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Reactive transport modeling of multicomponent cation exchange at the laboratory and field scale

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1 INTRODUCTION

As pointed out by Appelo (1996), multicomponent ion exchange models have not been widely used in geochemical or geochemical transport modeling of subsurface processes, despite their recognized importance in regulating soil and sediment pore water compositions. This is also somewhat surprising considering the demonstrated success of ion exchange models in describing sorption and subsurface transport (Ritchie, 1966; Pope et al., 1978; Valocchi et al., 1981a and 1981b; Griffioen, 1993; Appelo and Willemsen, 1987; Appelo, 1994; Lichtner et al., 2004; Steefel, 2004). The key strength of the ion exchange models over "simpler" formulations like the linear distribution coefficient (K_d), the Langmuir isotherm, or even the Freundlich isotherm, is that it captures competitive adsorption behavior through the use of a mass action expression. The total exchange capacity, which can not be exceeded in classical ion exchange, is incorporated as well. Since the ion exchange process involves electrically balanced exchange, complexities associated with the development of surface charge such as appear in the case of electrostatic surface complexation models are avoided. In some cases, it has been necessary to introduce multi-site models to account for the strong dependence of exchange on cation ion concentration (Brouwer et al., 1983; Comans et al., 1991; Poinssot et al., 1999; Zachara et al., 2002; Steefel et al., 2003). Other difficulties have arisen in heterovalent systems where the non-ideality of exchange has required the use of activity coefficients for exchangers (Sposito, 1981; Appelo, 1996; Liu et al., 2004).

2 MATHEMATICAL FORMULATION OF CATION EXCHANGE

An ion exchange reaction can be described via a mass action expression with an associated equilibrium constant (Vanselow, 1932; Sposito, 1981; Appelo and Postma, 1993). The exchange reaction can be written in generic form as

$$vACl_u(aq) + uBX_v(s) \leftrightarrow uBCl_v(aq) + vAX_u(s) \tag{1}$$

where X refers to the exchange site occupied by the cations A^{u+} and B^{v+}. The equilibrium constant, K_{eq}, for this reaction can be written as (Vanselow, 1932)

$$K_{eq} = \frac{(BCl_v)^u (AX_u)^v}{(ACl_u)^v (BX_v)^u} \tag{2}$$

where the parentheses () refer to the thermodynamic activities. Activity corrections for solutes can be described with various models (e.g., Debye-Huckel, Pitzer), but there has been less agreement on models for calculating activity corrections for exchangers. Several activity conventions are in wide use. Vanselow (1932) suggested the use of mole fractions to represent exchange species activities, which for our generic binary system are given by

$$N_A = \frac{\{AX_u\}}{\{AX_u\} + \{BX_v\}} \qquad N_B = \frac{\{BX_v\}}{\{AX_u\} + \{BX_v\}}, \tag{3}$$

where the brackets {} refer to the concentration in moles. As pointed out by Sposito (1981), however, the activity of a component in a mixture is equal to its mole fraction only if the mixture is ideal. If the mixture is not ideal, then the activities have to be related to their mole fractions by means of an activity coefficient. In the binary exchange reaction considered in Equations 1-3, these are given by

$$f_B = {(BX_v)}/{N_B} \qquad f_A = {(AX_u)}/{N_A}. \tag{4}$$

This implies that the empirical selectivity coefficient, K_v, is related to the equilibrium constant through the expression

$$K_v = K_{eq} \frac{f_A^{\ v}}{f_B^{\ u}}, \tag{5}$$

which, after converting to logarithms, can be written in differential form as (Argersinger et al., 1950; Sposito, 1981, Liu et al., 2004)

$$d \ln K_v = v d \ln f_A - u d \ln f_B. \tag{6}$$

This expression can be combined with the Gibbs-Duhem equation,

$$N_A d \ln(f_A N_A) + N_B d \ln(f_B N_B) = 0 \tag{7}$$

which states that changes in the activity of one component must be balanced by changes in the activity of another component as mass is conserved. This provides two equations which can be solved for the two unknowns, f_A and f_B (Sposito, 1981). As pointed out by Liu et al. (2004), however, the activity of water should be included explicitly as well

$$N_A d \ln(f_A N_A) + N_B d \ln(f_B N_B) + \frac{n_w}{\{AX_u\} + \{BX_v\}} d \ln a_w = 0 \tag{8}$$

where n_w is the moles of water in the exchanger and a_w is the activity of water. For a binary system, $N_A + N_B = 1$, so combining Equations 6 and 8 yields

$$u d \ln f_B + d\left[(1-\beta_B) \ln K_v\right] = -\ln K_v d\beta_B - uvn_w d \ln a_w, \tag{9}$$

$$v d \ln f_A + d\left[\beta_B \ln K_v\right] = -\ln K_v d\beta_B - uvn_w d \ln a_w, \tag{10}$$

where β_B is the equivalent fraction of cation B in the exchanger defined by

$$\beta_B = \frac{v\{BX_v\}}{u\{AX_u\} + v\{BX_v\}} = \frac{v\{BX_v\}}{CEC} \tag{11}$$

and *CEC* is the cation exchange capacity, here defined for only a single exchange site. The chief practical difficulty in using Equations 9 and 10 to calculate exchanger activity coefficients from selectivity coefficients (K_v) is associated with the experimental determination of the number of moles of water in the exchanger phase, although this parameter is important only where significant variations in the activity of water occur. Liu et al. (2004) presented an alternative approach to solving Equations 9 and 10 that avoids the need to determine the water content of the exchanger. Some of the apparent non-ideality of exchange can be elimi-

nated by considering multiple exchange sites with differing equilibrium constants (Zachara et al., 2002; Steefel et al. 2003; Liu et al., 2004).

3 LABORATORY STUDIES OF CATION EXCHANGE

A large number of both batch and column (flowthrough) laboratory studies of cation exchange have been carried out (e.g., Beekman and Appelo, 1990; Cernik et al., 1994; Voegelin et al., 2000; Steefel et al., 2003). Batch experimental studies have the advantage of being relatively rapid to conduct, making it possible to span a wide range of concentrations. A possible disadvantage is that it can be difficult to displace all of the cations from the exchanger in the batch experiment. Also problematic is the dissolution of soluble mineral phases, especially carbonate, that can yield erroneous determinations of the cation exchange capacity and the exchange population. This problem can be circumvented by accounting for mineral dissolution and/or precipitation by determining changes in alkalinity or other anionic species, or by using radiolabelled cations where applicable.

Flowthrough column experiments potentially circumvent the problem of incomplete exchange by eluting multiple pore volumes through the exchanger. If the eluent is collected and analyzed continuously, one can quantify the completeness of exchange. In addition to the need to collect and analyze a large number of samples, however, care must be taken to ensure that cation breakthrough curves can be determined with sufficient precision to determine cation exchange capacities and selectivity coefficients.

3.1 *Batch versus column experiment determination of selectivity coefficients*

A limited number of studies have compared determinations of selectivity coefficients and cation exchange capacity in batch and column experiments (e.g., Cernik et al., 1994; Steefel et al., 2003). Steefel et al. (2003) compared Cs^+-Na^+ exchange in Hanford sediment batch experiments reported by Zachara et al. (2002) with exchange equilibria determined in flowthrough column experiments and found that batch-derived selectivity coefficients consistently under predicted retardation in the flowthrough column experiments. There are several possible explanations for these discrepancies. One possibility is that slow, largely irreversible uptake of Cs^+ into intralamellar or frayed edge sites on illite in the sediment may account for the observation of higher selectivity for Cs^+ in the column versus batch experiments—column experiments are typically carried over longer periods of time. Alternatively, the discrepancy may be due in part to the failure to characterize completely the exchanger composition in the batch experiments. Because column experiments involve continuous elution of many pore volumes through the sediment, they are less subject to errors resulting from the failure to displace the initial exchange species population (Steefel et al., 2003).

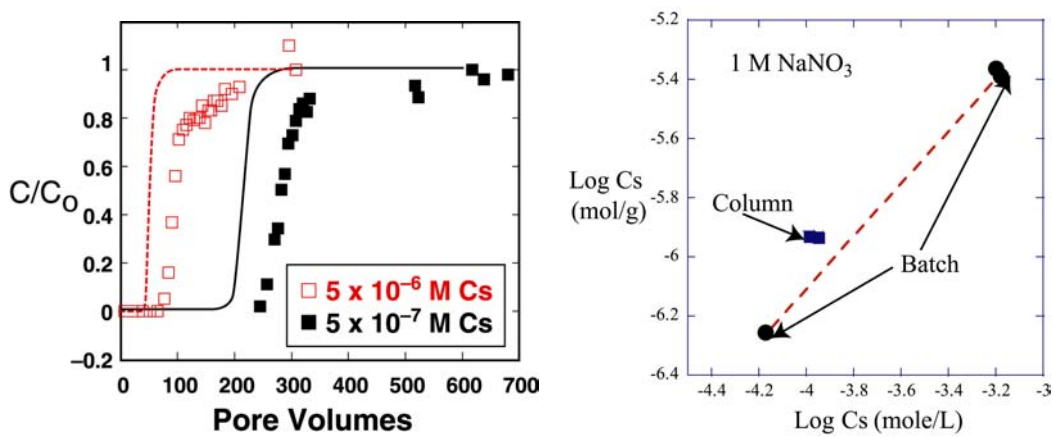

Figure 1: Left: Comparison of reactive transport simulations (lines) using selectivity coefficients determined in batch experiments with Cs^+ breakthrough determined in column experiments (symbols). Experiment conducted in 1 M $NaNO_3$. Right: Comparison of Cs^+ partitioning between solid and liquid at concentrations of Cs^+ close to 10^{-4} M. From Steefel et al., 2003.

4 FIELD EXAMPLES OF CATION EXCHANGE

Countless examples of the application of reactive transport modeling to field examples have been presented in the literature, but in most cases these have required the calibration of modeling parameters at the field site of interest. Far rarer is the application of laboratory (batch and column) experimental data to the field. Even where laboratory determinations of selectivity coefficients and the cation exchange capacity were not made in advance, however, the ability of the multicomponent cation exchange models to capture multiple, complicated cation breakthrough curves indicates that the theory upon which the models are based is relatively robust.

Appelo (1996) and Appelo and Postma (1993) offer the most comprehensive reviews of field examples of cation exchange, along with a lucid discussion of chromatographic theory. Noteworthy examples include the case of fresh water injected into a brackish water aquifer presented by Valocchi et al. (1981a and 1981b) and discussed further by Appelo (1994, 1996) and the case of a freshening of a saline aquifer in the Aquia aquifer in Maryland (Appelo, 1994; 1996). Other field examples include those discussed in Appelo et al. (1990), Griffioen and Appelo (1993), and Beekman and Appelo (1990).

4.1 *An example of field exchange: Cs^+ transport in the Hanford vadose zone*

More recently, combined laboratory and field studies have been undertaken to understand the controls on Cs^+ transport in the vadose zone at the Hanford reservation. Cs^+ occurs in significant concentrations as a contaminant in highly concentrated $NaNO_3$ plumes that have developed from leaks from single-shelled storage tanks at Hanford. Zachara et al. (2002) proposed that a multi-site cation exchange model could be used to explain the Cs^+ behavior in the vadose zone. Steefel et al. (2003) carried out flowthrough column studies to develop a set of selectivity coefficients and exchange site concentrations that could be applied to the field-scale contamination. An important question, however, is how well these laboratory-derived parameters apply to a field setting. To test this, the case of a plume developed in the vadose zone below a leak in the SX-115 high level waste tank was used. The advantage of considering the SX-115 leak is that both its volume (about 250,000 liters) and duration (1 week in 1965) is well known. Through analysis of water extractable ions, Serne et al. (2001) identified a well-defined chromatographic separation of cations in 299-W23-19, a borehole sited about two meters from the edge of the SX-115 tank, which can be attributed to the exchange of waste-derived cations.

A direct comparison of aqueous geochemical data collected from the 299-W23-19 borehole and the 3D simulations is shown in Figure 2. The simulations capture quite closely the leading edge of all the exchange fronts, although the match with the trailing portions of the plumes is not as good. However, the simulations even capture some aspects of the complicated shape of the cation plumes, including the sodium "shoulder" above the main part of the sodium plume in the aqueous phase. This presumably represents sodium being gradually eluted from exchange sites above the main zone of sodium in the aqueous phase. The simulated widths of the magnesium, calcium, and magnesium plumes are slightly too broad, although this may be the result of an overly coarse discretization. The relatively broader shape of the potassium plume, which shows up clearly in the data, is captured in an approximate fashion by the simulations. Cesium, although not detected in significant amounts in the 299-

W23-19 borehole, is known to occur very close to the bottom of the SX-115 tank (Raymond and Shdo, 1966).

It is important to point out that these results do not include any calibration of either the independently estimated hydrologic parameters (taken directly from Khaleel et al. 2001) or the laboratory-determined CEC and ion exchange selectivity coefficients. In order to match the absolute concentration of sodium in the borehole, the composition of the tank leak fluid had to be adjusted, however, with a "best fit" value representing a dilution of the estimate provided by Lichtner and Felmy (2003) by about a factor of 3.5. The exchanger calcium concentration required almost no adjustment from the value determined experimentally, while the exchange concentration of magnesium determined in the column experiments had to be adjusted downward by about a factor of 2 to obtain a match with the field data. Potassium had to be increased by a factor of 2 to 4 over the values estimated from the column experiments.

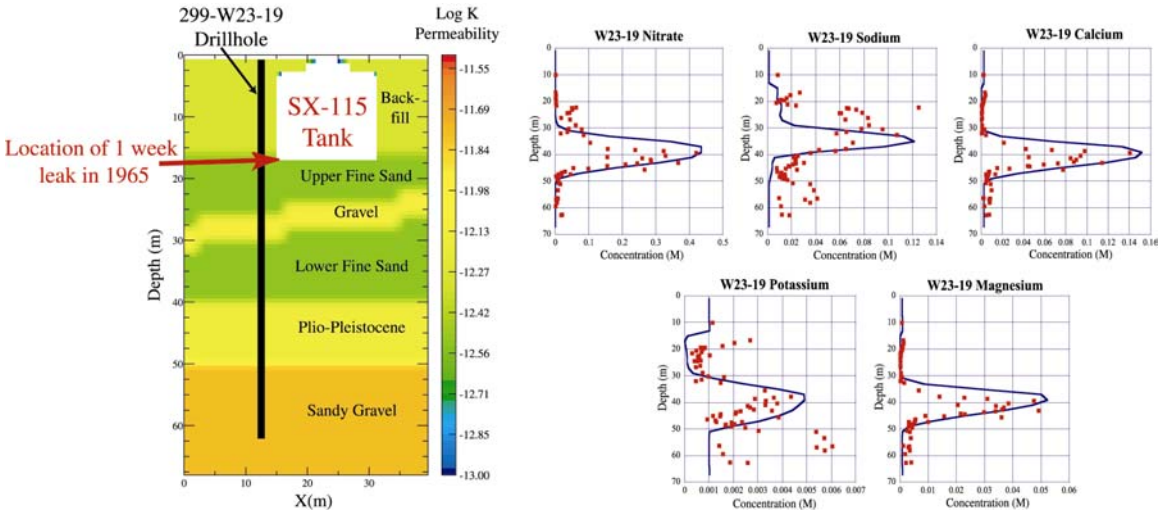

Figure 2: Left: Two-dimensional slice through 3D permeability field at SX-115 tank. Right: Comparison of 3D modeling results with pore water extracts from Borehole 299-W23-19 below the SX-115 tank at the Hanford Reservation, USA.

5 SUMMARY

Multicomponent ion exchange models have been successful in describing the chromatographic separation of cations in both laboratory and field settings. Their chief advantage lies in their ability to capture the competitive effects of other cations that may be present. By incorporating exchanger activity coefficients calculated on the basis of the Gibbs-Duhem equation applied to the exchanger phase, it is possible to correct for the non-ideality of exchange. The use of multiple exchange sites can also substantially improve the ability of the cation exchange models to describe adsorption and retardation. All of these benefits are associated with relatively little additional computational burden. Even where the cost of the multicomponent cation exchange calculations are considered too high, the models are useful in calculating distribution coefficients for the environmental conditions of interest.

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