



Research paper

Gypsum precipitation enhanced by electrokinetic method and porewater chemistry in compacted montmorillonite



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ABSTRACT

An understanding of chemical reactions in bentonite is important in completing a reliable safety assessment of the geological disposal of radioactive waste. In the present study, porewater chemistry and calcium reactivity in a compacted Na/Ca-mixed montmorillonite is explored through a gypsum precipitation reaction enhanced using an electrokinetic method. Results showed that CaSO_4 was sparsely precipitated as gypsum in up to 300- μm aggregates, and grew into the montmorillonite texture. A threshold ionic equivalent fraction of calcium, X_{Ca} , of the Na/Ca-mixed montmorillonite in the gypsum precipitation was experimentally found to be within a range between $X_{\text{Ca}} = 0.1$ and $X_{\text{Ca}} = 0.25$ under a dry density of 1.0 kg/dm^3 saturated with $0.5 \text{ M Na}_2\text{SO}_4$ solution. The saturation indices of gypsum for specimens following the precipitation experiments were evaluated based on a model including anion exclusion and cation exchange (Gains-Thomas selectivity coefficients, K_{GT}) between the montmorillonite and interparticle solution using the PHREEQC code. Gypsum precipitation regions obtained from the precipitation experiments are in good agreement with regions in which the saturation indices are greater than zero when assuming $K_{\text{GT}} = 200$, which is much greater than the $K_{\text{GT}} = 4.9$ reported from the batch experiment. The greater K_{GT} value implied in this study indicates that the thermodynamic properties of confined solutions are different from those of diluted or bulk solutions. The reason for the K_{GT} deviation remains unresolved; however, the precipitation tendency of gypsum may be explained by a model including anion exclusion and cation exchange between the montmorillonite and the interparticle solution when an adequate K_{GT} value is used in the calculation.

1. Introduction

When assessing the geological disposal of radioactive wastes, it is important to evaluate long-term interactions between clay materials and other engineered barriers. In this regard, cement/clay interactions (Gaucher and Blanc, 2006; Savage et al., 2007) and iron/clay interactions (Bildstein et al., 2006; Savage et al., 2010) have been investigated intensely throughout the world. The reactive transport of chemical species among these barriers (Watson et al., 2009; Wilson et al., 2015) and porewater compositions in clay materials (Gaucher et al., 2009; Wersin et al., 2016) have been predicted using geochemical calculation codes including cation exchange reactions between clay materials and porewater in compacted systems. A selectivity coefficient of the Gaines-Thomas convention, K_{GT} (Gaines and Thomas, 1953), obtained from diluted systems, such as a batch experiment, has often been used in the modeling of cation exchange reactions in compacted systems because of the experimental difficulty in obtaining in-situ K_{GT} . The applicability of the selectivity and other coefficients obtained from diluted systems to compacted systems is among the most important questions in

radioactive waste disposal.

Sodium bentonite is widely used as an engineered barrier, including Kunigel V1 (Oda and Shibata, 1999) and MX-80 (Karland, 2010). In cement/clay interactions, calcium ions arising from dissolution of cementitious materials will diffuse in the sodium bentonite accompanied by cation exchange and secondary mineral precipitation. Therefore, it is important to elucidate the calcium reactivity in Na/Ca-mixed compacted bentonite. In this context, precipitation of secondary minerals will decrease the clay porosity, referred to as clogging, sealing (Gaucher and Blanc, 2006) and/or cementation (Steefel and Lictner, 1994). Clogging of natural argillite porosity resulting from newly formed minerals including calcium silicate hydrates (C-S-H), calcite and gypsum is suggested in long-term in-situ experiments of cement/clay interactions (De Windt et al., 2008; Gaboreau et al., 2011; Techer et al., 2012). In addition, the impacts of cement water on the diffusion of compacted clay has been investigated in a laboratory experiment (Melkior et al., 2004), suggesting that the tritium water (HTO) effective diffusion coefficient decreases over a 12-month period because of clogging.

Although calcium precipitation is suggested in-situ (De Windt et al.,

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2008; Gaboreau et al., 2011; Techer et al., 2012) and in laboratory experiments (Melkior et al., 2004), little is known regarding the reaction mechanisms involving calcium precipitation in compacted bentonite, because of its micro- or nano-scale pore structures (Kozaki et al., 1998; Melkior et al., 2009) and strong negative charge. In this regard, diffusion mechanisms of anions and cations in compacted bentonite have been intensely investigated and discussed. Models incorporating different types of pore spaces such as interlayer between montmorillonite sheets, interparticle space among montmorillonite stacks and external surface are proposed to explain ion diffusion in bentonite (Bourg et al., 2008; Glaus et al., 2010; Kozaki et al., 2001; Tachi and Yotsuji, 2014; Tournassat and Appelo, 2011; Van Loon et al., 2007). The selectivity coefficient was introduced to evaluate cation exchange reactions between clays and interparticle solutions in compacted bentonite (Glaus et al., 2007; Tachi and Yotsuji, 2014). Models introducing the membrane behavior of clay have been proposed based on the Donnan effect (Birgersson, 2017; Birgersson and Karland, 2009; Leroy et al., 2006; Muurinen et al., 2004). Application of the concepts including multiple porosities and/or the Donnan effect to the models addressing reactive transport and porewater composition is becoming increasingly popular in recent studies (Alt-Epping et al., 2018; Alt-Epping et al., 2014; Wersin et al., 2016; Zheng and Samper, 2015). In contrast, there are few experimental options, such as long-term diffusion and permeability experiments, to investigate the chemical reactions in bentonite, which makes it difficult to understand its reactive transport and porewater chemistry.

Because of the quite low hydraulic conductivity and diffusional mass transport in clay materials, some in-situ and laboratory experiments regarding clay alterations have taken longer than one year (Melkior et al., 2004; Techer et al., 2012). For the same reason, it is quite difficult to verify the results of long-term evaluations between clay materials and other engineered barriers. In contrast, electrokinetic methods have an advantage of enhancing ion migration in bentonite and in turn drastically decreasing the test duration. Thus far, this method has been applied in many ways to compacted clay materials as follows: (1) evaluation of diffusion coefficients over a short duration (Maes et al., 1999), (2) investigation of chemical speciation (Beauwens et al., 2005), (3) determination of charge carriers (Higashihara et al., 2008), and (4) discussion regarding migration pathways of ions (Tanaka et al., 2008; Tanaka et al., 2011). In addition to these findings, the method has a possibility of enhancing chemical reactions as anions migrate in the opposite direction from that of cations under an electric potential gradient.

The purpose of this study was to investigate the porewater chemistry and calcium reactivity in compacted Na/Ca-mixed montmorillonite from a gypsum precipitation reaction enhanced by electrokinetic method. First, electromigration experiments of $^{22}\text{Na}^+$, $^{45}\text{Ca}^{2+}$, $^{35}\text{SO}_4^{2-}$ and HTO were conducted to determine migration coefficients (velocities, dispersion coefficients, transport numbers, etc.) under the same experimental conditions as those of the precipitation experiments. Based on these migration coefficients, an optimal condition for gypsum precipitation was determined. Second, the method was applied to gypsum precipitation in the compacted montmorillonite. An ionic equivalent fraction of calcium (X_{Ca}) in the montmorillonite was chosen as a variable for gypsum precipitation rather than the Na_2SO_4 concentration, because basal spacing in the montmorillonite at a dry density of 1.0 kg/dm^3 saturated with deionized water does not change with respect to X_{Ca} (Kozaki et al., 2010). In contrast, changing the Na_2SO_4 concentration in the montmorillonite will result in a drastic change in the microstructural characteristics. Therefore, the initial concentration was set to be $0.5 \text{ M Na}_2\text{SO}_4$ for all the precipitation experiments, and then a threshold X_{Ca} for gypsum precipitation was experimentally determined. Third, X-ray diffraction analysis (XRD) and electron probe X-ray microanalysis (EPMA) were conducted on specimens following the precipitation experiments to identify the mineral species, size, and form of the precipitates. Finally, saturation indices of gypsum were estimated

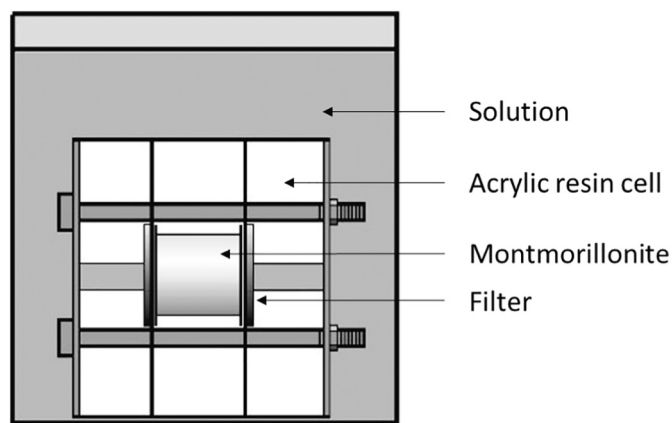


Fig. 1. Experimental apparatus for saturation of montmorillonite specimens. In the case of the Na/Ca-mixed montmorillonite, deionized water was used as solution. In the case of the Na montmorillonite, $0.5 \text{ M Na}_2\text{SO}_4$ solution labeled by S-35 radiotracer was used. The dry density was set as 1.0 kg/dm^3 in all experiments.

using the PHREEQC code to discuss the tendency of gypsum precipitation.

2. Experimental methods and materials

2.1. Preparation of montmorillonite specimens

Homoionized Na- and Ca-montmorillonite purified from Kunipia-F were mixed to obtain Na/Ca-montmorillonite mixtures. Detailed preparation procedures are described elsewhere (Kozaki et al., 1999). The ionic equivalent fraction of calcium, X_{Ca} , was set as 0.10, 0.25, 0.50, and 0.75. These were compacted as specimens 20 mm in diameter and 20 mm in length, with a dry density of 1.0 kg/dm^3 . The specimens were immersed in deionized water as shown in Fig. 1. The containers with the specimens and water were maintained in a vacuum desiccator for 15 min to prompt water saturation. Following this, these were maintained for > 30 days to complete saturation. The Na-montmorillonite was compacted with a dry density of 1.0 kg/dm^3 , and saturated with $0.5 \text{ M Na}_2\text{SO}_4$ solution labeled by the S-35 radioisotope in the same manner as shown in Fig. 1. The minimum saturation period (30 days) was predicted analytically based on an apparent diffusion coefficient of SO_4^{2-} ions in Na montmorillonite at a dry density of 1.0 kg/dm^3 saturated with $0.5 \text{ M Na}_2\text{SO}_4$ under the same initial and boundary conditions as shown in Fig. 1.

After saturation, the initial concentrations of Na (including exchangeable Na^+ in the montmorillonite, free Na^+ , and NaSO_4^- as an ion-pair) and SO_4 (including free SO_4^{2-} and NaSO_4^-) in the montmorillonite were determined. The saturated specimen was sliced, and all the Na and SO_4 was extracted using $1 \text{ M NH}_4\text{Cl}$ solution. The Na concentration was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the SO_4 concentration was determined from S-35 radioactivity measured using a liquid scintillation counter.

2.2. Electromigration of $^{22}\text{Na}^+$, $^{45}\text{Ca}^{2+}$, $^{35}\text{SO}_4^{2-}$ and HTO

Electromigration experiments of $^{22}\text{Na}^+$, $^{45}\text{Ca}^{2+}$, $^{35}\text{SO}_4^{2-}$, and HTO were conducted to obtain the migration coefficients of each species. A small amount of tracer ($^{22}\text{NaCl}$, $^{45}\text{CaCl}_2$, $\text{Na}_2^{35}\text{SO}_4$, or HTO) was applied to the contact surface of the montmorillonite specimens. During the experiments of the Na/Ca-mixed montmorillonite with different ionic equivalent fractions of calcium ($X_{\text{Ca}} = 0.25, 0.50, \text{ and } 0.75$), $^{22}\text{Na}^+$, $^{45}\text{Ca}^{2+}$, and HTO were used as tracers. During the experiments of Na-montmorillonite saturated with $0.5 \text{ M Na}_2\text{SO}_4$ solution, $^{22}\text{Na}^+$,

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