

Molecular dynamics study of montmorillonite crystalline swelling: Roles of interlayer cation species and water content



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ABSTRACT

Molecular dynamic simulations are employed to study the crystalline swelling behavior of montmorillonites (MMTs) with different interlayer Na⁺ and Ca²⁺ ion compositions, and the effect of temperature and pressure on the swelling behavior. Non-linear increases in *d*-spacing are observed with increasing water content. Plateaus in the swelling curve for Na-MMT around *d*-spacings of 12 and 15 Å demonstrate the formation of 1- and 2-layer hydrate structures. Ca-MMT and mixed Na/Ca-MMTs exhibit similar swelling behavior with exception of showing stronger swelling at water contents corresponding to the 1-layer hydrate in Na-MMT. The stronger swelling in the calcium containing systems is attributed to the preference of Ca²⁺ to be fully coordinated to water molecules, which favors a 2-layer hydrate structure and increased *d*-spacings. The larger hydration energy of Ca²⁺ ions relative to Na⁺ ions promotes increased water coordination numbers and more pronounced association of water molecules with Ca²⁺ ions. The 1- and 2-layer hydrates for Na-MMT and the 2-layer hydrate for Ca-MMT were relatively stable to changes in temperature and pressure.

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1. Introduction

Bentonite clay minerals are attracting great attention as buffer and backfill materials in spent nuclear fuel disposal because of their low hydraulic conductivity, and distinct cation exchange and swelling properties [1,2]. Montmorillonite (MMT), as the major component of bentonite clay minerals, mainly accounts for these properties. The MMT clay mineral is a layer-type aluminosilicate where each individual layer is composed of two tetrahedral sheets that sandwich an octahedral sheet. Isomorphous replacements with lower-valency metal cations, Mg²⁺ and Fe²⁺ substituting Al³⁺ in the octahedral sheet and, to lesser degree, Al³⁺ substituting Si⁴⁺ in the tetrahedral sheets, give the structure a net negative charge. The charge is compensated by cations held between individual layers in the interlayer space. Interlayer cations become hydrated as water enters the interlayer space and causes clay swelling [3].

Bentonite swelling as a critical factor in bentonite performance, has received extensive experimental [3–11] and theoretical [12–29] investigations. The investigations have shown that the swelling behavior is regulated by multiple factors, including the

composition of the bentonite mineral [4,6–8,12,13,22,23,26,30,31] and environmental factors [24,32,33]. The variation of interlayer cation species causes also differences in clay swelling [3,4,6,7,12,13,15,22,23,30]. Experimental studies [3,34] have revealed that the swelling of Na-MMT exhibits two regimes: crystalline swelling and osmotic swelling. Crystalline swelling occurs through the stepwise formation of 1-, 2- and 3-layer hydrates [10,12,13,21,22,28]. In crystalline swelling the *d*-spacing increases from about 10 Å in the dehydrated state up to about 19 Å, whereas in the osmotic swelling, the *d*-spacing increases onwards [3,11,35]. The swelling for Ca-MMT is limited to crystalline swelling. The natural clay minerals, however, usually contain simultaneously more than one species of cations [36]. There are comprehensive theoretical studies of interlayer swelling on one cation species but systems with the multiple cation species have received less attention by computational and theoretical methods.

In the present work, our aim is to investigate the swelling characteristics of MMT with different interlayer cation compositions in the regime of crystalline swelling. Through our simulation work, the arrangement of interlayer species and their interactions with clay layers are explored. Since environmental factors are also known to affect the swelling behavior of clay minerals [24,32,33], we will also demonstrate how the hydrated structures of clay minerals respond to changes in temperature and pressure.

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2. Models and methods

A unit-cell of MMT has a chemical composition of $(\text{Si}_{7.75}\text{Al}_{0.25})(\text{Al}_{3.5}\text{Mg}_{0.5})\text{O}_{20}(\text{OH})_4$ and a negative charge of $-0.75e$ [21]. The MMT super-cell model utilized in this work includes two clay layers where each layer contains 4×4 unit cells (Fig. 1). Hence, to balance the negative charge, cations with a total unit charge of +24 are incorporated into the system and evenly distributed into the two interlayer spaces. Different $\text{Na}^+/\text{Ca}^{2+}$ cation compositions are considered and four simulation systems were set up (Table 1). To mimic the swelling process, water molecules were added stepwise into the interlayers up to the water content of 0.4 g/g (grams of water per 1 g of clay). Four water molecules per step were added into each interlayer at low water contents, while eight water molecules per step were added for water contents higher than about 0.2 g/g. The cations and water molecules were placed randomly within the interlayer space in all simulations.

The molecular dynamics (MD) simulations were performed with GROMACS program and CLAYFF force field [21]. The flexible simple point charge (SPC) water model [37] was used. The simulations were carried out in an isobaric–isothermal (NPT) ensemble applying three dimensional periodic boundary conditions. The pressure and temperature were controlled by Parinello–Rahman [38] and Bussi's Velocity-rescale [39] methods, respectively. Leap-frog algorithm [40] was used for the integration of the equations of motions with a time step of 0.5 fs. The simulation systems were allowed to equilibrate for 200 ps of MD simulations. During the equilibration period, the convergence of total energy and temperature and pressure values were monitored to ensure that the thermodynamic equilibrium has been reached. The production run of 200 ps was preceded by this equilibration run, and data were collected after every 0.025 ps. The long-range Coulombic interactions were calculated using the Particle-Mesh Ewald electrostatics (PME) [41]. Cut-off distance for short range Coulomb and Lennard–Jones interactions was 9 Å.

The swelling of MMTs with different cation compositions was first studied at baseline conditions of 300 K and 0.1 MPa. The d -spacing was determined for each water content as an average of two individual d -spacings in the super-cell. Water contents for the 1-, 2-, and

Table 1
Simulated cation compositions.

Simulation system	Cation composition
Na-MMT	24 Na^+
Mixed I	16 Na^+ and 4 Ca^{2+}
Mixed II	8 Na^+ and 8 Ca^{2+}
Ca-MMT	12 Ca^{2+}

3-layer hydrates are obtained as minima in the derivatives of high order polynomial functions, which are fitted on the corresponding regions of the swelling curves. Density profiles and radial distribution functions between cations and water/clay oxygen atoms were calculated for characteristic water hydrates to reveal their atomic level structures in the interlayer space. Simulations were also performed under different temperatures (260, 340, and 380 K), while keeping the pressure constant (0.1 MPa), and under different pressures (4, 8, 12, and 16 MPa), while keeping the temperature constant (300 K). These temperatures and pressures represent extreme values that the buffer bentonite as a release barrier in geologic nuclear waste disposal may be exposed to over the long-term use [42,43]. The response to temperature and pressure changes was then evaluated by comparing the simulated d -spacings to the simulations at baseline conditions.

3. Results and discussion

A summary of dry and water-containing Na-MMT and Ca-MMT d -spacings reported in previous experimental and theoretical studies is shown in Fig. 2. The experimental data refers to ion-exchanged forms of MMT which were studied at standard conditions. For Na-MMT, the majority of the experimental studies reported the formation of 1-layer [3–6,30,44–52] and 2-layer hydrates [3–6,44,45,47,48,50–54], whereas the formation of the 3-layer hydrate was observed only in a few studies [3,45,47,50,53,54]. On the other hand, all the experimental studies reported the formation of the 2-layer hydrate for Ca-MMT [3,7,30,51,53,55–58], whereas the formation of 1-layer [7,51,56,57] and 3-layer hydrates was reported more rarely [3,30,51,53,55,57]. It may be because the 1-layer and 2-layer hydrates of Na-MMT and the 2-layer hydrate of Ca-MMT are more stable under the prevailing analysis conditions allowing easier detection. In general, the d -spacings reported by the theoretical studies agree reasonably well with the experiments, although they do slightly underestimate the d -spacings of the 2-layer and 3-layer hydrates of Ca-MMT (Fig. 2).

3.1. Swelling of Na and Ca montmorillonites

3.1.1. Sodium montmorillonite

The simulated d -spacing for Na-MMT is displayed in Fig. 3a as a function of water content. The results are in good agreement with previous experimental findings [5] and simulation results [12,21], and demonstrate the non-linear increase in the d -spacing with increasing water content. Plateaus are observed around water contents of 0.08 and 0.22 g/g which correspond to 1-layer and 2-layer hydrates at d -spacings of 12.1 and 15.1 Å, respectively.

3.1.2. Calcium montmorillonite

Simulation results for Ca-MMT are shown in Fig. 3b. Analogous to the Na-MMT simulations, two plateaus are observed in the swelling of Ca-MMT and the plateaus appear at water contents similar to those observed for Na-MMT. However, the d -spacing around the first plateau is about 0.5 Å larger than in Na-MMT. The different d -spacing suggests the hydrate structure formed in Ca-MMT differs

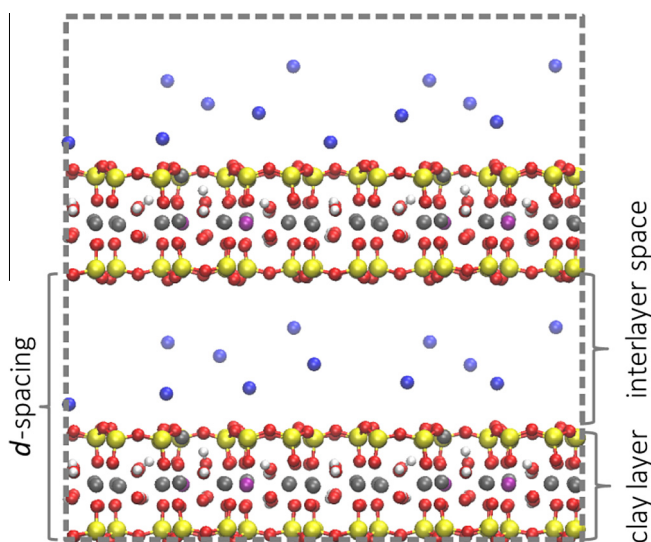


Fig. 1. Structure of the Na-MMT super-cell. The color code of the atoms is yellow for silicon, grey for aluminum, purple for magnesium, red for oxygen, white for hydrogen, and blue for sodium. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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