Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 22-23, 2025

Determination of Equilibrium Constants for Calcium-Sodium Exchange Reactions onto Bentonil-WRK Montmorillonite

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Keywords : Engineered barrier, Buffer, Ion-exchange, Thermodynamic sorption modeling

1. Introduction

Deep geological disposal (DGD) has been developed and widely recognized as the most viable method for safely isolating high-level radioactive waste (HLW) from the biosphere. The DGD system consists of multiple barrier components, with bentonite-based clay buffer and tunnel backfill serving as key engineered barriers; these barriers are designed to prevent groundwater ingress into the waste canister while simultaneously retarding the migration of released radionuclides into the biosphere. Montmorillonite, a swelling 2:1 phyllosilicate, is the main component of bentonite and largely governs the hydrogeochemical performance of clay material. Beyond its geological origin, bentonite (or montmorillonite) is generally classified based on its exchangeable cation composition, with the most abundant forms found in nature being Na- and Ca-types. To date, the thermal, hydrodynamic, mechanical, and chemical (THMC) properties of Na-bentonites (e.g., MX-80, Kunigel V1, etc.) have been extensively investigated as reference materials for engineered barriers in DGD plans for HLW developed in numerous countries, whereas Ca-bentonites have received comparatively less attention. However, recent studies [1,2] have demonstrated that the Ca-form can exhibit swelling pressure similar to or even greater than that of Na-form at high initial dry density, and most commercial Ca-bentonites indeed satisfy the hydromechanical criteria required for use as a buffer [3]. In 2021, Korea Atomic Energy Research Institute (KAERI) introduced a new reference research Ca-type bentonite, Bentonil-WRK (Clariant Korea), and not only its THM properties but also sorption capability for highly soluble radionuclides (e.g., Cs, Sr, Se, I, etc.) have been investigated. In particular, a thermodynamic modeling approach based on the principle of mass action law was adopted in the sorption study, with the aim of determining reliable equilibrium constant data, which are useful for mechanistic understanding and predictive evaluation of the associated sorption phenomena under a wide range of aqueous conditions [4,5]. In this study, beyond the radionuclide sorption, we aimed to examine the reaction thermodynamics of calcium-sodium interlayer exchange onto Bentonil-WRK montmorillonite, which are baseline data required to evaluate the geochemical alteration of surrounding environment of engineered barriers upon various long-term evolution scenarios, such as intrusion of seawater or Na-rich groundwater.

2. Experimental

All experiments were conducted at a temperature of 25 ± 2 °C. Aqueous batch samples were prepared with deionized water (Merck Millipore, Milli-Q Direct 8), while their background electrolyte composition was controlled using concentrated NaCl (Sigma-Aldrich, ≥ 99 %) and $CaCl_2$ (Sigma-Aldrich, ≥ 99 %) solutions. Bentonil-WRK Montmorillonite was separated from the raw bentonite through a mineral purification treatment, as detailed elsewhere [4]. The purified montmorillonite was further treated with 1 M NaCl solution for 7 days at a S/L ratio of 5 $g \cdot L^{-1}$, followed by centrifugation at 4696 g for 10 minutes (Thermo Scientific, Sorvall X1 Pro). This interlayer homogenization process was repeated three times, and the homoionic clay mineral suspension was dialyzed and lyophilized. The clay exchange experiment was conducted at a S/L of 2 $g \cdot L^{-1}$ for 270 hours (72 hours for pre-equilibrium and 198 hours for reaction), where initial concentrations of NaCl and $CaCl_2$ reactants were within the ranges of 1.83 – 90.63 mM and 0.2 – 10.43 mM, respectively. The measured pH values were corrected to actual molar proton concentrations ($-\log [H^+] = pH_c$) using an empirical method described elsewhere [6]; The pH of batch samples was maintained at 6.4 ± 0.6. After the reaction equilibrium was established, supernatants were separated by centrifugation at 4696 g for 120 minutes, and the remaining dissolved Na and Ca were quantified using inductively coupled plasma-optical emission spectrometry (Perkin Elmer, Optima 8300). A parameter estimation code PEST [7] coupled with PHREEQC [8] was employed to conduct inverse modeling of the exchange data obtained.

3. Results and discussions

The calcium-sodium interlayer exchange reactions generally reached an equilibrium state within 120 hours, while the retention of Na^+, Ca^{2+}, or Cl^- by polypropylene containers was confirmed to be negligible.

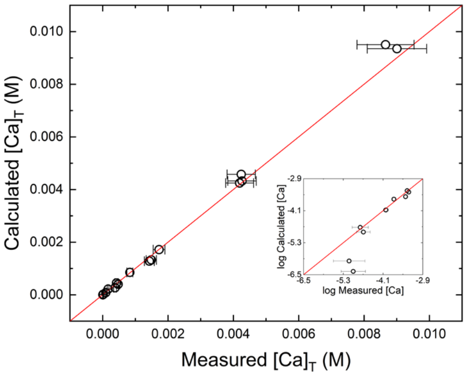

Fig. 1. Comparison of measured and calculated $[Ca]_T$ in batch samples after the interlayer exchange experiment.

At low background chloride concentrations ($[Cl]_T <$ ~10 mM), the experimental data indicated a direct stoichiometric exchange of sodium and calcium cations at the interlayer site (see eq. (1)). However, as chloride concentration increased, the amount of exchanged calcium per unit site gradually increased, suggesting that an additional calcium-chloride ion-pairing (see eq. (2)) also occurred. Indeed, adopting both the reaction mechanisms in the inverse modeling of obtained supernatant data allowed a more consistent fitting, and Fig. 1 shows the acceptable agreement between the measured and calculated concentrations of remaining calcium in supernatants after the batch experiment. For each mechanism, equilibrium constants, with their uncertainties corresponding to a 95 % of confidence level, were determined to be log K = 0.63 ± 0.20 and 2.46 ± 0.73, respectively.

$$(1)\quad 2XNa + Ca^{2+} \rightleftarrows X_2Ca + 2Na^+$$

$$(2)\quad XNa + Ca^{2+} + Cl^- \rightleftarrows XCaCl + Na^+$$

These values are comparable with previously reported exchange reaction parameters of other reference Na-montmorillonites [9,10], signifying that Bentonil-WRK clay exhibits a similarly high interlayer sorption capacity.

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