

## Background

Natural zeolite minerals exhibit favorable ion-exchange selectivity for cations. This property enables the use of natural zeolites in industrial and nuclear waste management applications, such as remediation of sites contaminated with radioactive strontium (Sr) and cesium (Cs). Natural zeolites also interact with groundwater and can be possible indicators of groundwater chemical evolution and processes, for example, at the potential high-level waste repository at Yucca Mountain, Nevada. There have been numerous studies of ion-exchange equilibria, but nearly all have focused on binary systems rather than the multicomponent systems found in nature and in many industrial processes.

## Objectives

- Generate experimental data for binary, ternary and quaternary cation-exchange systems
- Develop thermodynamic parameters for cations of interest through experimental analysis and correlation methods
- Develop a thermodynamic model that could be used to predict ion-exchange equilibria in multicomponent systems

## Methods and Approach

### Experimental

- Clinoptilolite, a commonly occurring zeolite mineral, was selected for use in the experiments
- Batch-type experiments were conducted at various concentrations and used several cations of interest, including Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup>
- For ternary and quaternary systems, a standardized experimental design was employed using constant ionic strength, solution volume, and solid mass

### Thermodynamic Modeling Approach

For the reaction



where  $z$  is the valence of the cation,  $A$  or  $B$ , and  $L$  is defined as the portion of zeolite framework holding unit negative charge, the equilibrium constant ( $K_{A,B}$ ) is:

$$K_{A,B} = \frac{(\bar{X}_A)^{z_B} (M_B)^{z_A} (f_A)^{z_B} (\gamma_B)^{z_A}}{(\bar{X}_B)^{z_A} (M_A)^{z_B} (f_B)^{z_A} (\gamma_A)^{z_B}}$$

where  $\bar{X}$  is the cationic mole fraction,  $M$  and  $\gamma$  are the molar concentration and activity coefficient, respectively, of the cation in solution, and  $f$  is the activity coefficient of the zeolite component.

### Non-ideal Behavior

A thermodynamic model was developed using the B-dot method (Helgeson, 1969) to account for non-ideality effects in the aqueous phase ( $\gamma$ ) and the Wilson model to address nonideality in the zeolite phase ( $f$ ).

The general form of the Wilson model is represented

$$\ln f_k = 1 - \ln \left( \sum_{j=1}^m \Lambda_{kj} \bar{X}_j \right) - \sum_{i=1}^m \left( \frac{\bar{X}_i \Lambda_{ik}}{\sum_{j=1}^m \Lambda_{ij} \bar{X}_j} \right)$$

which can be used to calculate zeolite component activity coefficients for multicomponent systems using empirical parameters,  $\Lambda_{ij}$ , derived from binary systems only.

### Correlation Method

A correlation method was employed to develop estimated thermodynamic parameters where experimental data were lacking. The method is based on the approach used by Brown et al. (1985) for predicting formation constants of aqueous hydroxo-metal complexes. The method employs an equation of the form

$$-\log K_{A,B} = \text{intercept} + \text{slope}[g_1(z/r^2 + g_2)]$$

(g-factor)

where  $r$  is the ionic radius and  $g_1$  and  $g_2$  are functions of the charge and electronic structure of the cation.

## Reference

- Brown P.L. et al. (1985) J. Chem. Soc. Dalton Trans. 1985, 723–730.  
 Chelishchev, N. (1973) Dokl. Akad. Nauk SSSR. 210, 1110–1112.  
 Helgeson, H.C. (1969) Amer. J. Sci. 267, 729–804.

## Acknowledgments

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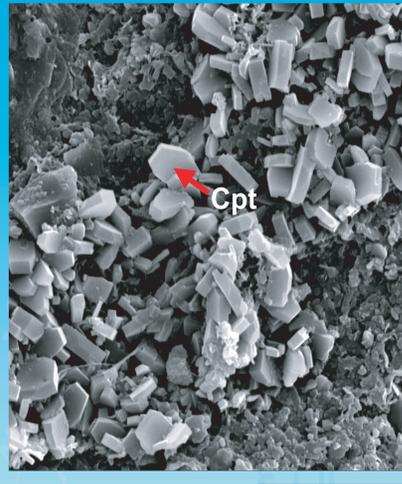


Figure 1. Clinoptilolite (Cpt), a commonly occurring natural zeolite, is highlighted by the red arrow in this scanning electron micrograph of an alluvial sediment sample from Yucca Mountain, Nevada, a potential repository site for high-level nuclear wastes.

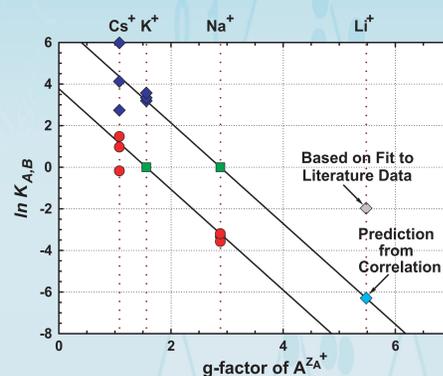


Figure 2. A correlation method using the approach of Brown et al. (1985) was used to constrain the value of the equilibrium constant for the Li<sup>+</sup>/Na<sup>+</sup> exchange system. The g-factor is a function of charge and electronic structure of an ion.

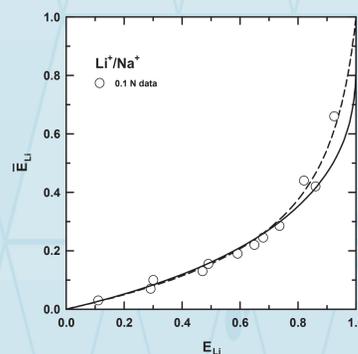


Figure 3. Comparison of calculated and experimental Li<sup>+</sup>/Na<sup>+</sup> isotherms. Circles are experimental data from Chelishchev et al. (1973). The dashed curve was derived by fitting  $K_{Li,Na}$  and the Wilson parameters,  $\Lambda_{Li,Na}$  and  $\Lambda_{Na,Li}$ , to ion-exchange data. The solid curve is the isotherm fit to experimental data, but with  $K_{Li,Na}$  constrained by the correlation method (Figure 2).

## Results

- Estimation method based on correlation between  $K_{A,B}$  and g-factor was successful in calculating thermodynamic parameters for univalent cations (Figures 2 and 3)
- The Wilson model was used successfully to predict binary system behavior for a range of solution conditions (Figure 4)
- Thermodynamic model parameters were used to predict ternary system solution chemistry from measured zeolite composition (Figure 4). Predicted and actual solution compositions show good agreement within total uncertainty
- Results of experiments at higher ionic strength emphasizes exchange for preferred cation (in this case K<sup>+</sup>) (Figure 5)
- Preliminary data for the quaternary Na<sup>+</sup>-K<sup>+</sup>-Ca<sup>2+</sup>-Sr<sup>2+</sup> system are shown in Figure 5

## Conclusions

- Binary, ternary and quaternary cation-exchange data were generated to test thermodynamic models of ion exchange
- Wilson equation parameters derived from binary ion-exchange data enabled
  - successful prediction of isotherms as a function of solution concentration
  - successful prediction of solution composition in multicomponent systems
- For systems with limited or no experimental data, thermodynamic parameters may be estimated using correlation methods

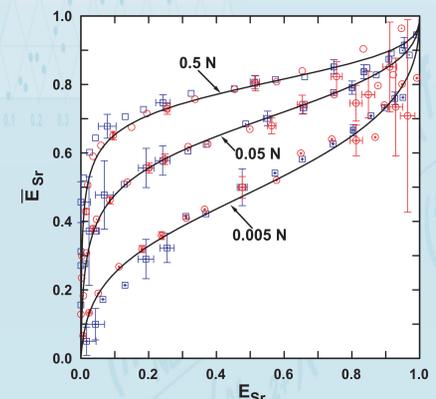


Figure 4. A Wilson model fit to Na<sup>+</sup>/Sr<sup>2+</sup> exchange data at 0.05 N was used to predict exchange isotherms at 0.5 N and 0.005 N. Cumulative uncertainty is shown by the error bars and can be significant at the isotherm extremes.

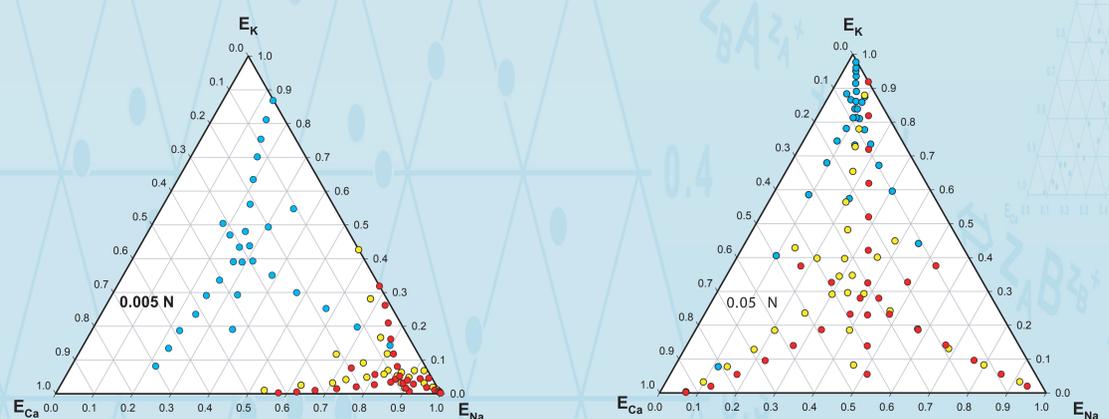


Figure 4. Equilibrium compositions in the Na<sup>+</sup>-K<sup>+</sup>-Ca<sup>2+</sup> system at total solution concentrations of 0.005 and 0.05 N. Zeolite and solution compositions are shown by blue and red circles, respectively. Shown as yellow circles are solution compositions calculated using the thermodynamic model, with measured equilibrium zeolite compositions as input. Predicted and actual solution compositions show good agreement within the uncertainty of the experiment.

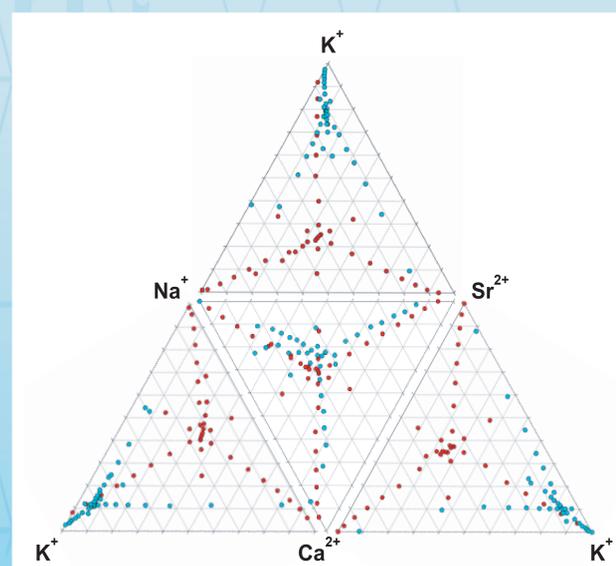


Figure 5. Equilibrium compositions of aqueous solution (red circles) and zeolite (blue circles) in the quaternary Na<sup>+</sup>-K<sup>+</sup>-Ca<sup>2+</sup>-Sr<sup>2+</sup> system at 0.05 N total concentration.