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Research paper

Molecular dynamics simulation of hydrated Na-montmorillonite with inorganic salts addition at high temperature and high pressure

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ABSTRACT

The swelling behaviors of Na-montmorillonite (Na-Mt) in non-ambient environment have been the subject of considerable speculation due to the difficulties associated with their study. Inorganic salts are often used to minimize clay mineral hydration. The influence of inorganic salts addition (NaCl, $CaCl_2$, KCl) on the hydration of Na-Mt at high temperature and high pressure (HTHP) was investigated by molecular dynamics simulation at 6 GPa and different temperatures (200, 300, 400, 500 and 600 K) in an isobaric isothermal ensemble (NPT). Water model and force field used in the clay-water system are SPC/E model and universal force field (UFF), respectively. The results show that after adding inorganic salts into Na-Mt, the mobility of the interlayer species increases, and the hydration shell of the interlayer cations decreases with a rise in temperature. The influence of temperature on the diffusion of water molecules is much greater than that of the ions present in the interlayer. Temperature increase and hydration degree play an important role on the diffusion behavior of the interlayer species. The size, valence, mass and hydration energy of cations present between the layers affect the structure of Na-Mt interlayer. The inorganic salts are able to inhibit the hydration of Na-Mt by reducing the mobility of the interlayer species and the basal spacing. After analyzing the effect of each salt on Na-Mt, it was found that, the most stable state of Na-Mt at HTHP is achieved with KCl addition, compared with NaCl and $CaCl_2$. It is expected the results obtained from this study would help to understand the inhibition effect of inorganic salts on Na-Mt, and predict the swelling of Na-Mt at HTHP.

1. Introduction

Clay minerals are the ubiquitous components in the earth's geologic deposits, terrestrial weathering environments and marine sediments. They play important roles in many industrial processes such as catalysis, hydrocarbon drilling, diagenetic, metamorphic, petrologic, geochemical processes, soil mechanics and physics, agronomy, properties and behavior of soils, retention and transport of contaminants, waste management, and in petroleum exploration and recovery, borehole instability, adsorption of stabilizing additives and polymers, overpressure and migration of hydrocarbons (Magara, 1974; Steiger, 1982; Hall et al., 1986; Huggett and Shaw, 1993; Velde, 1995; Rutherford et al., 1997; Cotter-Howells and Patterson, 2000). Montmorillonites are 2:1 clay minerals consisting of an octahedral sheet between two tetrahedral sheets. Isomorphic substitution of Mg^{2+} for Al^{3+} in octahedral site and isomorphic substitution of Al^{3+} for Si^{4+} in tetrahedral result site in the negative charges in the montmorillonites which are balanced by counter ions such as Na^+, Ca^{2+} and K^+. These interlayer cations are exchangeable with other cations in water solution by the cation exchange (CEC) process. Na-Mt has a high ability to swell in wet environments, and can exhibit two different regimes which are crystalline and osmotic swellings (Norrish, 1954; Boek et al., 1995; Karaborni et al., 1996; Cygan et al., 2004; Tambach et al., 2004; Warr and Berger, 2007; Salles et al., 2008; Zheng et al., 2011). These characteristics are well known from experimental and simulation studies (Sposito et al., 1983; Yamada et al., 1994; Chávez-Páez et al., 2001) under normal conditions, but less are known at HTHP (de Carvalho and Skipper, 2001) due to the lack of information. To understand the swelling behavior and the effect of inorganic salts addition on Na-Mt, we need to study the mechanism of water adsorption on its surface and gain knowledge of the interlayer cations hydration, dynamics of intercalated species, layer charge, substitution type and distributions, environmental conditions, temperature as well as pressure (Zhang et al., 1993; Segad et al., 2012). Tuck et al. (1984) have used the quasi-elastic neutron scattering to measure the diffusion of water molecules in a two layered Ca-Mt at three different temperatures. Morodome and

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Kawamura (2009) have used the X-ray diffraction to study the swelling behavior of Na-, Ca-Mt at temperatures up to 150 °C. de Carvalho and Skipper (2001) have used Monte Carlo simulation in the grand canonical ensemble to show that none of K-Mt hydrates are stable under 353 K and 625 bar. Zheng and Zaoui (2013) have employed molecular dynamics simulation to study the effect of temperature on the diffusion of water and monovalent counter ions in hydrated montmorillonite under temperature range between 260 and 400 K. In the present work, our aim is to investigate the swelling characteristics of Na-Mt at HTHP in the regime of crystalline swelling with inorganic salts addition. The effect of temperature and pressure on the diffusion of interlayer species, the interaction between water-oxygen and interlayer cations, the effect of inorganic salts on the stability of Na-Mt and the change that occurred on its structure at increasing temperature and constant pressure.

2. Methodology

2.1. System set up

The clay mineral model used in this study was taken from the model derived by Skipper and co-workers (Skipper et al., 1995). The unit-cell formula was:

$$Na_{0.75}[Si_{7.75}Al_{0.25}](Al_{3.25}Mg_{0.75})O_{20}(OH)_4 \qquad (1)$$

Na-Mt model was constructed, and the atomic coordinates were derived from the space group of monoclinic C2/m with a = 5.23 Å, b = 9.06 Å, c = 9.60 Å (with no water in interlayer spaces), c value changed with water molecule content between the layers, α = 90°, β = 99.00°, γ = 90°, and the symmetrical L2PC structure (Wang, 2005). The clay mineral layers were considered as rigid molecules and mirror image. The atomic charge assigned to each atom sites in the clay were given by Smith (1998). Based on the primitive unit cell, the supercell of the model (4a × 2b × 1c) was built (Fig. 1).

The measure of the three-dimensional, periodic boundary conditions applied to the system was 20.92 × 18.12 Å^2, which consists of 320 atoms in each of clay mineral layers equivalent to 8 unit cells and 6 atoms of sodium.

2.2. Molecular dynamics simulation

Molecular simulation was performed under the module “Forcite” of Materials Studio 5.0 software to investigate the effect of inorganics salts on the hydration process of Na-Mt at HTHP. The interaction between the atoms was described by Universal Force Field (UFF). Metal-Oxygen interactions were based on a Lennard-Jones potential combined with electrostatics. For the water behavior SPC/E model of Berendsen et al. (1987) was used. The simulation was carried out at P = 6 GPa and temperatures changing from 200, 300, 400, 500 to 600 K in the isobaric isothermal ensemble (NPT) in which the temperature and pressure were constant via a Nose-Berendsen thermobraostat, while the volume of the system was allowed to vary (Frenkel and Smit, 2002; Cramer, 2013). We chose to output the atomic positions every 0.5 ps during production runs, the total simulation time were set to 1000 ps, the number of steps was 2,000,000, and the frame output was obtained every 5000 steps. The short range van der Waals forces were applied with a 6 Å cut-off radius. To calculate the long range electrostatics, the Ewald summation method was used. The total potential energy was given by the summation of all interaction sites of the system:

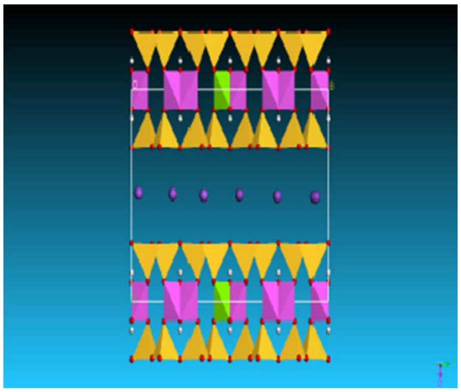

Fig. 1. A snapshot of Na-Mt, Si = yellow, Al = purple, Mg = green, O = red, H = white and Na = blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$U = \sum_i \sum_j \left(q_i q_j / r_{ij} + 4\varepsilon_{ij} \left[\left(, \sigma_{ij}/r_{ij}\right)^{12} - \left(, \sigma_{ij}/r_{ij}\right)^{6} \right] \right) \qquad (2)$$

where q_i and q_j are the charges on atom i and j, r_{ij} is the distance between atom i and j, ε_{ij} and σ_{ij} are Leonard-Jones parameters deduces from Lorentz-Berthelot rules. All the interaction terms of Leonard-Jones are from the combination of these relationships (Smith, 1998):

$$\sigma_{ij} = 1/2(\sigma_i + \sigma_j) \qquad (3)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \qquad (4)$$

The potential parameters used for oxygen and hydrogen were those used in water (Salles et al., 2008). The method of velocity initialization used for the dynamics calculation was Random. The water content considered in these simulations was 48, 72 and 128 water molecules for one, two and three hydration layers, respectively. From the output data obtained, radial distribution functions (RDFs), total energy, basal spacing and mean square displacement (MSD) profiles were calculated.

2.3. Analysis of simulation results

The basal spacing (c) was calculated from the NPT simulations (Zhou et al., 2011):

$$c = \langle V \rangle/(2 \times S) \qquad (5)$$

where $< V >$ denotes the statistically averaged volume of the simulated system, and S is the basal surface area.

The RDF of water molecules around the interlayer cations was calculated as (Kotkoskie et al., 1992):

$$g(r) = 1/(4\pi\rho r\text{\^{}}2\ )\, dN/dr \qquad (6)$$

where ρ is the number density of water molecules, dN is the average number of particle of water molecules lying at the region of $r + dr$ from a cation. N is the coordination number $n(r)$ of water molecules around the cation.

The self-diffusion coefficient D of the interlayer species was calculated with a two-dimension Einstein relation (Chang et al., 1997):

$$D = 1/4d/dt\,\langle r(t)^2 \rangle \qquad (7)$$

where $\langle r(t)^2 \rangle$ is the mean square displacement of the particle defined by $r(t) = R(t) - R(0)$, with $R(t)$ is the particle position at time t, and $R(0)$ is the initial particle position.

3. Results and discussion

3.1. Interaction between interlayer cations and water oxygens

3.1.1. NaCl addition into hydrated Na-Mt

After investigating the RDF of Na-O(w) in one, two and three hydration layers, it was observed that for the temperature rising from 200 to 600 K at 6 GPa, the RDF peaks of Na-O(w) in each layer decreased with the rise of temperature (Fig. 2). The decrease in the peaks of the RDF of Na-O(w) was due to the decrease of the amount of water molecules around Na cations when the temperature and the hydration degree increased. The increase in temperature led to reduction of the size of the hydration shell of Na cations, and facilitated their movement