances were applied in a 0.01N (or 200 ± 10 mg/L) $CaCl_2$ solution, which also contained $^{60}Co$, $^{137}Cs$ and $^{85}Sr$ as radioactive tracers. Both influent and effluent were characterized by EDTA titration for $CaCl_2$, by a specific ion electrode for iodide, and by radioanalysis for $^{60}Co$, $^{137}Cs$ and $^{85}Sr$.

Lucite columns of 40 cm x 3.8 cm i.d. were packed with approximately 30 cm (500 g) of compacted tuff. The columns were operated under vacuum to maintain a uniform moisture profile of about 20 percent. Influent solutions were applied at a flow rate of about 30 $cm^3/d$ by precision peristaltic pumps[5]. Columns were run in two temperature-controlled chambers one at 5° and the other at 25°C. Duplicate columns were run at each temperature condition. During the addition of the pulse of solutes the flow rate was higher (about 48 $cm^3$/day) at 25°C than that at 5°C (about 33 $cm^3$/day).

In order to simplify evaluation of tracer sorption the tuff was preconditioned with 0.01N $CaCl_2$ solution. Once the columns were packed, 0.01N $CaCl_2$ was passed through the columns for at least three column pore volumes which was higher than the minimum requirement for conditioning. During this conditioning period the vacuum and the respective flow rates were adjusted to target values. Next a 48-hour pulse of a composite of the selected solutes and tracers in 0.01N $CaCl_2$ solution was applied to all the columns, immediately followed by the continuous addition of 0.01N $CaCl_2$ solution and by continuous effluent sampling. The total amounts of solutes added was greater at 25°C than at 5°C because of the faster flow rate at 25°C during the addition of the pulses. The amounts added as indicated by the pore volumes of the pulses were 1.00 and 1.02 for the duplicates at 25°C and 0.66 and 0.56 for the duplicates at 5°C. Effluent sampling varied between 4 and 72 hours in accordance with changes in the breakthrough of solutes.

## RESULTS AND DISCUSSION

A concern in conducting these experiments was reproducibility of the duplicate columns. At each temperature columns were prepared, treated, and operated in duplicate. Figures 1 and 2, respectively, depict the breakthrough curves for the duplicates at 5°C and at 25°C. Comparison of the breakthrough curves at 5°C indicates good reproducibility. Comparison of breakthrough curves at 25°C indicates good reproducibility for all but one of the solutes; that solute was cobalt. Although the migration of cobalt at 25°C produced a similar tailing, for the duplicates the leading ends appeared at significantly different times. That difference in arrival times could possibly be explained qualitatively on the basis that some of the cobalt sorbs very slowly compared to strontium and cesium[2] and that the flow conditions do not allow equilibrium sorption of cobalt to occur. Under those conditions transport tends towards that of a nonsorbing solute. The difference in arrival times of cobalt at 25°C between duplicates could reflect variability in flow rates as well as average differences in flow rate. The flow rate in the first duplicate column was slightly higher than that in the second duplicate column. Also variability in flow at the beginning of the experiment was greater in the first duplicate column. Thus one could expect a faster arrival time of cobalt in the first column, which is consistent with the experimental data.
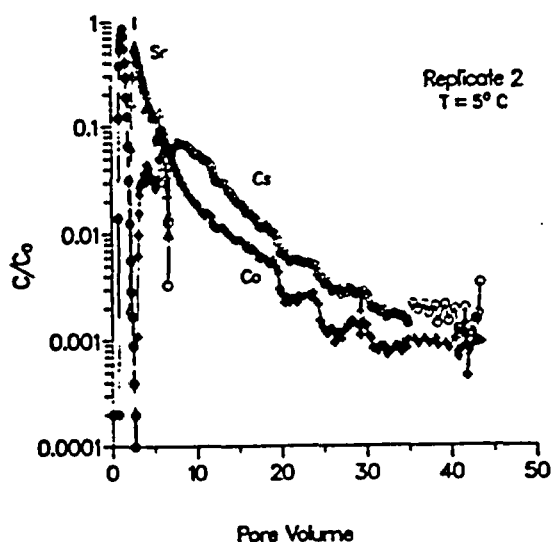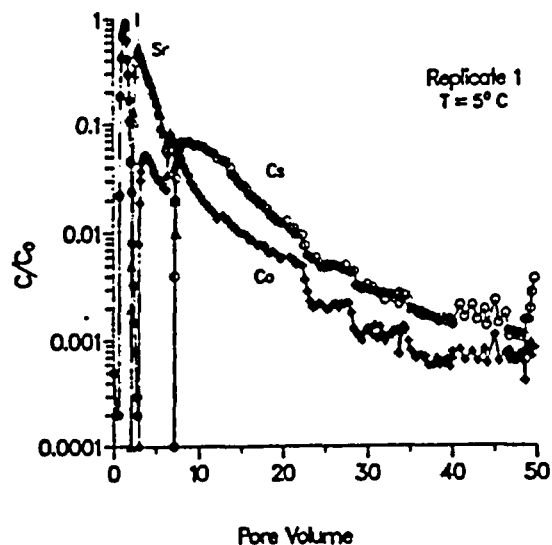


Fig. 1. Comparison of breakthrough curves at 5°C.

The breakthrough curves (peak arrivals) for iodide, strontium, cesium, and cobalt at 25°C (Fig. 2) indicate that of the nonconservative solute strontium is transported the fastest and cobalt the slowest. This sequence is consistent with that predicted from batch experiments[1,2]. The data in Fig. 2 indicate that chemical dispersion is least for strontium and greatest for cobalt. Chemical dispersion is indicated by a combination of peak height and width. Dispersion due to flow dynamics is taken into consideration in evaluating chemical dispersion. The small amount of chemical dispersion of strontium is consistent with that predicted from theory and batch data. However those studies predicted the chemical dispersion of cesium to be greater than that of cobalt. An explanation for this apparent discrepancy in dispersion is that the prediction assumed sorption equilibrium when in fact nonequilibrium sorption was the likely behavior. Under nonequilibrium sorption and flow dynamic conditions, dispersion should be enhanced. The effects of nonequilibrium sorption should be greater on cobalt transport than on cesium transport. Thus the experimental results of transport appear to be

consistent with that predicted.
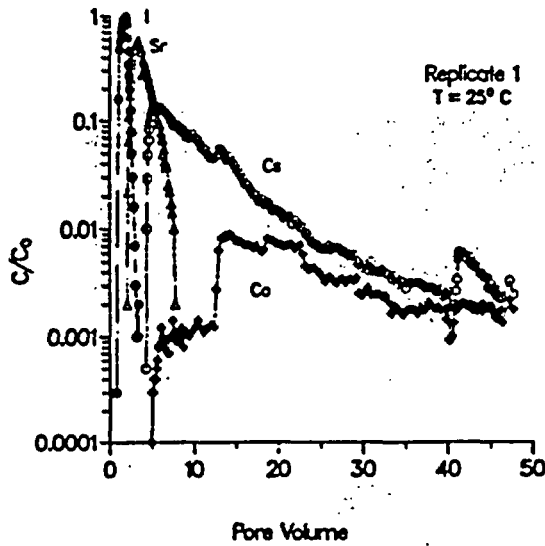
to be sensitive to the change. The effect of the differences in pulse size because of differences in flow rates during the addition of the pulses were interpreted to have little influence on the overall differences in transport between 5°C and 25°C.
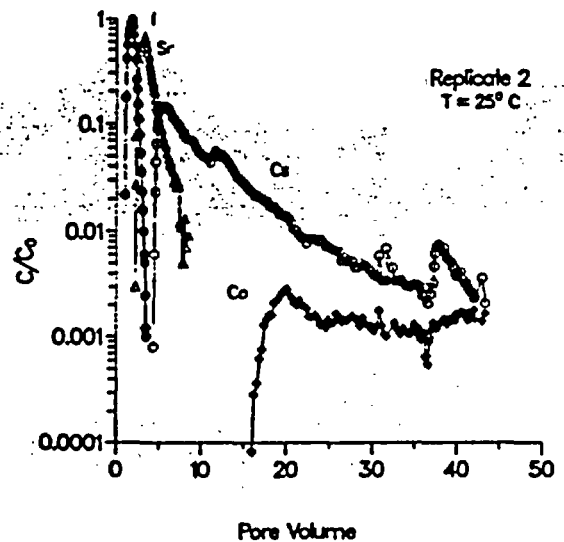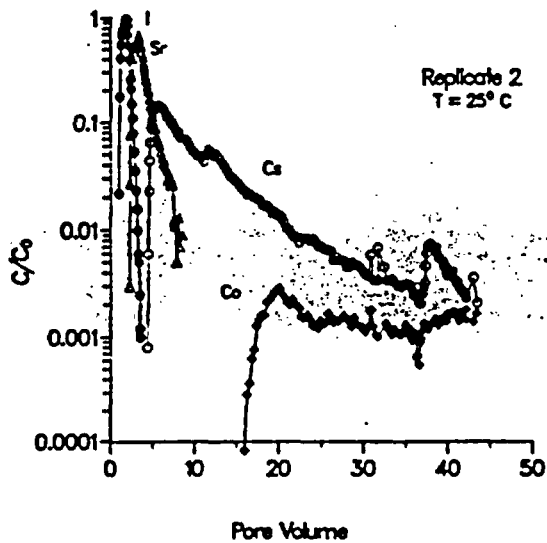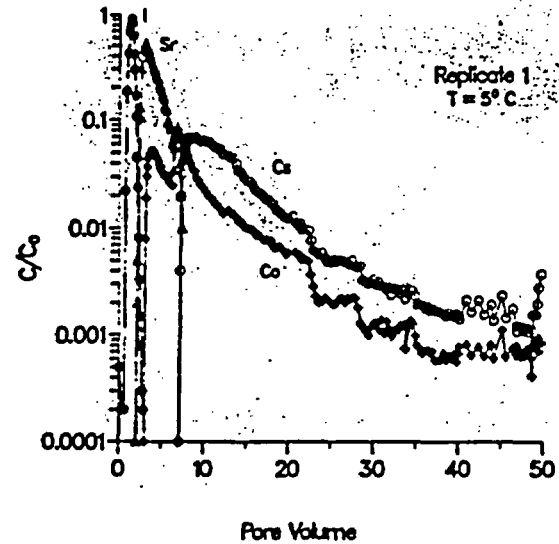


Fig. 2. Comparison of breakthrough curves for replicates at 25°C.



Fig. 3. Comparison of breakthrough curves at 5°C and 25°C.

The effect of temperature on the transport of iodide, strontium, cesium, and cobalt is shown in Fig. 3. Only one duplicate at each temperature, 5°C and 25°C, is shown for the set of breakthrough curves. This choice for analysis was based on the fact that the duplicates at 5°C are alike and that the one duplicate at 25°C will provide conservative conclusions. Similar breakthrough for iodide implies that any effect on physical processes is not significant for the range of temperatures tested. However, the effect of temperature on the rest of tracers, namely, the nonconservative ones is much more dramatic. Cobalt is affected most by the change. A lower temperature mobilizes cobalt which also appears at a much earlier time with a sharper peak. Cesium is mobilized more at higher temperatures for which it also has an earlier appearance time and a sharper peak. The tailing fronts for cesium at the two temperatures are approximately alike. Finally, strontium does not seem

The above results are consistent with theory and can be explained on the basis of effect of temperature changes and on the degree of sorption equilibrium relative to flow rates. Previous work[1,2] indicates that under the flow conditions strontium sorption is controlled by equilibrium conditions during transport and that its rates of sorption are fast. Under these conditions theory predicts temperature to have little, if any, affect on rate of sorption and thus on transport. Those predictions were confirmed by these column studies. Cobalt, on the other hand, should have much slower rates of sorption and thus temperature should have a much greater effect on transport; the rates of sorption should be considerably less at 5°C. If the rates of sorption are extremely slow relative to the flow,

then the transport of cobalt would tend towards that of a nonsorbing solute. Under these conditions cobalt breakthrough could occur sooner at 5$^{\circ}$C than at 25$^{\circ}$C. The previous work[1,2] indicates that the rates of sorption of cesium should be less than those of strontium and greater than those of cobalt. Thus sorption of cesium should be slower at the lower temperature, but faster than that of cobalt. If the reduced rates of sorption are still relatively fast for the flow conditions, then theory would predict a decrease in the transport of cesium with a decrease in temperature. That prediction is consistent with the transport of cesium in these laboratory column studies.

It is shown that environmental temperature changes can significantly and to different extents affect the chemical interactions of nonconservative solutes in transport through porous media. Also, the effect of temperature changes can be predicted in a qualitative manner from batch equilibrium and nonequilibrium data and from the theory of sorption used in deriving the modified Freundlich isotherm equation. However it should be noted that additional specifically designed column experiments are needed in order to validate the applicability of the theory to dynamic flow conditions.

## CONCLUSIONS

This study strongly suggests that sorption of solutes can alter their transport by dispersion as well as retardation. Also this study strongly suggests that temperature effects within environmental ranges may cause significant modifications of the migration of nonconservative solutes. Modifications may occur with respect to arrival time and peak spread. Because these temperature changes (in time or in space domains) occur in many spills and land waste disposal cases, proper consideration should be given to them because modeling, site selection and management decisions, among others, may be considerably impacted. The interpretation of sorption and temperature data suggest that the effects of temperature changes and sorption on transport may be predicted in a qualitative manner from batch equilibrium and nonequilibrium data and the theory of sorption used in deriving the modified Freundlich isotherm equation.

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