Experimental and Thermodynamic Modeling Study of Multicomponent Ion-Exchange of Alkali and Alkaline-Earth Metals in Clinoptilolite

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Ion-exchange processes in natural systems generally involve more than two cations, but little published data are available for multicomponent ion-exchange reactions. Experimental data on ternary and more complex mixtures are needed to develop and evaluate thermodynamic models that can be used to predict ion-exchange equilibria in natural systems. In this study, ternary and quaternary ion-exchange experiments were conducted involving the alkali and alkaline-earth cations Na^+, K^+, Cs^+, Sr^{2+}, and Ca^{2+} and clinoptilolite, a zeolite mineral that is locally abundant in the saturated and unsaturated zones of Yucca Mountain, Nevada, which is the potential site for a high-level waste repository. The clinoptilolite used in the experiments was prepared by pulverizing a sample of clinoptilolite-rich tuff from Death Valley Junction, California, and purifying the 200–325 mesh fraction. Homoionic forms of Na^+-, K^+-, and Ca^{2+}-clinoptilolite were prepared by reacting at 75 °C [167 °F} the purified zeolite with 3 M chloride solutions of Na^+, K^+, or Ca^{2+}. The ternary ion-exchange experiments consisted of reacting weighed amounts of homoionic clinoptilolite powder with known volumes of solution mixtures of Na^++K^++Cs^+, Na^++K^++Sr^{2+}, and Na^++K^++Ca^{2+} at constant solution normality. The quaternary ion-exchange experiment studied a Na^++K^++Ca^{2+}+Sr^{2+} system.

A thermodynamic model based on the Wilson equation was used to model the ion-exchange data. The parameters for the Wilson equation and the equilibrium constants for the binary ion-exchange reactions were derived from published binary ion-exchange data. A correlation method that has been applied to predictions of formation constants of aqueous hydroxo-metal complexes was used to help constrain the equilibrium constants derived from the binary isotherm data. The Wilson model, with parameters derived only from binary ion-exchange data, was used to predict ternary and quaternary ion-exchange equilibria. A comparison of experimental data for ternary and quaternary systems and thermodynamic model predictions indicates that the Wilson model adequately reproduces multicomponent ion-exchange equilibria. The results suggest that it is possible to use the Wilson model to evaluate multicomponent ion-exchange involving alkali and alkaline-earth metals in natural systems.

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