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Modeling Ion Exchange in Clinoptilolite Using the EQ3/6 Geochemical Modeling Code

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Modeling ion exchange in clinoptilolite using the EQ3/6 geochemical modeling code

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ABSTRACT: Assessing the suitability of Yucca Mtn., NV as a potential repository for high-level nuclear waste requires the means to simulate ion-exchange behavior of zeolites. Vanselow and Gapon convention cation-exchange models have been added to geochemical modeling codes EQ3NR/EQ6, allowing exchange to be modeled for up to three exchangers or a single exchanger with three independent sites. Solid-solution models that are numerically equivalent to the ion-exchange models were derived and also implemented in the code. The Gapon model is inconsistent with experimental adsorption isotherms of trace components in clinoptilolite. A one-site Vanselow model can describe adsorption of Cs and Sr on clinoptilolite, but a two-site Vanselow exchange model is necessary to describe K contents of natural clinoptilolites.

1 INTRODUCTION

Assessing the suitability of Yucca Mtn., Nevada as a potential repository for high-level nuclear waste requires the means to simulate ion-exchange behavior of clays and zeolites. Clinoptilolite is the most abundant cation exchanger at Yucca Mtn. Its cation-exchange properties will affect the partitioning of radionuclides between fluid and solid phases. The distribution of cations occupying the exchange site of an ion-exchanger may be described and simulated using either solid-solution or cation-exchange models.

Solid-solution models simulate compositional changes in clinoptilolite during dissolution/precipitation and are necessary to compute changes in clinoptilolite compositions during reaction path modeling simulations. Cation-exchange models allow ion exchange to be simulated independently of dissolution/precipitation, and are necessary for simulating ion exchange for phases that are not in overall equilibrium with the fluid, for phases for which thermodynamic stability data is lacking, and for multi-phase exchangers such as soils.

Additional solid-solution models and a new cation-exchange option have been implemented in geochemical modeling codes EQ3/6 (Wolery et al. 1990) to simulate the interrelated processes of dissolution/precipitation and ion exchange, respectively. The newly implemented Vanselow and Gapon exchange models and an ideal site-mixing solid-solution model were compared to each other and examined with respect to their ability to match field and experimental data for Yucca Mtn. tuffs.

2 CATION-EXCHANGE MODELS

The cation-exchange option implemented in EQ3/6 allows exchange to be modeled for up to three exchangers or a single exchanger with three independent sites according to either the Vanselow or Gapon exchange conventions. The exchanger is treated as an aqueous ligand; thus, only instantaneous ion exchange is considered.

The Vanselow and Gapon models differ in the stoichiometry of the exchanger components used to define the exchange reaction. Only ideal exchange is considered, and thus for both models, the *activity* of the exchanger component is equal to its *mole fraction* in the exchanger.

The Vanselow exchange component is $M\text{-}Z_m$, where M is a cation of valence m and Z represents one equivalent of exchanger. For heterovalent exchange (e.g. Na-Ca) involving z equivalents of exchanger, the Vanselow model exchange reaction is

$$zNa\text{-}Z + \frac{z}{2}Ca^{++} = \frac{z}{2}Ca\text{-}Z_2 + zNa^{+} . \qquad (1)$$

For ideal exchange, the activity of the exchange component, $M\text{-}Z_m$, is equal to

$$a_{M\text{-}Z_m} \equiv X_{M\text{-}Z_m} = x_M \ , \qquad (2)$$

where $X_{M\text{-}Z_m}$ is the mole fraction of *component* $M\text{–}Z_m$ in the exchanger and x_M is the *mole fraction of cation M* on the exchange site. Thus, the activity of the exchange component in the ideal Vanselow model is equal to the mole fraction of the cation on the exchange site.

The Gapon exchange component is $M_{1/m}\text{-}Z$. For Na–Ca exchange, the reaction is

$$zNa\text{–}Z + \frac{z}{2}Ca^{++} = zCa_{1/2}\text{–}Z + zNa^{+} \ , \qquad (3)$$

and for ideal exchange, the activity of the exchange component is equal to

$$a_{M_{1/m}\text{-}Z} \equiv X_{M_{1/m}\text{-}Z} = E_M \ , \qquad (4)$$

where $X_{M_{1/m}\text{-}Z}$ is the mole fraction of *component* $M_{1/m}\text{–}Z$ in the exchanger and E_M is the *equivalent fraction of cation M* on the exchange site. Thus, the activity of the exchange component in the ideal Gapon model is equal to the equivalent fraction of the cation on the exchange site.

Activity coefficients for Vanselow and Gapon aqueous exchanger complexes, consistent with Eqs. (2) and (4), are equated in EQ3/6 to the terms $1/\sum_{k}^{n} c_{M_k\text{-}Z}$, and $1/T_Z$, respectively, where $c_{M_k\text{-}Z}$ is the molal concentration of the *kth* Vanselow complex and T_Z is the total equivalents of exchanger in the simulation. The activity coefficient for the exchanger ligand is set to unity. The association constants for the exchanger/cation complex are set so that the concentration of uncomplexed exchanger ligand is small.

The EQ3/6 input files were modified to allow the user to specify the amount of exchanger or site, its initial composition, and the logK_{ex}'s or the free energies of the binary exchange reactions.

3 SOLID-SOLUTION MODELS

The activity of a component end-member in a solid solution can be described in terms of the occupancy of atoms and vacancies that mix on the crystallographic sites in the solution. In the simplest case, ideal site-mixing (ISM), the mixing of atoms on the site is ideal (Helgeson & Aagaard 1985).

If the entity that mixes on the site is a *coupled cation-vacancy*, $M_{1/m}V_{(1-1/m)}$, where M is a cation of valence m and V is a vacancy, then the activity of a component in the solid solution can be shown to be (Viani & Bruton 1992)

$$a_k = X_k^N \ , \qquad (5)$$

where N is the number of energetically equivalent positions in the site on which mixing of cations can occur and X_k is the mole fraction of the *kth* component in the solid solution. We equate N to the negative charge on the clinoptilolite framework. This modification of the ISM model is *numerically equivalent to the Gapon exchange model.* Implementation of the model into EQ3/6 followed the method outlined by Bourcier (1985).

If the entity that mixes on the site is $MV_{(m-1)}$, the activity of a component is (Viani & Bruton 1992)

$$a_{k=L} = \left[\frac{X_L/m_L}{\sum_k (X_k/m_k)} \right]^{N/m_L} \qquad (6)$$

where X_L represents the mole fraction of component $k = L$ in the solid solution and m_L is the valence of the cation occupying the exchange site in that component. This modification of the ISM model is equivalent to the *Vanselow exchange model* and is currently being implemented in EQ3/6.

4 EFFECT OF A THIRD CATION ON BINARY EXCHANGE

Assuming a single exchange site and ideal exchange, normalized non-preference ($K_{ex} = 1$) binary isotherms were computed for Na–Ca exchange at 1.0 N total normality according to the Gapon, Vanselow, and ISM models in the absence of any other cation (solid lines), and in the presence of a constant equivalent fraction (dashed lines) of a third cation (M^{++}) (Fig. 1).

Isotherms calculated according to the Gapon model are independent of the presence of a third cation on the exchanger. In contrast, the ISM and Vanselow models predict that binary isotherms depend on the concentration of other cations in the exchanger. This dependency arises because the activity of a given component in these models is a function of the mole fractions of all other components in the exchanger/solid solution. Ternary exchange data are not available to distinguish between these models for clinoptilolite.

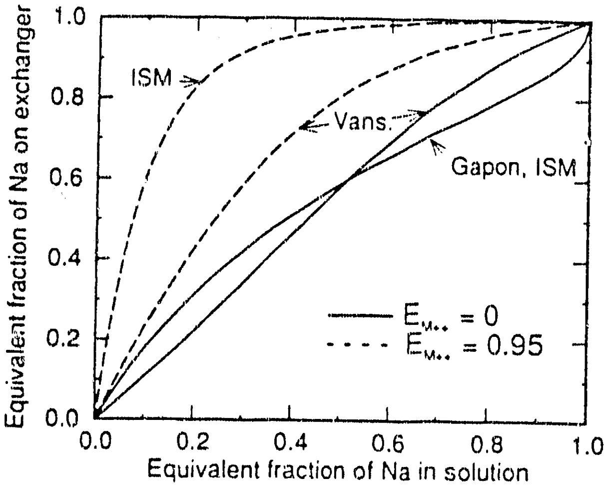

Fig. 1. Non-preference isotherms for Gapon, Vanselow and ISM models. E_{M++} = equivalent fraction of second divalent cation on the exchanger.

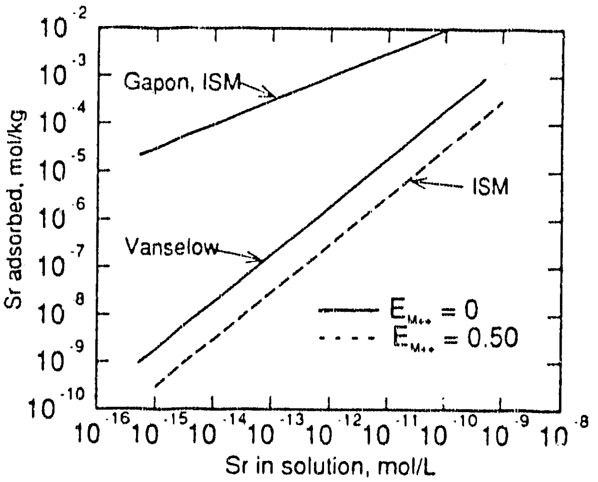

Fig. 2. Adsorption isotherms calculated using Gapon, Vanselow, and ISM models. E_{M++} = equivalent fraction of second divalent cation.

5 EXCHANGE AT TRACE LEVELS

Ion-exchange models must be able to predict adsorption at trace levels of exchange in order to predict radionuclide adsorption. Adsorption isotherms for a divalent cation (e.g. Sr) that have been calculated from normalized non-preference binary exchange isotherms (0.001N) are shown in Fig. 2. In the absence of a second divalent cation, the Gapon and ISM models predict that the adsorption of trace quantities of Sr is non-linear (parabolic; slope of 0.5 on a log-log plot). This contrasts with the observation that trace quantities of Sr or other divalent cations display linear (unit slope) adsorption on clinoptilolite and clinoptilolite-bearing materials (Thomas 1987). When a second divalent cation is present on the exchanger, the adsorption isotherm predicted using the ISM model is linear, while that predicted using the Gapon model (not shown) remains parabolic. Adsorption isotherms predicted using the Vanselow model are always linear.

In Fig. 3, experimental adsorption isotherms (symbols) for Sr and Cs on clinoptilolite-bearing tuff from Yucca Mtn. (sample YM-38) in contact with groundwater (well J-13) (Thomas 1987) are compared to isotherms simulated using the cation exchange option of EQ3 (lines) assuming a one-site Vanselow exchange model. Exchange energies, quantity and initial composition of clinoptilolite, and total concentration of Cs and Sr used in the simulations were taken from Ames (1964a, 1964b) and Thomas (1987) (details reported in Viani & Bruton 1992). No attempt was made to "fit" the experimental data by varying the exchange energies or the quantity and composition of the clinoptilolite exchanger used in the simulations. The simulated adsorption isotherms closely match the experimental data. Simulated adsorption isotherms for Sr computed using the Gapon model (not shown) are non-linear and hence, can not match the Sr adsorption data.

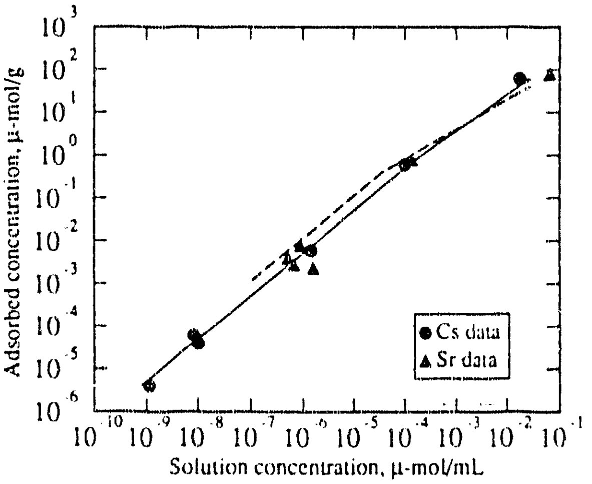

Fig. 3. Cs and Sr adsorption on clinoptilolite-bearing tuff (symbols) simulated using EQ3 and one-site Vanselow model (lines).

6 TWO-SITE EXCHANGE MODEL FOR CLINOPTILOLITE

Although Fig. 3 suggests that a simple one-site exchange model is adequate to describe adsorption of Cs and Sr on clinoptilolite, structure refinements have shown that three crystallographically distinct sites are present in clinoptilolite (Smyth et al. 1990). In natural samples, K appears to be restricted to one of those sites with Na and Ca distributed over the remaining sites. This observation explains why Bruton and Viani (1990) found that a one-site exchange model under-predicted K contents in clinoptilolites from Yucca Mtn. A *two-site ideal exchange model* was developed to explicitly account for the site that has high specificity for K. Because the remaining crystallographic sites do not appear to be occupied by a specific cation, they are represented as a single site in the exchange model. The observation that Cs adsorption can be accurately modeled by a one-site model but K cannot is consistent with the finding that Cs is distributed over five low-occupancy sites and shows a large amount of positional disorder (Smyth et al. 1990).

6.1 *Na–Ca and Na–K exchange at 25 °C*

Binary exchange isotherms and equilibrium constants were reported by Pabalan (1991) for Na–Ca and Na–K exchange at 0.05 and 0.5 N. For two independent exchange sites

$$\log K_{ex} = f_1 \log K_1 + f_2 \log K_2 \ , \qquad (7)$$

where K_{ex} is the equilibrium exchange constant for the overall exchange as reported by Pabalan (1991). f_1 and f_2 are the fractions of the total exchanger charge associated with sites 1 and 2, and K_1 and K_2 are the exchange constants for each site. Assuming ideal Vanselow exchange, expressing the mass action equation for reaction (1) in terms of equivalent fractions in solution and on the exchanger (e.g. Sposito 1981, pg. 135), and combining with Eq. (7), an expression is obtained that was fit to Pabalan's data by varying K_i and f_i. Estimates of the site-specific exchange parameters that best fit the isotherm data at both normalities are shown in Table 1. A comparison of the model isotherm (solid lines) and experimental data (symbols) for Na–Ca exchange is shown in Fig. 4.

The fit between model and data appears to be as good as that obtained when the data is fit to a one-site non-ideal model (Pabalan 1991). Thus, exchange on individual sites is close to ideal, thereby greatly simplifying calculations required to simulate clinoptilolite/fluid interaction.

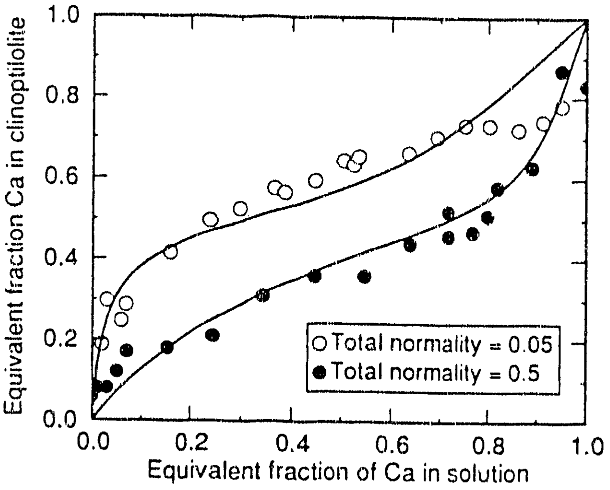

Fig. 4. Na–Ca isotherm. Data (symbols) from Pabalan 1991; two-site Vanselow model (lines) calculated with parameters in Table 1.

Table 1. Parameters used in two-site model

		Exchange constant, K_{ex}	
Site	$f^{(1)}$	Na –> K$^{(2)}$	Na –> ½Ca
Site 1	0.55	4.811	1.667
Site 2	0.45	81.62	0.086
Total	1.0	17.2$^{(3)}$	0.439$^{(3)}$

(1) Fraction of charge associated with site. f_1 and f_2 were obtained by fitting the Na–Ca exchange data, and were fixed at those values when fitting the Na–K exchange data.
(2) Na–clinop. + K^+ = K–clinop. + Na^+
(3) Overall K_{ex}'s from Pabalan (1991)

6.2 *Predicted vs. observed clinoptilolite compositions at Yucca Mtn., NV*

Cation occupancies of the two exchange sites were computed using the two-site model for a clinoptilolite in equilibrium with groundwaters (J-13 and USWH-3) from Yucca Mtn. As expected from the difference in the site-specific K_{ex}'s (Table 1), over 98% of the K is predicted to be in site 2, over 90% of the Ca is in site 1, and Na is distributed between the sites.

One- and two-site Vanselow exchange models were used to predict clinoptilolite compositions in equilibrium with reported groundwater compo-

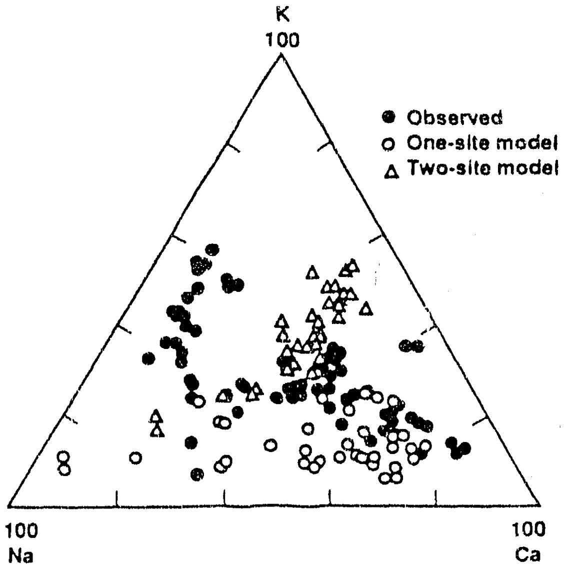

Fig. 5. Measured (see text for references) and predicted (using one- and two-site Vanselow models in EQ3) clinoptilolite compositions.

sitions from Yucca Mtn. (Benson & McKinley 1985, Ogard & Kerrisk 1984) and compared with observed clinoptilolite compositions (Broxton et al. 1986, Levy 1984; Levy, unpub. data) (Fig. 5). Measured clinoptilolite compositions are analyses of clinoptilolites from drill-hole samples collected from the saturated zone at Yucca Mtn. The underestimation of K by the one-site model is evident. Although predictions with the two-site model do not match observed data trends, it is clear that a multisite model is necessary to capture the compositional variability of clinoptilolites at Yucca Mtn. Some of the discrepancy between prediction and observation may be due to poor spatial correspondence between fluid and clinoptilolite samples, and because compositions of fluids sampled from water wells may not reflect the true variability of the in-situ groundwater composition.

7 CONCLUSIONS

Cation-exchange and solid-solution models are required to model the compositional variability of clinoptilolite. Based on limited experimental data, the Vanselow and ISM models appear to be the most appropriate *ideal* models to use for modeling clinoptilolite/fluid interactions. A two-site ideal Vanselow model, derived from experimental isotherms, appears promising for modeling the variation of Na, K and Ca in clinoptilolite.

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