Research paper

Molecular dynamics study of the dissolution mechanism of kaolinite basal surfaces in alkali media

Zeinab Naderi Khorshidi, Xiaoli Tan, Qi Liu, Phillip Choi*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada

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ABSTRACT

The geopolymerization process involves the dissolution of aluminosilicates in an alkali solution followed by the polymerization of the dissolved aluminate and silicate oligomers to form an amorphous geopolymer. It is generally accepted that the dissolution determines the nature of the oligomers formed, thereby the properties of the resultant geopolymer. Accordingly, in this work, a series of molecular dynamics (MD) simulations were carried out in the isothermal-isobaric (NPT) ensemble at 298 K and 1 atm to study the initial stage of dissolution process that takes place at the two basal surfaces (partially deprotonated octahedral and tetrahedral) of kaolinite in alkali media. Three different alkali media containing sodium (Na^+), potassium (K^+) and a mixture of 50/50 Na^+/K^+ cations were modeled at low (1 M) and medium (5 M) concentrations. The MD results showed that cations migrated to the vicinity of the deprotonated sites, trigging the dissociation of the nearby surface hydroxyl groups and increasing the interatomic distances between the aluminum atom that were adjacent to the deprotonated site and those attached such aluminum atom, thereby dissolving them in the form of aluminates into the alkali solution. Radial distribution functions and structural analyses indicated that the crystallinity of the model kaolinite decreased as simulation time and alkali solution concentration increased. The distortion occurred mostly on the octahedral surface that was attributed to the change of the coordination of aluminum from 6-fold octahedral to 5- and 4-fold tetrahedral. However, Na^+ and K^+ exhibited different dissolution mechanisms. In particular, Na^+ with a higher charge density induced more dissociation of the surface hydroxyl groups, whereas K^+ with a lower charge density resulted in more dissociation of aluminum atoms in the form of aluminates. In the case of the solution containing 50/50 Na^+/K^+, there was a synergistic effect of both cations that the solution led to more surface structure distortion as quantified by the number of 5- and 4-fold aluminum atoms.

1. Introduction

Over the past few decades, geopolymerization has attracted tremendous interests to alter the industrial wastes to geopolymers which can be used as construction materials. Properties of these materials are comparable to those of the Portland cement. One major advantage of the geopolymerization process, compared with the Portland cement production process, is that the process requires much less energy, thereby less greenhouse gases emission. Studies showed that the geopolymerization process reduces CO_2 emission by about 80% (Gartner, 2004; Habert et al., 2011). A geopolymer is essentially formed by the initial dissolution of the aluminosilicate source material in an alkali solution followed by the reaction of the dissolved aluminate and silicate oligomers to form a three-dimensional, amorphous structure interlinked tetrahedrally, alternatively sharing all oxygen atoms (Davidovits, 1994). The tetrahedrally coordinated aluminum carries a negative charge that is balanced by an alkali cation (e.g., sodium (Na^+))

(Davidovits, 1994; Rovnaník, 2010).

In the dissolution step, it is believed that the alkali solution (i.e., high pH) activates octahedral surfaces of the aluminosilicate source material by deprotonation (Huertas et al., 1999). This surface activation is considered as a necessary step for the subsequent dissolution of the aluminum (Al) and silicon (Si) containing species (oligomers) (Duxson et al., 2007; Grutzeck and Siemer, 1997). According to Xu et al. (Xu and van Deventer, 2003) the final strength of a geopolymer highly depends on the Si/Al ratio of the gel phase (i.e., the oligomer solution) that is formed during the dissolution process. It is worth noting that Si/Al ratios in the range of 2 to 3 generally yield geopolymers with higher compressive strengths. Therefore, understanding the dissolution process is essential for optimizing the geopolymerization processes and the resultant geopolymers (Catauro et al., 2014; Van Jaarsveld et al., 1998; Xu and Van Deventer, 2000).

Researchers have evaluated the dissolution process of aluminosilicate source materials under different conditions in terms of alkali type,

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concentration, pH and temperature. In most studies, kaolinite was used as the aluminosilicate source material. Kaolinite, $Al_4[Si_4O_{10}](OH)_8$, is a typical mineral with a 1:1 type layered structure, which comprises aluminum octahedral sheet and silicon tetrahedral sheet. These two sheets are connected together by bridging oxygens (Al−O−Si). For the tetrahedral sheet, a silicon atom is bound to three other silicon atoms through bridging oxygens (Si−O−Si) leading to the formation of the tetrahedral surface. This arrangement of tetrahedral silicones forms six-membered silica ring on the surface that is called tetrahedral cavity. For the octahedral sheet, each aluminum atom is connected to two oxygens of the tetrahedral sheet and shares four hydroxyl moieties with adjacent aluminum atoms. Three of these hydroxyl moieties are oriented toward the external surface giving rise to the octahedral surface while the fourth one is oriented inward in the direction of the tetrahedral cavity (Huertas et al., 1999; Vasconcelos et al., 2007). All layers in kaolinite structure are kept together by weak hydrogen bonds between hydroxyl moieties extending from the octahedral surface of a layer to the basal oxygen atoms on the tetrahedral surface of the adjacent layer.

Studies have shown that the bridging oxygen atoms on silicate surface tend to be highly hydrophobic (Iler, 1979; Šolc et al., 2011). Blum and Niss (1991) showed that adsorption of proton at the silicate surface of kaolinite is very weak and the (Si−OH−Si)$^+$ sites at the tetrahedral layer will not be detectable by surface titration in the pH range studied. Huertas et al. (1999) studied the dissolution of kaolinite at ambient temperature and pressure over the pH range of 1 to 13. Their findings confirm that the adsorption of protons at the Si sites of the kaolinite surface and edges is negligible and the limiting step for the dissolution of kaolinite in an alkali solution is the formation of an AlO$^-$ surface complex and the detachment of the Al atom from the structure. In fact, the octahedral surface becomes deprotonated at high pH (> 9). Bauer and Berger (1998) studied the kinetics of the kaolinite dissolution in a solution containing K$^+$ cations ranging from 0.1 to 4 M at various solid-solution ratios. It was reported that the rate-limiting step is the dissolution of the octahedral layer of kaolinite. Carroll and Walther (1990) studied the dissolution of kaolinite at 25, 60 and 80 °C at various pH ranging from 1 to 12. They found that at high pH, the detachment of Si from the kaolinite structure is slower than that of Al. On the other hand, Walther's studies showed that under alkali conditions, formation of SiO$^-$ complexes controls the rate of the dissolution of kaolinite (Brady and Walther, 1989; Walther, 1996). Panagiotopoulou et al. (2007) studied the dissolution of different industrial aluminosilicate minerals and by-products in the alkali media. The experimental results showed that the extent of dissolution of Al and Si atoms of the reactive materials, such as metakaolin, in the sodium hydroxide (NaOH) solution was ∼40% higher than the KOH solution. However, in the case of kaolin, the KOH solution yielded ∼10% more dissolution of Al and Si atoms than the NaOH solution. Nevertheless, in both cases, more Si atoms were released to the solution. Xu and Van Deventer (2000) investigated the extent of dissolution of 16 different minerals in the alkali solutions and the subsequent geopolymerization processes. It was concluded that in the presence of K$^+$ and calcium (Ca^{+2}) cations, the Si/Al ratio reached to 2. Hajimohammadi et al. (2010) have found that the release of alumina in the early stage of the reaction leading to a more homogeneous geopolymer gel.

In view of the apparent conflicting results of the interaction/dissolution of kaolinite in alkali media reported in the literature, in the present research, molecular dynamics (MD) simulation was utilized to study the interaction/dissolution mechanism of two basal surfaces of kaolinite at low (1 M) and medium (5 M) concentrations of three different alkali solutions at ambient condition (i.e., 298 K and 1 atm). Here, it should be noted that alkali solutions with concentrations > 1 M have a pH close to 14 at room temperature. Since NaOH and KOH solutions are widely used in the geopolymerization process (Aldabsheh et al., 2015; Xu and Van Deventer, 2000), in this study, alkali media containing Na$^+$, K$^+$ and a mixture of 50/50 Na$^+$/K$^+$ were studied.

2. Simulation method

Interactions between kaolinite's basal surfaces and the alkali solutions were modeled using the CLAYFF force field. The CLAYFF force field is commonly used to model structural and dynamical properties of hydrated clay systems and their interfaces with fluid phases by other researchers (Cygan et al., 2004; Greathouse and Cygan, 2005; Wang et al., 2005). The force field treats clay minerals made up of flexible structures. In particular, interactions between the oxygen and metal atoms in the clay lattice are described by short-range 12-6 Lennard-Jones (LJ) potentials and long-range Coulombic potential using ab initio atomic partial charges (Payne et al., 1992). Therefore, interaction energy between metal and oxygen atoms is given by the sum of LJ and Coulombic potentials:

$$E_{total} = E_{coul} + E_{LJ} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i\neq j} \frac{q_i q_j}{r_{ij}} + \sum_{i\neq j} D_{0ij} \left[\left(\frac{R_{0ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{0ij}}{r_{ij}} \right)^6 \right]$$

(1)

where e is the charge of the electron, ε_0 is the permittivity of vacuum, q_i and q_j are ab initio partial atomic charges, r_{ij} is the distance between atoms i and j. D_{0ij} and R_{0ij} are empirical parameters. All non-bonded and bonded parameters for the CLAYFF force field (Cygan et al., 2004) used in this study are presented in Tables 1 and 2.

In the CLAYFF force field, interactions between water molecules are described by the simple point charge (SPC) water model, which has been used to study properties of bulk water and aqueous systems (Berendsen et al., 1981; Smith and Haymet, 1993; Teleman et al., 1987; Wallqvist and Teleman, 1991). The atomic structure of kaolinite was taken from the crystal structure refinement data determined from neutron diffraction studies performed at 1.5 K with well-characterized hydrogen position data (Bish, 1993). According to reference (Bish, 1993) kaolinite has triclinic lattice structure with C1 symmetry and the lattice parameters are a = 5.1535 Å, b = 8.9419 Å, c = 7.3906 Å, and α = 91.926°, β = 105.046°, γ = 89.797°. Three-dimensional periodic boundary conditions were employed to all simulations reported here and all dimensions of the cell were free to vary independently. The simulation cell was built by repeating the kaolinite unit cell along the three axes (12 × 12 × 6 units in *x*, *y*, and *z* dimensions) which led to the formation of contained 864 kaolinite unit cells. The aqueous part of simulation cells in this study contained 4020 water molecules and 84 and 420 cations for 1 M and 5 M solutions, respectively. First, the cell of 4020 water molecules with the dimension of 61.7 Å × 107.2 Å × 18.6 Å was built based upon the density of water at ambient condition and was assembled with the basal surface of kaolinite (the *ab* plane) to create the solid-aqueous solution interface with the dimension of 61.7 Å × 107.2 Å × 65.1 Å. It is worth noting that kaolinite has two different (001) basal surfaces and building a simulation cell in this way allowed us to simultaneously study the interactions at both interfaces using molecular dynamics (MD) simulation. Afterwards, cations were inserted in the solution region of the simulation cell in three different initial configurations, i.e., i. random distribution of cations in the solution region, ii. positioning of cations in

Table 1
Nonbonded parameters used in the CLAYFF force field[23].

Force field type	Symbol	Charge (e)	D_0 (kcal/mol)	R_0 (Å)
Water hydrogen	h*	0.410		
Water oxygen	o*	−0.820	0.1554	3.5532
Hydroxyl hydrogen	ho	0.425		
Hydroxyl oxygen	oh	−0.950	0.1554	3.5532
Bridging oxygen	ob	−1.050	0.1554	3.5532
Tetrahedral silicon	st	2.100	1.8405×10^{-6}	3.7064
Octahedral aluminum	ao	1.575	1.3298×10^{-6}	3.7064
Aqueous sodium ion	Na	1.000	0.1301	2.6378
Aqueous potassium ion	K	1.000	0.1000	3.7423