Interaction of Zinc Ions with Hydrated Calcium Silicate Surfaces

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Abstract: Cement materials with calcium silicate hydrate (CSH) gel as the main hydration product have good ability to immobilize heavy metal contaminants. In order to fundamentally understand the curing mechanism of cement materials, the atomic intensity distribution, kinetic properties of Zn$^{2+}$ ions near the interface of CSH gels were investigated by molecular dynamics method by building a realistic CSH gel nanopore model and aqueous ZnCl$_2$ solution. The simulation results show that the interaction between zinc ions and hydrated calcium silicate surface is mainly through the desorption of calcium ions, which leads to the negative charge of the whole hydrated calcium silicate matrix, and thus the adsorption of Zn$^{2+}$ by coulombic force, and thus the immobilization effect of Zn$^{2+}$.

Keywords: CSH heavy metal contaminants adsorption cement materials.

1. Introduction

Among the hazardous heavy metals, zinc (Zn) is considered a hazardous contaminant and is present at high levels in most contaminated sites in the world [1-2]. Zinc is retained in contaminated soil in the chemical form of free ions (Zn$^{2+}$), zinc carbonate (ZnCO$_3$), zinc sulfate (ZnSO$_4$), zinc sulfide (ZnS) and zinc complex ions [3]. It can enter the human body and pollute the surrounding environment through various "indirect contact" or "direct contact" pathways such as the food chain and groundwater, leading to risks to human health and the environment [4-5]. Studies have shown that excessive intake of Zn through "indirect contact" or "direct contact" will stimulate the proliferation of prostate tissue and cause malignant tumor diseases such as lung cancer and digestive tract cancer in humans. Therefore, the remediation of heavy metal contaminated soil is urgent.

Cement is the most widely used inorganic material for the remediation of heavy metals in the world, and calcium silicate hydrate (C-S-H) is the main reaction product during the hydration of cement particles, accounting for 60%-70% of the hydration products of cement particles, and is the most critical bonding phase in cement paste, with a multiscale porous structure allowing water molecules and ions to reside in it [6-7]. Therefore, it is of great importance to study the interaction between water molecules and zinc ions on the hydrated calcium silicate surface from the molecular scale.

2. Model Construction

In this paper, Hamid 11Å tobermorite cells with the chemical formula Ca$_4.5$[Si$_6$O$_{15}$(OH)$_3$]$\cdot$2H$_2$O were used as the initial configuration[8]. To create orthogonal supercells, monoclinic cells are transformed into orthogonal cells. a, b, c, α, β, and γ have cell parameters of 11.2, 7.4, 22.8, 90°, 90°, and 90°, respectively. Based on the above-mentioned crystals, a realistic C-S-H model is constructed by the following steps. First, all interlayer water molecules are removed. The silicate chains were then shortened by randomly removing the bridging site silicate tetrahedra. Some dimeric structures were also removed, making the resulting structures match the Qn distribution, Ca/Si ratio of the CSH of the cement material. Subsequently, the unit cell was cut along the [0, 0, 1] direction and the orthorhombic cell was then repeated at 3 × 5 × 2 to obtain a C-S-H model with dimensions of 33.5 Å (x), 37 Å (y), and 32.5 Å (z). Giant canonical Monte Carlo simulation simulations (GCMC) were applied to the modified model so that water molecules were adsorbed in the structure until a density similar to the experiment was reached at room temperature (300 K) with a chemical potential μ of 0 eV applied in GCMC. The energy of the C-S-H model was minimized using lammps by the fastest descent method and geometric optimization to reach equilibrium (as in Figure 1). The final calcium to silicon ratio (1.625), Qn distribution (Q0 = 13%, Q1 = 67%, Q2 = 20%) and density (2.73 g/cm$^3$) of the final C-S-H model are close to the experimental results.

3. Analysis of Results
Figure 2 records the transformation of Zn$^{2+}$ and Cl- ions from solution to the C-S-H interface region during 1000 ps. In the first 500 ps, Zn$^{2+}$ and Cl - ions diffuse toward the calcium silicate surface. Around 1000 ps, most of the Zn$^{2+}$ ions are adsorbed on the calcium silicate substrate, which indicates a strong adsorption of Zn ions. On the other hand, some of the surface calcium atoms were desorbed from the C-S-H surface and diffused into the solution. The zinc ion...
adsorption and calcium ion desorption processes indicate that
cation exchange occurs between the liquid and solid phases. 
And it can be seen in Figure 2.c that some of the zinc ions on 
the CSH gel surface are surrounded and form ionic clusters.

Figure 3. Atomic intensity distribution of chloride and 
zinc ions

The atomic intensity distribution shown in Fig. 3 provides quantitative information on the atomic structure of the interface. z=0 is the bottom of the model, and the position of the interface CaO-Os is defined as the solid-liquid boundary (z=20.2Å,49.1Å ), which is shown by the black line, as shown in Fig. 3. The intensity peaks in Fig. 3 show that zinc ions are mainly concentrated on the surface of the CSH gel and there is also Zn$^{2+}$ distribution inside the hydrated calcium silicate, which means that zinc ions not only stay stably in the region near the matrix interface, but also inside the Zn$^{2+}$ hydrated calcium silicate matrix due to a large number of defective sites in CSH. As can be seen from the chloride ion peaks in Figure 3, the chloride ions are mainly concentrated in the middle region of the matrix, probably mainly due to the desorption of calcium ions resulting in the hydrated calcium silicate being negatively charged, thus repelling the chloride ions from moving in the surface region.

4. Conclusion

The interaction of zinc ions with the surface of hydrated calcium silicate is mainly through the desorption of calcium ions, which leads to the negative charge of the whole hydrated calcium silicate matrix, thus fixing a large amount of zinc ions on the surface of calcium silicate through the adsorption of Zn$^{2+}$ by coulombic forces. And there are a large number of defective sites inside the CSH, thus adsorbing zinc ions and water molecules into the internal cavity of the hydrated calcium silicate.

References