



Molecular dynamics study on the Tri-calcium silicate hydration in sodium sulfate solution: Interface structure, dynamics and dissolution mechanism

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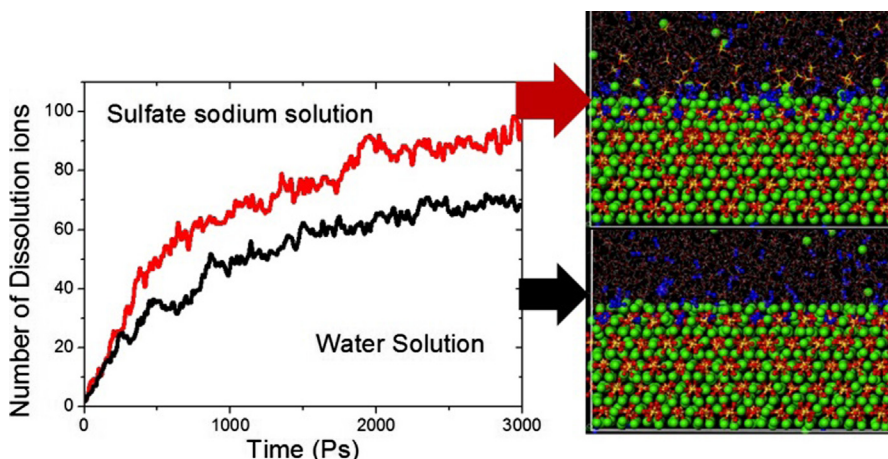
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HIGHLIGHTS

- Surface water forms hydration layer tessellated on C_3S surface.
- The OH and Ca ions diffuse from the C_3S surface and dissolve in solution.
- Sulfate ions are adsorbed on the C_3S surface.
- Sulfate solution inhibits the dissolution of OH and Ca ions.
- Ca ions, SO_4 and Na ions form ionic cluster near the C_3S surface.

GRAPHICAL ABSTRACT

The surface adsorbed sulfate and sodium ions form ionic and hydrate layers, inhibiting the dissolution of ions in C_3S .



ARTICLE INFO

Article history:

Received 10 January 2018

Received in revised form 28 February 2018

Accepted 2 March 2018

Keywords:

H-bond
Dissolution
Sulfate ions adsorption
Molecular dynamics
Calcium silicate gel

ABSTRACT

The hydration and dissolution of tri-calcium silicate mineral is of great importance for guiding the material design. In order to understand the hydration mechanism of C_3S mineral in sodium sulfate solution, molecular dynamics was employed to construct three interface models of C_3S and Na_2SO_4 solution of 0 mol/L, 0.79 mol/L and 1.58 mol/L and the structure, dynamics and dissolution properties of the interfacial species were investigated. Due to hydrophilic nature of C_3S surface, the water molecule in hydrate layer deeply tessellated on the vacancy surface region shows high intensity packing, ordered arrangement, enlargement of the dipolar moment value and orientation preference. With progressively increasing simulation time, the hydroxyl groups and calcium atoms in the high reactive surface gradually escape from the substrate bonding restriction and diffuse away to the solution region. Furthermore, both ions prefer to adsorbing on the surface of tri-calcium silicate mineral: the highly solvated surface calcium ions associate with the oxygen sites in the sulfate ions, forming the $Ca-SO_4$ ionic pairs in the interfacial region; the sodium ions are attracted by the non-bridging oxygen in the silicate monomers, forming Na–O connection. The surface adsorbed water molecules, sulfate and sodium ions, strongly associated

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with the calcium atoms and hydroxyl groups, form a ionic and hydrate layer, stabilizing the tri-calcium silicate surface and inhibiting the dissolution of ions in C_3S . With increasing ions' concentration, the sulfate and sodium ions in the solution are more probable to form cation-anion pairs and further accumulate to the ionic cluster.

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1. Introduction

Water plays critical important role in the hydration and dissolution process of the mineral that ubiquitously exists in wide range of geological, environmental, biological and chemical fields: such as carbonate accumulation in marine sediments and global cycle of chemical elements [1], the production and utilization of some construction and building materials [2], retrograde filling biocompatible and bioactive material in apical surgery [3], and immobilization of the heavy metal containment [4] and so on. Tri-calcium silicate (C_3S) is the main mineral component in the Portland cement. The complex hydration reaction taking place between C_3S and water is considered as the main reason for hardening of the cement paste [5] and the reaction is responsible for the mechanical properties and durability of the material. Cement-based concrete materials, serving in the marine environment such as bridges and subbottom tunnel, suffer the sulfate ions attacking from the sea water. The detrimental ions influence the hydration of cement-based material, and further destroy the micro-structure of the cement hydrate, finally resulting in the durability degrade for the marine concrete structure. Understanding the mechanism of cement hydration in detrimental environment can help explore the effective techniques to design sustainable materials that have better strength and longer service time. Considering that the production and utilization of the cementitious material result in about 8%~10% of greenhouse gas emission [6], reduction of cement material production by improving the hydration properties is meaningful.

The hydration and dissolution reactions of C_3S are greatly dependent on the interaction between the minerals and the interfacial water. The properties of water in the vicinity of the mineral substrate have been probed by various experimental techniques. Near infrared spectroscopy (NIR), providing information on the vibration and bending of hydrogen bonds, quantitatively distinguished the water state by the H-bond strength and characterized the state evolution of water during the hydration of tri-calcium silicate paste [7]. By using the 1H nuclear magnetic resonance (NMR) [8–10], the water in the C_3S /water system was categorized into three types: chemical bound water that is incorporated into the structure and form strong chemical bound with calcium silicate structure, physical bound water that is deeply adsorbed near the surface and capillary water without bound and diffuse freely in the capillary pore. Quasi Elastic Neutron Scattering (QENS) can also monitor the water conversion during the mineral hydration and differentiate the bound, constrained and “free” water in the mineral environment by probing the relaxation dynamics of water molecules [11]. Based on QENS method, Fratini [12] evidenced that the diffusion coefficient decreases from $4.0 \times 10^{-9} \text{ m}^2/\text{s}$ to $4.0 \times 10^{-10} \text{ m}^2/\text{s}$ for water/ C_3S system after 2 day hydration. The one order magnitude of the diffusion coefficient reduction is induced by water transforming from free state to surface associated state during the hydration. The experimental study on the C_3S hydration provides insights of the complex H-bonds structure and diffusion behavior of surface associated water molecule.

Furthermore, computational method, such as ab initio and molecular dynamics, can give the complementary interpretation of the mineral hydration and dissolution process. Hydration

reactivity of calcium silicate polymorphs were investigated by Wang et al. [13] Based on the adsorption energy surface analysis from the ab initio calculation, DFT energy barriers and the number of reactive sites were proposed as the key aspect that controls hydration reactivity of the mineral surface. The water rotation, dissociation and diffusion were observed in the reactive sites of the silicate mineral. Manzano et al. [14] further disclosed the hydration mechanism of silicate polymorphs by the molecular dynamics simulation. They found that hydrogen from the dissociated water molecule penetrated into the mineral, forming the calcium silicate hydrate layer. The topology of the mineral structure can hide the water molecule by tessellation, stabilizing against dissolution. The molecular dynamics research unraveled the hydration mechanism of C_3S in water solution more deeply. In many cases, besides the water solution, the tri-calcium silicate mineral hydrates in the ionic solution to moderate the hydration ability and ions dissolution rate. Hence, it is necessary to study the coupled effect by water molecules and solvated ions on the hydration and dissolution of silicate mineral.

In this study, molecular dynamics was utilized to model the interaction between sulfate sodium solution and tri-calcium silicate mineral. The interface structure for the water molecules and solvated ions was characterized by the density profile, H-bond distribution and spatial correlation functions. The dynamic properties of the interfacial species were further analyzed by the mean square displacement and time correlation function. Furthermore, the dissolution of tri-calcium silicate mineral at sulfate concentration was studied to unravel the influence of sulfate ions on the hydration process of silicate mineral.

2. Simulation method

2.1. Model construction

The tri-calcium silicate mineral model is based on C_3S crystal determined by Mumme in 1995 [15]. In order to efficiently implement in MD simulation, Heinz [16] transformed from triclinic coordinates to orthorhombic coordinates. The orthorhombic structure of C_3S is shown in Fig. 1a. Cleavage of the tri-calcium silicate structure in [0 4 0] direction results in the calcium atoms and dangling oxygen atoms. The dangling atoms near the surface boundary are transformed to Ca–OH by adding hydrogen atoms or hydroxyl groups. The oxygen atoms in the tri-calcium silicate mineral solid are described by the symbol Onb for analysis and discussion in following sections.

In the simulation, the supercell of tri-calcium silicate model contains $4 \times 4 \times 2$ crystallographic unit cells. The dimension of the supercell is $\mathbf{a} = 48.74 \text{ \AA}$, $\mathbf{b} = 28.12 \text{ \AA}$, $\mathbf{c} = 50.55 \text{ \AA}$ and $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. After cleavage of the super-cell, a vacuum region with thickness larger than 50 \AA was built along \mathbf{y} direction for three models. For the first model, only 4800 water molecules are added into the vacuum region of the tri-calcium silicate substrates. The water molecules were initially distributed randomly in the simulation box. As proposed in most cases of water and ions simulation in the nano pore [17–19], the number of water molecules in the pore is required to satisfy the density of bulk aqueous solution under ambient conditions ($\sim 1 \text{ g/cm}^3$). Besides pure water solution

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