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Evaluation of K^+ Ion-Exchange Selectivity in Ca-Bentonite

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1. Introduction

Long-term safety of high-level radioactive waste (HLW) disposal relies not only on engineered design but also on the chemical stability of the buffer system under evolving groundwater conditions. In this context, bentonite is selected because its swelling behavior, low permeability, and strong interaction with cationic species provide multiple, coupled barrier functions. However, these properties are not immutable: bentonite's high cation exchange capacity (CEC) implies that shifts in porewater chemistry can actively reorganize the population of exchangeable interlayer cations, triggering changes that may propagate from the nanometer-scale interlayer to macroscopic buffer performance.

Sustained cation exchange can alter interlayer hydration and clay microstructure, thereby affecting swelling behavior, transport properties, and the sorption capacity for radionuclides. Such concerns become more pronounced in chemically perturbed or saline environments, where the dominant exchangeable cations may evolve over long timescales. Among common alkali cations, K^+ is of particular interest because its uptake can promote reduced hydration and interlayer reorganization relative to divalent cations, potentially influencing both the reversibility of exchange and the long-term functional stability of Ca-type bentonite systems.

Accordingly, this study quantitatively evaluates the extent and selectivity of K^+ ion exchange in Ca-bentonite under systematically controlled reaction conditions. To obtain robust selectivity parameters while minimizing transport-related artifacts, we conducted well-mixed batch experiments using powdered Ca-bentonite at a fixed solid-to-liquid ratio (1:2 w/v) and a consistent equilibration protocol. The initial KCl concentration was varied over a wide range (1×10^{-4} to 2.0 M) to span dilute to highly saline conditions. Equilibrium aqueous compositions were used to determine exchanger-phase composition and to derive the K^+/Ca^{2+} exchange selectivity coefficient. Finally, the derived selectivity parameter was implemented as an input for ion-exchange modeling and validated against the experimental observations. This combined experimental–modeling approach provides quantitative constraints on K–Ca exchange behavior in Ca-bentonite and supports improved predictive capability for geochemical performance assessments relevant to HLW disposal.

2. Methods and Results

2.1 Ca-Bentonite

A Ca-type bentonite (Bentonil-WRK) was used in this study. The dominant clay mineral responsible for the key physicochemical functions of bentonite (e.g., swelling and cation exchange) is montmorillonite, a dioctahedral 2:1 smectite. The structural formula of the montmorillonite in the present material can be expressed as $[Ca_{0.2}K_{0.1}]\ [Al_{1.3}Mg_{0.4}Fe_{0.3}]\ [Si_{3.8}Al_{0.2}]\ O_{10}(OH)_2 \cdot nH_2O$, and its cation exchange capacity (CEC) is 73.32 cmol(+)/kg.

2.2 Experimental method

All ion-exchange experiments were performed in batch mode at room temperature. Powdered bentonite was used to reduce solid-phase heterogeneity and minimize spatial variability in solid–solution reactions, thereby improving experimental reproducibility and facilitating attainment of exchange equilibrium under well-mixed conditions.

For each test, 50 g of bentonite was contacted with 100 mL of KCl solution and agitated for 10 days, which was considered sufficient for reaching equilibrium. After agitation, the suspensions were centrifuged at 15,000 rpm for 4 min. The supernatant was collected and filtered through a 0.22 μm syringe filter prior to aqueous chemical analysis.

The reacted solids were recovered and thoroughly rinsed with ultrapure water until residual salts were removed. The washed solids were then freeze-dried and subsequently milled to obtain a homogenized powder for further characterization.

2.3 Ion-exchange selectivity

Because the K^+–Ca^{2+} exchange is a heterovalent (monovalent–divalent) reaction, ion-exchange selectivity was quantified on an equivalent basis using the Gaines–Thomas convention. The exchange reaction was written as [1]:

$$CaX_2 + 2K^+ \rightleftharpoons 2KX + Ca^{2+}$$

where X denotes an exchange site. For each batch system (i.e., for each initial KCl concentration / ionic strength condition), the exchanger-phase composition was obtained from aqueous mass balance of K and Ca. Equivalent (charge-based) amounts on the exchanger were defined as:

$$E_K = n_K,\ \ E_{Ca} = 2n_{Ca}$$

and the corresponding equivalent fractions were calculated as:

$$X_K = E_K\ /\ (E_K + E_{Ca}),\ \ X_{Ca} = E_{Ca}\ /\ (E_K + E_{Ca})$$

Aqueous activities were expressed as $a_i = \gamma_i\, c_i$, where c_i is the measured equilibrium concentration and γ_i is the activity coefficient computed using a consistent activity model (Davies/extended Debye–Hückel/B-dot/Pitzer). The Gaines–Thomas selectivity coefficient (K_{GT}) was then calculated as:

$$K_{GT} = [X^2_K \cdot a_{Ca2+}]\ /\ [X_{Ca} \cdot\ a^2_{K+}]$$

The selectivity coefficient was determined separately for each experimental condition, thereby yielding K_{GT} or (S) as a function of K^+ activity / ionic strength across the investigated KCl range (1×10⁻⁴ to 2.0 M).

To validate the derived selectivity parameters, Geochemist’s Workbench (GWB) 2025 was used to perform ion-exchange modeling. The K^+–Ca^{2+} exchange reaction and the experimentally derived selectivity coefficient(s) were implemented in the GWB ion-exchange framework, and simulations were run using the same initial conditions as the batch tests (solid mass, solution volume, and KCl concentration). Model predictions (equilibrium aqueous K and Ca concentrations and exchanger-phase compositions) were then compared with the experimental results to assess the consistency and predictive capability of the selectivity-based ion-exchange model.

The extent of K–Ca ion exchange in Ca-bentonite increased with increasing KCl concentration in the contacting solution. However, above approximately 0.1 M KCl, no further significant increase in exchange was observed, suggesting that the system approached an equilibrium state. Consistent with this behavior, the selectivity coefficient also increased with KCl concentration at lower concentrations, but converged to similar values beyond a threshold reaction concentration.

3. Conclusions

From the perspective of long-term safety in HLW geological disposal, the chemical evolution of the buffer cannot be treated as a secondary issue: owing to the intrinsic ion-exchange capacity of clay minerals, cation exchange has the potential to govern key buffer functions over repository timescales. In this study, K^+ was explicitly considered as a chemically conservative (i.e., performance-challenging) cation, and the extent of K^+–Ca^{2+} exchange in Ca-bentonite was quantified under systematically controlled conditions. The resulting selectivity-based parameters provide a defensible basis for describing how groundwater chemistry may translate into changes in exchanger composition. The extent of K–Ca ion exchange in Ca-bentonite increased with increasing KCl concentration in the contacting solution. However, no further significant increase in ion exchange was observed above approximately 0.1 M KCl, suggesting that the system approached equilibrium under highly concentrated conditions. Accordingly, the selectivity coefficient increased with KCl concentration at lower concentrations, but converged to similar values beyond a threshold concentration.

Importantly, establishing quantitative ion-exchange characteristics in advance enables their use as mechanistic inputs for subsequent coupled-process assessments. The selectivity coefficients and exchange modeling framework developed here are expected to facilitate integration with thermo–hydro–mechanical (THM) analyses and, ultimately, support the construction of more comprehensive THMC (thermo–hydro–mechanical–chemical) models for evaluating buffer performance and long-term stability in HLW repository environments.

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