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BINARY AND TERNARY ION-EXCHANGE EQUILIBRIA IN ZEOLITIZED TUFF: Cs-Sr-Co SYSTEM

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ABSTRACT

Sorption isotherms for the ternary system Cs-Sr-Co using 'Nonscents,' a zeolitized volcanic tuff material from southeast Arizona, as sorbent were measured with a columnar flow technique. The isotherms were correlated with an ion-exchange phase-equilibrium model, and the triangle rule of ion exchange has been validated. Sorbent-phase selectivity for the ternary system has been successfully predicted from a knowledge of the selectivity of constituent binary pairs. The study helps in the understanding of multisolute sorption behavior during host rock-ground water interactions relevant to a high-level nuclear waste repository.

INTRODUCTION

It is generally recognized that one needs to understand the mechanisms of radionuclide transport and retardation in tuff as well as develop a comprehensive data base of sorptive behavior during host rock-ground water interactions in order to make the required performance-assessment calculations of possible releases from a high-level nuclear waste repository. Though a multiple barrier approach is used in the design of a high-level nuclear waste repository, the host rock of the repository itself is expected to provide sufficient retardation to radionuclide migration via sorption processes. If credit is taken for sorption, one must make sure the sorption parameters used in the performance assessment calculations do not underestimate radionuclide migration.

Los Alamos National Laboratory has been mainly responsible for geochemistry and transport processes in the site characterization activities of the Yucca Mountain project. They made extensive sorption measurements of major radionuclides in J-13 well water on Yucca Mountain tuff samples (1). Most of these measurements were of single-solute sorption, made in batch experimental mode, with very dilute concentrations of solute nuclides in the aqueous phase. In some of their experimental runs, phase equilibrium was not attained. It is well known that single-solute ionic sorption measurements are not representative of sorption characteristics of the solute nuclide in a multisolute sorption environment. Sorbent-phase selectivity plays a very important part in the sorption characteristics of multicomponent ionic systems. The presence of a solute ion in the system that is highly favored on the sorbent phase will considerably reduce the values of sorption parameters of other solute ions that are obtained from correlations of single-solute sorption measurements. It was shown that radionuclide cobalt in synthetic ground water also containing strontium and cesium nuclides sorbed 'irreversibly' on Bandelier tuff, and sorption capacities of strontium and cesium were considerably reduced (2). One needs to be aware of scenarios that reduce sorption parameters used in the performance acessment calculations so that retardation of radionuclides is not overestimated.

Geochemists, the most predominant group of scientists working in this area of radionuclide retardation by sorption processes along flow paths to the accessible environment, have been using mathematical models such as linear, Langmuir, Freudlich, and modified Langmuir to describe sorption isotherms. Parameters used in these models, K_D and ß, are not fundamental constants but vary with experimental conditions such as solid to liquid ratio and the initial compositions of the competing solute ions in both the sorbent and liquid phases (3). Mechanistic models such as the triple-layer surface complexation model have also been used for describing sorption processes (4). Such models have not been applied to multicomponent mixtures, particularly over a wide range of solution compositions. Model parameters for natural environmental conditions are not usually available. The ease with which these models can be coupled with transport equations to account for retardation of a radionuclide in a multicomponent system is questionable.

THEORY

Radionuclides dissolved in groundwater are usually charged species, and their sorption on zeolites and clay minerals found in the host rock is best described by an ion-exchange mechanism. Both zeolites and clay minerals have surfaces with fixed charges.

A typical binary exchange process with ion A initially in aqueous phase exchanging with ion B in sorbent phase can be described as

$$\upsilon_B\,A(aq) + \upsilon_A\,\overline{B} \rightleftharpoons \upsilon_B\,\overline{A} + \upsilon_A\,B(aq),$$

where ν_A and ν_B are stoichiometric coefficients of ions A and B, $\overline{A}$ and $\overline{B}$ are solute ions in the solid phase.

The thermodynamic equilibrium constant for the above binary ion exchange can be expressed as

TABLE 1. PREDICTION OF TERNARY EQUILIBRIUM DATA: Cs-Sr-Co-NONSCENTS SYSTEM

Serial No.	Sorbent Column	Charge Fractions (Aqueous Phase)			Charge Fractions (Sorbent Phase)					
					Experimental			Calculated		
		X_{Cs}	X_{Sr}	X_{Co}	$\bar{X}_{Cs}$	$\bar{X}_{Sr}$	$\bar{X}_{Co}$	$\bar{X}_{Cs}$	$\bar{X}_{Sr}$	$\bar{X}_{Co}$
1	R-2	0.10	0.05	0.85	0.60	0.19	0.21	0.56	0.21	0.23
2	Q-2	0.10	0.10	0.80	0.51	0.23	0.26	0.51	0.27	0.22
3	L-9	0.10	0.30	0.60	0.40	0.36	0.24	0.43	0.39	0.18
4	Q-3	0.10	0.45	0.45	0.47	0.38	0.15	0.42	0.43	0.15
5	Z3-2	0.05	0.10	0.85	0.46	0.31	0.23	0.46	0.32	0.22
6	Z1-2	0.05	0.35	0.60	0.47	0.38	0.15	0.46	0.37	0.17
7	Z2-3	0.05	0.50	0.45	0.37	0.49	0.14	0.35	0.50	0.15

phase selectivity plays an important role in determining sorption characteristics of mixtures of solutes, and the selectivity would be different for different minerals.

The isotherm data of the binary pairs Cs-Sr, Cs-Co, and Sr-Co were correlated by the ion-exchange phase-equilibrium model presented in the theory section, and solid-phase ionic activity coefficients of each binary pair were also calculated as a function of solid-phase ionic composition. The results of these correlations were reported in two earlier papers (7, 8). The computed values of the three thermodynamic equilibrium constants are given below:

$$K^E_{Sr\text{-}Co} = 70, \quad K^E_{Cs\text{-}Sr} = 27, \quad K^E_{Cs\text{-}Co} = 1470.$$

If one applies triangle rule to the Cs-Sr-Co system,

$$K^E_{Cs\text{-}Sr} \cdot K^E_{Sr\text{-}Co} \cdot K^E_{Co\text{-}Cs} = 27 \times 70 \times 1/1470 = 1.285.$$

In the case of well-behaved ion-exchange systems, particularly with synthetic ion exchanges, one can expect the triangle rule of a ternary ionic system to hold well for the three constituent binary equilibrium constants (6).

$$K^{E}_{AB} \bullet K^{E}_{AB} \bullet K^{E}_{AB} = 1$$

One can predict ternary ion-exchange equilibria from binary equilibria. Binary equilibrium measurements are simpler, and relatively fewer experimental measurements are needed to fully characterize a binary exchange isotherm. In the case of quaternary or multicomponent systems of higher order, prediction of multicomponent equilibria using the binary equilibrium parameters is the preferred method. One needs analytical expressions for ionic activity coefficients in the sorbent phase in each of the constituent binaries. In order to predict sorbent-phase composition ($\overline{X}_i$ $\overline{X}_j$ $\overline{X}_k$) from a knowledge of solution-phase composition (X_i X_j, X_k), an iterative technique is required to solve the equations on a computer. In this study, a far simpler procedure is used to predict the ternary equilibria from constituent binary experimental isotherms. A sample calculation is shown in the Appendix.

EXPERIMENTAL METHOD

In the present study, the sorbent used, called 'Nonscents,' is a zeolitized volcanic tuff material, mined from southeast Arizona, and was supplied by Nonscents of Houston, Texas. It is a mixture of minerals, with clinoptilolite constituting 51%. The sorbent samples were crushed, ground, and sieved to a Tyler mesh size of -20 +80. The sorbent was converted to a homogenic form (NH_4^+) by washing with 1 M NH_4Cl solution in a columnar mode. Five grams of air-dried sorbent sample was equilibrated with a solution containing mixtures of cobalt, strontium, and cesium ions of known composition in a columnar mode. An equilibrium condition between solid and liquid phases was ensured by employing concentrated solutions (0.3 N Cl^-), continuous-flow technique (flow rate of 25-30 mL/h), and relatively long periods of equilibration (3 to 4 weeks). At the end of the sorption run, the sorbent bed was washed free of any adhering electrolyte with deionized water, and the sorbed solute ions were eluted back into aqueous phase by washing with 1 M NH_4Cl solution. The eluted fractions were analyzed for the solute ions using atomic absorption spectrometry. All the isotherm measurements were made at a temperature of 27 ± 1°C. A schematic of the experimental setup and details of the procedure were presented elsewhere (7). Several separate sorbent columns were employed in gathering isotherm data for both binary and ternary systems. Also, some of the columns were reused several times in obtaining the sorption data.

RESULTS AND DISCUSSION

Experimental data for Sr-Co, Cs-Sr, and Cs-Co isotherms were presented earlier (7,8). The results clearly showed that the sorption process was highly nonideal. Strontium is very strongly favored over cobalt by the sorbent phase, whereas cesium ion is the more favored species in Cs-Sr and Cs-Co binaries. One would expect that the order of preference in the sorbent phase of the solute ions in a ternary system would be Cs>Sr>Co. This is indeed the case (see Table 1) with the experimental ternary data. Two sets of ternary data are presented keeping the cesium charge or equivalent fraction in the solution phase constant at 0.05 and 0.1 and varying strontium and cobalt fractions. In all the runs, cesium is clearly the most favored ion in the sorbent phase, and cobalt was the least favored ion. In the case of Bandelier tuff, cobalt is the most favored ion on the sorbent phase, and the order of selectivity is Co>Cs>Sr>>Ca. Solid-

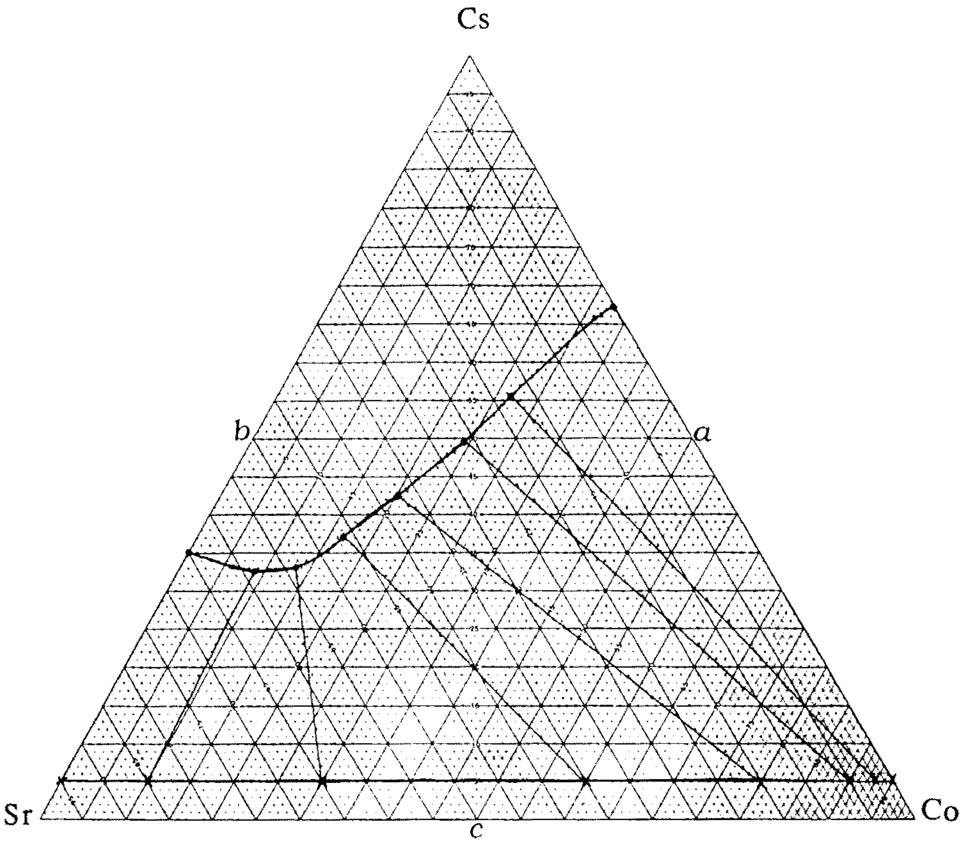

FIGURE 1. Predicted Values of Ternary Equilibria: Cs-Sr-Co- Nonscents System (tie-lines at constant $X_{Cs} = 0.05$).

This result is in excellent agreement with theory, considering the present sorbent is a heterogeneous volcanic tuff, and not a well-behaved synthetic ion exchanger. The author is not aware of any reports in the literature of successful application of triangle rule to zeolite sorbents.

In the present study, ternary equilibria of the Cs-Sr-Co- Nonscents System were predicted from the component binary isotherm data.

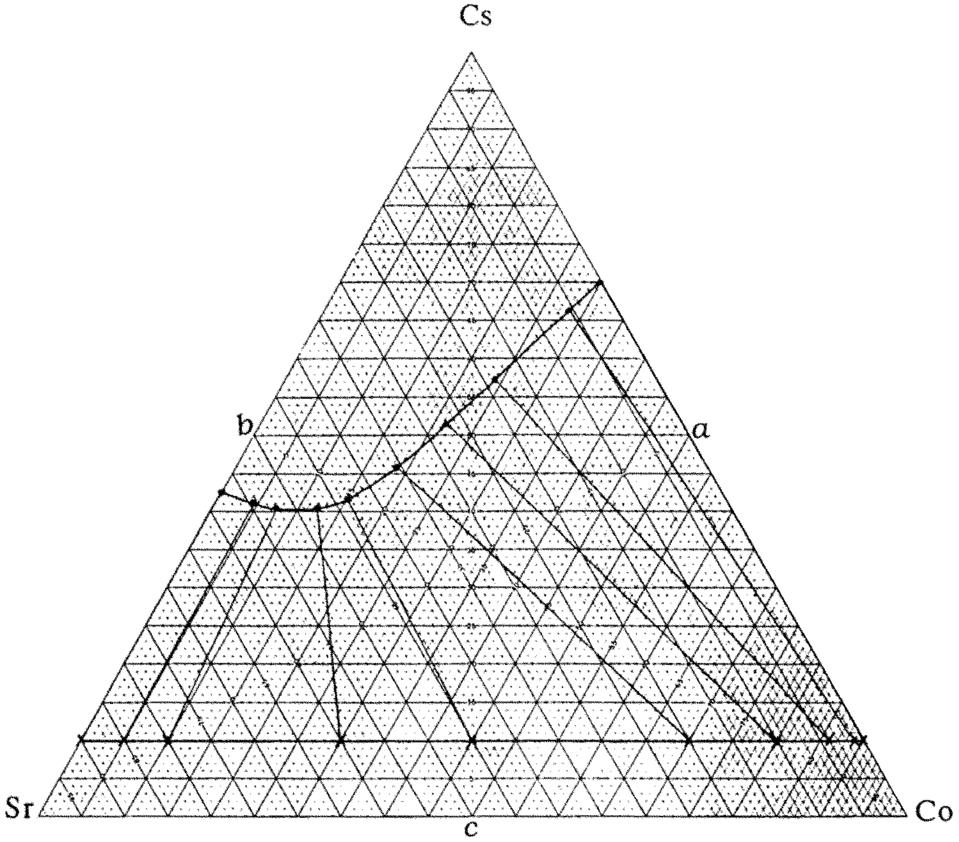

FIGURE 2. Predicted Values of Ternary Equilibria: Cs-Sr-Co-Nonscents System (tie-lines at constant $X_{Cs} = 0.10$).

Actually, two component binaries containing the most favored ion are sufficient to predict the ternary isotherm. Cs-Sr and Cs-Co isotherms were used to predict ternary equilibria of seven experimental runs. A sample calculation is given in the Appendix. Again, the agreement between predicted and experimental values of the ternary equilibria is very good considering experimental uncertainties in accurately measuring the concentrations (at ppm levels) of solute ions. Also, both the binary and ternary data were obtained using several different columns of a not entirely homogeneous sorbent. Predicted values of ternary equilibria at constant values of X_{Cs} 0.05 and 0.1 over a wide range of Sr and Co compositions are plotted in Figures 1 and 2, respectively. There are more rigorous methods available for prediction of ion-exchange equilibria for ternary systems from binary exchange data (9, 10). These methods involve correlation and mathematical modeling of ionic activity coefficients in the sorbent phase and also iterative computation procedures. Some of these techniques will be tried in the present study also at a later time.

It is clear that sorbent phase selectivity play an important part in determining the sorption characteristics of binary and ternary ionic systems. Ion-exchange equilibria of ternary, quaternary, or higher systems can be predicted from binary sorption isotherms which are easier to measure. The approach used in the present investigation is useful in developing an understanding of the retardation of mixtures of radionuclides by sorption processes during host rock-ground water interactions, in the event of a catastrophic leak of radionuclides from a high-level radioactive waste repository.

APPENDIX

Prediction of ternary equilibrium data given charge fractions in the aqueous phase

$$X_{Cs} = 0.05,\ X_{Sr} = 0.10,\ X_{Co} = 0.85$$

Since Cs ion is the most favored in the sorbent phase, select the experimental isotherms of two binary pairs, Cs-Sr and Cs-Co

On the third ion-free basis in Cs-Sr binary

$$\alpha_{Cs} = X_{Cs}/\,(X_{Cs} + X_{Sr}) = 0.05/(.05 + .1) = 0.33$$

From Cs-Sr binary isotherm data, obtain the corresponding sorbent phase composition $\bar{\alpha}_{Cs}$,

$$\bar{\alpha}_{Cs} = \bar{X}_{Cs} / (\bar{X}_{Cs} + \bar{X}_{Sr}) = 0.59$$

Similarly, β_{Cs} in Cs-Co binary,

$$\beta_{Cs} = X_{Cs} / (X_{Cs} + X_{Co}) = 0.05/(0.05 + 0.85) = 0.056 \tag{1}$$

The corresponding sorbent phase binary from Cs-Co binary isotherm,

$$\bar{\beta}_{Cs} = \bar{X}_{Cs} / (\bar{X}_{Cs} + \bar{X}_{Co}) = 0.67 \tag{2}$$

$$\bar{X}_{Cs} + \bar{X}_{Sr} + \bar{X}_{Co} = 1.0 \tag{3}$$

From the three equations above, one can obtain

$$\bar{X}_{Cs} = 0.457, \quad \bar{X}_{Co} = 0.225, \quad \bar{X}_{Sr} = 0.318$$

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REFERENCES

1. K.W. Thomas, Summary of Sorption Measurements Performed with Yucca Mountain, Nevada Tuff Samples and Water from Well J-13, LA 10960-MS, Los Alamos National Laboratory, Los Alamos, NM, 1987.

2. M.G. Rao, H.R. Fuentes, W.L. Polzer, and E.H. Essington, J. Contam, Hydrol. 6, 69 (1990).

3. W.L. Polzer, M.G. Rao, H.R. Fuentes, and R.J. Beckman, Environ. Sci. Technol. 26, 1780 (1992).

4. J.C. Westall, in Aquatic Surface Chemistry, W. Stumm, Ed., Wiley; New York, 1987, Chapt. 1.

5. G.L. Gains and H.C. Thomas, J. Chem Phys. 21, 714 (1953).

6. F. Helfferich, Ion Exchange . McGraw-Hill, New York, 1992, Chapt. 5.

7. M. Gopala Rao, P.C. Das, E.U. Honga, and A.E. Helou, Proceedings of the 3rd Annual Int'l Conference on High-Level Radioactive Waste Management, Las Vegas, NV, 2, 1587 (1992).

8. M.Gopala Rao, Proceedings of the 4th Annual Int'l Conference, High-Level Radioactive Waste Management, Las Vegas, NV, 2, 1496 (1993).

9. R.K. Bajpai, A.K. Gupta, and M.G. Rao, J. Phys. Chem. 77, 1288 (1973).

10. R.M. Allen and P.A. Addison, Chem. Eng. J. 44, 113 (1990).