Role of Mg Impurity in the Water Adsorption over Low-Index Surfaces of Calcium Silicates: A DFT-D Study

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Abstract: Calcium silicates are the most predominant phases in ordinary Portland cement, inside which magnesium is one of the momentous impurities. In this work, using the first-principles density functional theory (DFT), the impurity formation energy ($E_{fo}$) of Mg substituting Ca was calculated. The adsorption energy ($E_{ad}$) and configuration of the single water molecule over Mg-doped β-dicalcium silicate (β-C$_2$S) and M3-tricalcium silicate (M3-C$_3$S) surfaces were investigated. The obtained Mg-doped results were compared with the pristine results to reveal the impact of Mg doping. The results show that the $E_{fo}$ was positive for all but one of the calcium silicates surfaces (ranged from −0.02 eV to 1.58 eV), indicating the Mg substituting for Ca was not energetically favorable. The $E_{ad}$ of a water molecule on Mg-doped β-C$_2$S surfaces ranged from −0.598 eV to −1.249 eV with the molecular adsorption being the energetically favorable form. In contrast, the $E_{ad}$ on M3-C$_3$S surfaces ranged from −0.699 eV to −4.008 eV and the more energetically favorable adsorption on M3-C$_3$S surfaces was dissociative adsorption. The influence of Mg doping was important since it affected the reactivity of surface Ca/Mg sites, the $E_{ad}$ of the single water adsorption, as well as the adsorption configuration compared with the water adsorption on pristine surfaces.

Keywords: calcium silicates; first-principles DFT; Mg doping; water adsorption; structural and electronic properties

1. Introduction

Population growth has driven the exponential increase in infrastructure demand, especially in developing countries like China and India [1,2]. As the main ingredients within construction materials, ordinary Portland cement (OPC) is thus attracting considerable attention. Many studies have been conducted not only for the efficient use of OPC, but also to reduce energy consumption and CO$_2$ emission during OPC production [3,4]. However, the fine-tuning of OPC requires a more fundamental understanding of its hydration mechanism, which is vital for the sustainable development of the cement industry and effective application of cement-based materials [5].

OPC consists of four main compounds, namely alite (50–70 wt.%), belite (15–30 wt.%), aluminate (5–10 wt.%), and ferrite (5–15 wt.%). Alite and belite are the impurity-modified constituents of tricalcium silicate ($\text{Ca}_3\text{SiO}_5$ or C$_3$S) and dicalcium silicate ($\text{Ca}_2\text{SiO}_4$ or C$_2$S), respectively. In contrast to aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) and ferrite ($\text{Ca}_2\text{Al}_x\text{Fe}_{2-x}\text{O}_5$, $0 \leq x \leq 1.4$) [6], C$_3$S and C$_2$S are often referred to as calcium silicates and, in most cases, control the hydration characteristics of OPC [7]. Since phenomenological
experiments could only provide an overall indicator for the cement hydration reactions, the theoretical method is a promising alternative to reveal the hydration mechanism of calcium silicates [8].

The structural and electronic properties of calcium silicates have been theoretically investigated using first-principles calculations or molecular dynamics [9–15]. For example, Durgun et al. [16] utilized first-principles calculations to reveal the relationship between the reactivity and electronic structure of calcium silicates. It was found that the high reactivity of C3S originated mainly from the reactive sites around its more ionic oxygen atoms compared with that of C2S. Laanaiya et al. [17] conducted a density functional theory (DFT) study to analyze the ground state properties of C3S, with an emphasis on investigating the reaction mechanism of C3S. Apart from the structural and electronic properties of calcium silicates, the water adsorption on calcium silicates surfaces, which is often regarded as the initial step for cement hydration [18,19], has also been studied. For example, Zhang et al. [13] conducted a DFT study to reveal the single water adsorption on C3S low-index surfaces and analyzed the electronic properties of the adsorption. Qi et al. [12] investigated the molecular and dissociative water adsorption on low-index surfaces of both β-C3S and M3-C3S. Other relevant studies regarding the water adsorption on calcium silicates surfaces include, but not limited to, Zhang et al. [20,21], Qi et al. [22], and Wang et al. [23]. However, the above studies mainly focus on the structural and electronic properties of pure calcium silicates, which is rarely observed in practice [7].

It is known that the most common impurities include Mg2+, Al3+, and Fe3+, which can substitute Ca2+ in calcium silicates [11]. Understanding the role of impurities is vital to reveal the hydration mechanism of calcium silicates [24]. A number of studies have thus been conducted to investigate the impact of chemical impurities on the structural and electronic properties of bulk calcium silicates [11,16,25–27]. For example, Tao et al. [26] investigated the Zn incorporation into silicate clinker using DFT calculations and proposed two indicators to characterize the Zn-doping mechanism. It was found that the preference of the zinc substitution was mainly controlled by the overall crystal deformation and local structural distortion. However, the impact of chemical impurities in the water adsorption over low-index surfaces of calcium silicates has not been well studied at the atomic level using first-principles DFT calculations.

In this work, the adsorption of a single water molecule over Mg-doped low-index surfaces of calcium silicates was investigated. Bader charge analysis was performed for the selection of doping sites and the impurity formation energy (Eiad) was calculated. The water adsorption was investigated in both a molecular and dissociative way. The adsorption energy (Ead) was calculated and the adsorption configuration was analyzed. Electronic properties, i.e., Bader charge, the partial density of states (PDOS), and decomposed charge density, were studied to reveal the binding mechanism of the water molecule over Mg-doped calcium silicate surfaces. A detailed comparison was conducted on the structural and electronic properties before and after water adsorption, and the results of water adsorption over Mg-doped calcium silicates surfaces were compared with that over pristine calcium silicates surfaces.

2. Computational Methods

In this work, β-C3S and M3-C3S morphologies were investigated due to their frequent occurrence during industrial applications of OPC [28,29]. All first-principles DFT calculations were conducted using the projector augmented-wave (PAW) method implemented in the VASP code [30–32]. The exchange-correlation potential was approximated by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [33]. Valence electrons of 3p64s2, 3s2, 3s23p6, 2s22p6, and 1s1 were selected for Ca, Mg, Si, O and H, respectively. After convergence tests, the kinetic energy cutoff was determined to be 600 eV and the energy tolerance was set to be 1.0 × 10−5 eV/atom. The structural relaxation of bulk calcium silicates was conducted until the maximum residual force on each atom was smaller than 0.01 eV/Å. Interested readers can refer to our previous work [12] for a detailed discussion about the bulk structures of β-C3S and M3-C3S.

Starting from the relaxed unit cells, low-index surfaces were cleaved with the retaining of the in-plane crystalline periodicity. Stoichiometry and neutrality were maintained during the surface cleavage. Moreover, the SiO4 tetrahedron is preserved since it is energetically costly to break the Si-O
covalent bond. Multiple cuts were tested to ensure the lowest energy configuration, and the slab and vacuum thicknesses were verified by convergence tests. The surface relaxation was performed without considering the symmetry between the top surface and the bottom surface \[10\]. Dipole correction was applied during surface calculations and the maximum residual force on each atom = 0.03 eV/Å was used as the converging criterion. For all DFT calculations, the electronic minimization was performed following the blocked Davidson iteration scheme and the ions updating was performed using the conjugate gradient algorithm. The surface energy for all low-index surfaces was calculated. Table S1 summarizes the calculation details (i.e., the Brillouin zone mesh) and the surface energy ($\gamma$) of pristine low-index surfaces of calcium silicates.

To determine the doping site of Mg, the chemical reactivity of Ca atoms was investigated. In this work, the Bader charge was calculated for surface Ca atoms since it is well regarded as an effective way to indicate surface reactivities \[34,35\]. The surface Ca atom with the highest chemical reactivity, namely the lowest Bader charge, was selected as the doping site of Mg. The substitution of Ca$^{2+}$ with Mg$^{2+}$ was performed, and then the surface slab was relaxed. The same DFT settings, i.e., energy cutoff and maximum residual force, were applied for the Mg-doped surface relaxation. The authors note that the determination of the substitution site using chemical reactivity was mainly due to the availability of computational resources. Impurity formation energy ($E_{\text{for}}$) was used as the indicator to understand the solubility of the dopants inside host lattice, which can be calculated as follows \[36\]:

$$E_{\text{for}} = E_S(\text{Mg}) - E_S(\text{pristine}) - \mu_{\text{Mg}} + \mu_{\text{Ca}}$$  \[1\]

where $E_S(\text{Mg})$ is the total energy of the Mg-doped slab, $E_S(\text{pristine})$ is the total energy of the pristine slab model, and $\mu_{\text{Mg}}$ and $\mu_{\text{Ca}}$ are the chemical potential of Mg and Ca atoms, respectively. The $\mu_{\text{Mg}}$ and $\mu_{\text{Ca}}$ were calculated from the total energy per atom in their stable structures, which were relaxed using the same DFT settings for the unit cell relaxation of calcium silicates.

Molecular water adsorption involved the placement of a free water molecule 3 Å above the Mg atom (Figure 1a). In terms of the dissociative water adsorption, one hydroxyl group was placed 3 Å above the Mg atom and the remaining proton was placed 1 Å above the adjacent dominating O atom, whose reactivity was determined by the Bader charge (Figure 1b). For the water adsorption calculations, the van der Waals correction D3 was also employed \[37–39\]. The adsorption energy ($E_{\text{ad}}$) can be obtained using the following equation:

$$E_{\text{ad}} = E_{\text{total}} - E_{\text{clean}} - E_{\text{water}}$$  \[2\]

where $E_{\text{total}}$ is the total energy of the (water + surface) system after adsorption, $E_{\text{clean}}$ is the total energy of the clean surface slab before adsorption, and $E_{\text{water}}$ is the energy of an isolated H$_2$O in a vacuum. Thermochemically speaking, the more negative of $E_{\text{ad}}$, the more favorable of the adsorption.
A negative surface was marginally favorable in energy. Therefore, Mg substitution was unlikely to form under thermodynamically equilibrium conditions for most low-index surfaces of calcium silicates. On the contrary, only the Mg substitution on the M3-C3 surfaces.

### 3. Computational Results

#### 3.1. Impurity Formation Energy

Table 1 summarizes the calculated $E_{\text{for}}$ of Mg substituting for Ca in low-index calcium silicates surfaces. Almost all cases, except Mg substitution in M3-C3 (111) surface, were characterized by the positive $E_{\text{for}}$. More specifically, the $E_{\text{for}}$ ranged from 0.51 eV to 1.21 eV for β-C2S, with 0.51 eV being observed at (101) and (111) surfaces while 1.21 eV was observed at the (001) surface. In the case of the Mg substitution in M3-C3 surfaces, the largest $E_{\text{for}}$ occurred at the (101) surface (1.58 eV). A negative $E_{\text{for}}$ of −0.02 eV, though quite small, was observed at the M3-C3 (111) surface. From a thermodynamic point of view, a positive $E_{\text{for}}$ means the substitution is not energetically favorable [36]. Therefore, Mg substitution was unlikely to form under thermodynamically equilibrium conditions for most low-index surfaces of calcium silicates. On the contrary, only the Mg substitution on the M3-C3 (111) surface was marginally favorable in energy.

| Calcium Silicate Phase | Low-Index Surfaces | $E_{\text{for}}$ (eV) | Calcium Silicate Phase | Low-Index Surfaces | $E_{\text{for}}$ (eV) |
|------------------------|--------------------|----------------------|------------------------|--------------------|----------------------|
| β-C2S                  | (100)              | 0.82                 | (100)                  | 0.46               |
|                        | (010)              | 0.74                 | (010)                  | 0.53               |
|                        | (001)              | 1.21                 | (001)                  | 0.76               |
|                        | (110)              | 0.78                 | (110)                  | 0.19               |
|                        | (101)              | 0.51                 | (101)                  | 1.58               |
|                        | (011)              | 0.94                 | (011)                  | 0.48               |
|                        | (111)              | 0.51                 | (111)                  | −0.02              |

#### 3.2. Adsorption Energy

In this section, we present our theoretical results for the $E_{\text{ad}}$ of the H2O over Mg-doped surfaces of β-C2S and M3-C3S. The calculated $E_{\text{ad}}$ are listed in Table 2.
Table 2. $E_{ad}$ (eV) of a single H$_2$O over Mg-doped surfaces of $\beta$-C$_2$S and M3-C$_3$S.

| Surface   | Dissociated | Free   | Dissociated | Free   |
|-----------|-------------|--------|-------------|--------|
| $\beta$-C$_2$S | (100) $-1.249$ (D) | (001) $-0.994$ (M) | (110) $-0.952$ (M) | (111) $-0.982$ (M) |
|           | (010) $-0.869$ (D) | (011) $-0.598$ (D) | (101) $-0.765$ (M) | (111) $-0.817$ (M) |
| M3-C$_3$S | (100) $-1.624$ (D) | (001) $-0.915$ (M) | (110) $-0.302$ (D) | (101) $-4.008$ (D) |
|           | (010) $-1.786$ (D) | (111) $-0.817$ (M) | (101) $-1.708$ (D) | (111) $-1.454$ (D) |

Note: Dissociated and free represent the initial configuration of the H$_2$O, M, and D in the brackets represent molecular and dissociative adsorption, respectively, after relaxation.

For the H$_2$O adsorption over $\beta$-C$_2$S surfaces, the $E_{ad}$ ranged between $-1.249$ eV (dissociative adsorption on $<100>$ surface) and $-0.598$ eV (dissociative adsorption on $<011>$ surface). The hydroxyl group and the proton approached each other and formed a water molecule on $\beta$-C$_2$S (001, (110), (011), and (111) surfaces. In contrast, dissociation of the H$_2$O was only observed over the $\beta$-C$_2$S (100) surface. Although the dissociative adsorption over the $\beta$-C$_2$S (100) surface was found to be the most energetically favorable, molecular adsorption was generally more favorable considering the $E_{ad}$ of other $\beta$-C$_2$S surfaces.

Though molecular adsorption was observed for the adsorption of water on $\beta$-C$_2$S (001, (110), and (111) surfaces regardless of the initial water configuration, the final adsorption configuration was different. Figure S1 illustrates the final adsorption configuration on the $\beta$-C$_2$S (001) surface as an example. The difference in the adsorption configuration led to the difference in the Ead.

Dissociative water adsorption was found to be more energetically favorable than molecular water adsorption over M3-C$_3$S surfaces. The most negative $E_{ad}$ ($-4.008$ eV) was obtained at the dissociative adsorption over the M3-C$_3$S (101) surface while the least negative $E_{ad}$ ($-0.699$ eV) was obtained at the molecular adsorption over the M3-C$_3$S (100) surface. The dissociation of the H$_2$O was observed at M3-C$_3$S (101), (011), and (111) surfaces while no reformations of H$_2$O from the hydroxyl group and the proton were observed. The above results imply the dissociative adsorption was more stable and energetically favorable on M3-C$_3$S surfaces, which agrees well with the results in the literature [12,22]. Moreover, the $E_{ad}$ of M3-C$_3$S surfaces was much more negative than that of $\beta$-C$_2$S surfaces, indicating the H$_2$O adsorption on M3-C$_3$S surfaces was stronger than that on $\beta$-C$_2$S surfaces.

3.3. Adsorption Configuration

Table 3 summarizes the adsorption configuration of the H$_2$O over $\beta$-C$_2$S surfaces. In most cases, bonding was found between the surface Mg atom and the O atom from the water molecule (O$_w$). The O$_w$ was attracted to surface Ca atoms in the molecular adsorption on (011) and (111) surfaces, indicating the Ca-O$_w$ bond was more favorable than the Mg-O$_w$ bond in these two cases. Both Ca-O$_w$ and Mg-O$_w$ bonds can be formed simultaneously for dissociative adsorption, which was not observed during the molecular adsorption.
Table 3. Adsorption configurations of the H$_2$O over Mg-doped β-C$_2$S surfaces with respect to the adsorption energy in eV.

| Surfaces | Summary of Bonding |
|----------|--------------------|
| (100)    | −1.249D: Mg−O$_w$, Ca−O$_w$, O$_s$−H$_d$, O$_w$−H$_d$ |
| (010)    | −0.869D: Mg−O$_w$, O$_s$−H$_d$, O$_w$−H$_d$; −0.937M: Mg−O$_w$, O$_s$−H |
| (001)    | −0.994M and −0.915M: Mg−O$_w$, O$_s$−H |
| (110)    | −0.952M: Mg−O$_w$, O$_s$−H |
| (101)    | −0.765M and −0.831M: Mg−O$_w$, O$_s$−H |
| (011)    | −0.598D: Mg−O$_w$, Ca−O$_w$(2), O$_s$−H$_d$, O$_w$−H$_d$; −1.116M: Ca−O$_w$ |
| (111)    | −0.982M: Ca−O$_w$, O$_s$−H(2); −0.817M: Ca−O$_w$, O$_s$−H |

Note: abbreviations in bold represent the adsorption energy (the number) and adsorption type (D stands for dissociative adsorption; M stands for molecular adsorption; ‘−’ represents O atoms from the water molecule, O$_w$ represents surface O atoms, H$_d$ represents the dissociated proton, ‘−’ represents bond formation, ‘–’ represents the two atoms are attracted to each other without bond formation; the hydroxyl group from the water molecule is not shown for clarity.

The dissociated proton (H$_d$) was attracted to a surface O atom (O$_s$) of the calcium silicates. Moreover, the dissociative configuration was also influenced by O$_w$ and O$_s$ atoms. Although the adsorption configuration was mainly influenced by the Ca−O$_w$ or the Mg−O$_w$ bond for the molecular adsorption, the attraction between O$_s$ and H$_d$ was also crucial, such as on β-C$_2$S (010) and (111) surfaces.

Table 4 summarizes the adsorption configuration of the single water molecule on M3-C$_3$S surfaces. As shown, the dissociative adsorption was mainly characterized by the Ca−O$_w$ bond, the Mg−O$_w$ bond, the O$_s$−H$_d$ bond, or was influenced by the attraction between O$_s$ and H$_d$. In contrast, the configuration of the molecular adsorption was influenced by the Mg−O$_w$ bond, and in some cases such as (010) and (001), also influenced by the attraction between O$_s$ and H. The adsorption configurations for the most energetically favorable dissociative and molecular adsorptions are illustrated in Figure 2 as an example.

3.4. Partial Density of States

To reveal the bonding mechanism between the water molecule and surfaces, the partial density of states (PDOS) of atoms involved in the fresh-bond formation was analyzed. Figure 3a illustrates the bonding associated with the O$_w$ atom during the dissociative adsorption over the β-C$_2$S (100) surface. O$_w$ 2p orbital overlapped with Ca 4s and Ca 3p orbitals near the Fermi energy during the O$_w$−Ca bond formation. Similarly, overlapping was observed between O$_w$ 2p orbital and Mg 3s orbital for the O$_w$−Mg bond. It is noted that the O$_w$ 2p orbital also overlapped marginally with H$_d$ 1s orbital, indicating the O$_w$ and H$_d$ were attracted to each other.

Table 4. Adsorption configurations of the H$_2$O over Mg-doped M3-C$_3$S surfaces with respect to the adsorption energy in eV.

| Surfaces | Summary of Bonding |
|----------|--------------------|
| (100)    | −1.624D: Mg−O$_w$, Ca−O$_w$(2), O$_s$−H$_d$; −0.699M: Mg−O$_w$ |
| (010)    | −1.786D: Mg−O$_w$, Ca−O$_w$, O$_s$−H$_d$; −0.938M: Mg−O$_w$, O$_s$−H |
| (001)    | −1.708D: Mg−O$_w$, Ca−O$_w$(2), O$_s$−H$_d$, O$_w$−H$_d$; −0.868M: Mg−O$_w$, O$_s$−H |
| (110)    | −3.028D: Mg−O$_w$, Ca−O$_w$, O$_s$−H$_d$, O$_w$−H$_d$; −1.089M: Mg−O$_w$ |
| (101)    | −4.008D: Mg−O$_w$, Ca−O$_w$, O$_s$−H$_d$; −2.711D: Mg−O$_w$, Ca−O$_w$(2), O$_s$−H$_d$ |
| (011)    | −2.192D: Mg−O$_w$, Ca−O$_w$, O$_s$−H$_d$, O$_w$−H$_d$ |
| (111)    | −1.454D: Ca−O$_w$, O$_s$−H$_d$, O$_w$−H$_d$ |

Note: abbreviations are explained in Table 3.
Figure 2. Water adsorption configuration of: (a) dissociative adsorption on the β-C2S (100) surface, (b) molecular adsorption on the β-C2S (011) surface, (c) dissociative adsorption on the M3-C2S (101) surface, and (d) molecular adsorption on the M3-C2S (100) surface. Note: 1—side view and 2—top view.

The O\textsubscript{w}-H\textsubscript{d} bonding was mainly originated from the overlapping between O\textsubscript{w} 2p and H\textsubscript{d} 1s orbitals (Figure 3b). Moreover, O\textsubscript{w} 2s orbital overlapped marginally with H\textsubscript{d} 1s orbital at around −5 eV. In the case of the molecular adsorption over β-C2S (011) surface, the orbital overlapping was similar to that during the dissociative adsorption, which was the O\textsubscript{w} 2p orbital overlapping with Ca 4s and Ca 3p orbitals (Figure 3c). Similar orbital overlapping was observed during the water adsorption on other low-index surfaces of calcium silicates.

To summarize, the Ow-Mg bonding originated from the overlapping between O\textsubscript{w} 2p orbital and Mg 3s orbital, the Ow-Ca bonding originated from the overlapping between O\textsubscript{w} 2p orbital and Ca 4s/3p orbitals, and the O\textsubscript{w}-H\textsubscript{d} bonding mainly originated from the overlapping between O\textsubscript{w} 2p and H\textsubscript{d} 1s orbitals. The authors note that the PDOS results might show some difference with the results in the literature, such as in [40] and [27], due to the difference in DFT computational settings. Moreover, the PDOS near the conduction band minimum was not discussed since the overlapping was not as significant as that near the valence band maximum.
Figure 3. Partial density of states (PDOS) of the water adsorption on the Mg-doped β-C2S (100) and (011) surfaces: (a) dissociative adsorption on the Mg-doped β-C2S (100) surface—Ow bonding, (b) dissociative adsorption on the Mg-doped β-C2S (100) surface—Hd bonding, and (c) molecular adsorption on Mg-doped β-C2S (011) surface. Note: right sub-figures are enlarged representations of regions in the box and the Fermi energy was set at 0.00 eV.

4. Discussion

4.1. What Does the Positive $E_{for}$ Imply?

As indicated in Table 1, the $E_{for}$ of Mg substituting for Ca was positive for most cases, indicating such a substitution was energetically unfavorable. However, Mg substitution in the current study was only used to investigate the influence of Mg substitution on water adsorption. In reality, the Mg substitution occurs in the solid solution during the cement production. Under such circumstances, the raw materials are heated up to 1400 °C [7,41], which can promote the Mg substitution in bulk and at the surface.

Moreover, the main objective of Mg substitution is in the polymorphic modification. A higher proportion of MgO during C3S crystallization stabilizes the M3 phase [7]. In the case of C2S, Chan et al. [42]
found that the ionic substitution is vital in stabilizing the polymorphic form of C₂S other than γ, the only stable form at room temperature without impurities [7].

### 4.2. Comparison before and after Water Adsorption

In this section, the change of structural and electronic properties of low-index surfaces after water adsorption is analyzed. Figure 4 illustrates the bond length distribution of surface Mg-O before and after water adsorption. An increase in surface Mg-O bond length was observed after water adsorption, indicating the weakening of surface Mg-O bonds [12]. More specifically, the average Mg-O bond was increased by 0.007 Å after the dissociative water adsorption over β-C₂S low-index surfaces. In contrast, the average Mg-O bond was increased by 0.043 Å after the molecular water adsorption over β-C₂S low-index surfaces. The above results imply the molecular adsorption could weaken the surface Mg-O bond to a larger extent for β-C₂S surfaces.

![Figure 4](image-url) Distribution of surface Mg-O bond length that was involved in water adsorption: (a) dissociative adsorption on β-C₂S surfaces, (b) molecular adsorption on β-C₂S surfaces, (c) dissociative adsorption on M3-C₃S surfaces, and (d) molecular adsorption on M3-C₃S surfaces.

In the case of the Mg-O bond length on M3-C₃S surfaces, a 0.043 Å and 0.006 Å increase was found for the dissociative adsorption and molecular adsorption, respectively. Dissociative adsorption was better at weakening surface Mg-O bonds than molecular adsorption for M3-C₃S surfaces. Since the weakening of surface bonds implies the increasing probability of bond breakage, the dissolution of Mg was promoted after the water adsorption [22]. Furthermore, molecular adsorption is more beneficial to Mg dissolution in β-C₂S surfaces while dissociative adsorption is more beneficial to Mg dissolution in M3-C₃S surfaces.
Figure 5 illustrates the effect of water adsorption on the Bader charge of surface atoms that were involved in the bond formation. As shown, the Bader charge of surface Mg, Ca, and O increased after water adsorption, indicating a decrease of electrons. In contrast, the O$_w$ and H$_2$ accepted electrons, resulting in a decrease of the Bader charge. Taking β-C$_2$S as an example, the Bader charge of Mg, Ca, and O$_w$ was increased from 1.665 eV, 1.564 eV, and −1.590 eV, respectively, to 1.670 eV, 1.585 eV, and −1.495 eV. The above results indicate that the electron is transferred from the surface to the H$_2$O upon adsorption, which agrees well with the results in the literature [12,13,22].

Figure 5. The influence of water adsorption on the Bader charge of surface atoms that were involved in the bond formation: (a) β-C$_2$S surfaces, and (b) M3-C$_3$S surfaces. Note: numbers in the box are mean values.

The electron transfer can also be indicated by the decomposed charge density. In the current study, the decomposed charge density distribution around the top of the valance band ($\rho_{TVB}$, −6 eV to 0 eV) and around the bottom of the conduction band ($\rho_{BCB}$, 0 to 3 eV) was analyzed before and after water adsorption. Figure 6 illustrates the results of the molecular adsorption over the β-C$_2$S (011) surface as an example. The $\rho_{TVB}$ and $\rho_{BCB}$ of surface and water atoms were changed during the water adsorption. The comparison between the density of $\rho_{TVB}$ and $\rho_{BCB}$ before and after adsorption indicates the electron transfer from the surface to the H$_2$O.

4.3. Comparison with Pristine Low-Index Surfaces of Calcium Silicates

In this section, the Mg-doped surfaces are compared with pristine surfaces to reveal the role of Mg doping in the water adsorption over calcium silicate surfaces. As shown in Figure 5, the average Bader charge of Mg in β-C$_2$S surfaces and M3-C$_3$S surfaces was 1.665 eV and 1.635 eV, respectively. Compared with the Bader charge of surface Ca atoms (around 1.5 eV as shown in Figure 5 and in the literature [12]), the Mg site might be less reactive than the corresponding Ca site. The reactivity of surface Mg and Ca sites can also be revealed by the decomposed charge density. It can be seen from Figure 6c that the $\rho_{BCB}$ was mainly distributed around surface Ca atoms, implying the surface Ca atoms were more reactive than surface Mg atoms under nucleophilic attack.

Figure 7 illustrates the comparison of the $E_{ad}$ of the single water adsorption on pristine and Mg-doped β-C$_2$S and M3-C$_3$S surfaces. Generally speaking, the $E_{ad}$ became less negative after the Mg impurity (lighter color in the upper two rows compared with the lower two rows, as shown in
In the case of $\beta$-C$_2$S (100), $\beta$-C$_2$S (001), M3-C$_3$S (101), and M3-C$_3$S (011) surfaces, the $E_{ad}$ became more negative.

**Figure 6.** Decomposed charge density of the molecular adsorption on the $\beta$-C$_2$S (011) surface: (a) $\rho_{TVB}$ before adsorption, (b) $\rho_{TVB}$ after adsorption, (c) $\rho_{BCB}$ before adsorption, and (d) $\rho_{BCB}$ after adsorption. Note: isosurface level was 0.05 eV for $\rho_{TVB}$ illustration and 0.02 eV for $\rho_{BCB}$ illustration.

**Figure 7.** Comparison of $E_{ad}$ of a single water molecule on pristine and Mg-doped surfaces of: (a) $\beta$-C$_2$S, and (b) M3-C$_3$S. Note: the dis and free in the $y$-axis represents dissociated water and free water in the initial configuration.
The authors note that the more negative $E_{ad}$ after Mg impurity on $\beta$-C$_2$S (100), $\beta$-C$_2$S (001), M3-C$_3$S (101), and M3-C$_3$S (011) surfaces is not due to the Mg-O$_w$ bonding was more energetically favorable than Ca-O$_w$. Instead, more bonds were formed on these Mg-doped surfaces. More specifically, the coexistence of Mg-O$_w$ and Ca-O$_w$ bonds, as well as the attraction between H and O$_w$ even for the molecular adsorption, led to the more negative $E_{ad}$.

The influence of Mg doping on the water adsorption can also be indicated by the water configuration. For one thing, the water adsorption could be influenced by the adjacent Ca site to a larger extent on the Mg-doped surfaces than the pristine surfaces. In some cases, the water molecule is absorbed into the adjacent Ca site even if it is placed above the Mg site in its initial configuration (Figure 2b). Figure 8 illustrates the difference between the dissociative adsorption configuration over the M3-C$_3$S (111) surface. As shown, the O$_w$ was attracted to one adjacent Ca site on the Mg-doped surface, instead of shared by three Ca sites on the pristine surface. The reason for such a difference in adsorption configuration is due to the relatively low reactivity of the Mg site, as discussed in Section 4.1. Therefore, the adjacent Ca site could be much more reactive compared with the Mg site, resulting in the water adsorption around the adjacent Ca site.

**Figure 8.** The dissociative adsorption configuration on the M3-C$_3$S (111) surface of: (a) pristine surface, and (b) Mg-doped surface.

Another influence of Mg doping on the adsorption configuration could be revealed by comparing Tables 3 and 4 with Table 6 in the literature [12]. As shown, water reformation from H$^+$ and OH$^-$ was not as frequently observed on Mg-doped $\beta$-C$_2$S surfaces than on those pristine ones. On the pristine $\beta$-C$_2$S surfaces, water reformation was observed on most surfaces, except the (011) surface. However, such water reformations were not observed on the (100), (010), and (011) Mg-doped surfaces. Moreover, water dissociation occurred on the $\beta$-C$_2$S Mg-doped (100) surface, which was not observed on the pristine surface. The frequency of water dissociation on M3-C$_3$S was quite similar on pristine and Mg-doped surfaces, even though occurring at different surfaces. The water reformation and dissociation are influenced by the relaxed surface structure, which in turn affect the energy barrier for
such a process. Thus, a detailed discussion about the influence of Mg doping on the water reformation and dissociation would require further calculations and analysis.

5. Conclusions

In this work, using first-principles DFT calculations, we investigated the influence of Mg doping on the water adsorption over calcium silicates surfaces. Both molecular and dissociative adsorption were analyzed, and the influence of water adsorption was investigated. A detailed comparison between Mg-doped and pristine surfaces, both in terms of surface structures and water adsorption, was conducted. The following conclusions can be summarized based on the calculated results:

1. The \( E_{\text{for}} \) of Mg substituting for Ca ranged 0.51 to 1.21 eV on \( \beta\text{-C}_2\text{S} \) surfaces and \(-0.02\) to 1.58 eV on \( M_3\text{-C}_3\text{S} \) surfaces.

2. The \( E_{\text{ad}} \) of an \( H_2O \) over Mg-doped surfaces of \( \beta\text{-C}_2\text{S} \) and \( M_3\text{-C}_3\text{S} \) ranged from \(-0.598\) to \(-1.249\) eV and \(-0.699\) to \(-4.008\) eV, respectively. Generally speaking, molecular adsorption was more energetically favorable on \( \beta\text{-C}_2\text{S} \) surfaces and dissociative adsorption was more favorable on \( M_3\text{-C}_3\text{S} \) surfaces.

3. Molecular adsorption was characterized by the Mg-O\(_w\) bond and/or the Ca-O\(_w\) bond, and in some cases, was also influenced by the attraction between O\(_s\) and H. Dissociative adsorption was mainly characterized by the Ca-O\(_w\) bond, Mg-O\(_w\) bond, O\(_s\)-H\(_d\) bond, or was influenced by the attraction between O\(_s\) and H\(_d\).

4. Ow-Mg bonds were originated from the O\(_w\) 2\( p\) orbital and the Mg 3\( s\) orbital, Ow-Ca bonds were originated from the O\(_w\) 2\( p\) orbital and the Ca 4\( s\)/3\( p\) orbitals, and O\(_s\)-H\(_d\) bonds was mainly originated from the O\(_s\) 2\( p\) and the H\(_d\) 1\( s\) orbitals.

5. Water adsorption increased the bond length of surface Mg-O and promoted the Mg dissolution. Such a bond-weakening effect was more evident for the molecular adsorption over \( \beta\text{-C}_2\text{S} \) surfaces and the dissociative adsorption over \( M_3\text{-C}_3\text{S} \) surfaces. The electron transfer was observed from the surface to \( H_2O \) upon adsorption.

6. Mg doping influenced the reactivity of surface Ca/Mg sites, the \( E_{\text{ad}} \) of the single water adsorption, as well as the adsorption configuration compared with the water adsorption on pristine surfaces.

In the future, the influence of Mg concentration on the water adsorption should be investigated. Moreover, a systematic study should be performed to determine the substitution site for more representative results. Finally, more adsorption sites could be investigated to better reveal the influence of Mg substitution on the water adsorption.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/8/665/s1, Figure S1: Water adsorption configuration on \( \beta\text{-C}_2\text{S} \) (001) surface: (a) \(-0.994\) eV, and (b) \(-0.915\) eV. Please refer to Figure 1 for the atom type, Table S1: Calculation details and the surface energy of pristine low-index surfaces of calcium silicates.

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References

1. Singh, S.K.; Singh, A.; Singh, B.; Vashistha, P. Application of thermo-chemically activated lime sludge in production of sustainable low clinker cementitious binders. J. Clean. Prod. 2020, 264, 121570. [CrossRef]

2. Wang, D.L.; Zhang, Q.L.; Chen, Q.S.; Qi, C.C.; Feng, Y.; Xiao, C.C. Temperature variation characteristics in flocculation settlement of tailings and its mechanism. Int. J. Miner. Metall. Mater. 2020. [CrossRef]
3. Feng, Y.; Chen, Q.; Zhou, Y.; Yang, Q.; Zhang, Q.; Jiang, L.; Guo, H. Modification of glass structure via CaO addition in granulated copper slag to enhance its pozzolanic activity. Constr. Build. Mater. 2020, 240, 117970. [CrossRef]

4. Chen, X.; Shi, X.; Zhou, J.; Yu, Z.; Huang, P. Determination of mechanical, flowability, and microstructural properties of cemented tailings backfill containing rice straw. Constr. Build. Mater. 2020, 246, 118520. [CrossRef]

5. Chen, X.; Shi, X.; Zhang, S.; Chen, H.; Zhou, J.; Yu, Z.; Huang, P. Fiber-Reinforced Cemented Paste Backfill: The Effect of Fiber on Strength Properties and Estimation of Strength Using Nonlinear Models. Materials 2020, 13, 718. [CrossRef][PubMed]

6. Tao, Y.; Zhang, W.; Li, N.; Wang, F.; Hu, S. Atomic occupancy mechanism in brownmillerite Ca2FeAlO5 from a thermodynamic perspective. J. Am. Ceram. Soc. 2019, 103, 635–644. [CrossRef]

7. Taylor, H.W. Cement Chemistry, 2nd ed.; Thomas Telford Publishing: London, UK, 1997.

8. Qi, C.; Fourie, A.; Chen, Q.; Liu, P.-F. Application of first-principles theory in ferrite phases of cemented paste backfill. Miner. Eng. 2019, 133, 47–51. [CrossRef]

9. Huang, J.; Valenzano, L.; Singh, T.V.; Pandey, R.; Sant, G. Influence of (Al, Fe, Mg) Impurities on Triclinic Ca3SiO5: Interpretations from DFT Calculations. Cryst. Growth Des. 2014, 14, 2158–2171. [CrossRef]

10. Durgun, E.; Manzano, H.; Kumar, P.V.; Grossman, J.C. The Characterization, Stability, and Reactivity of Synthetic Calcium Silicate Surfaces from First Principles. J. Phys. Chem. C 2014, 118, 15214–15219. [CrossRef]

11. Zhang, Y.; Lu, X.; Song, D.; Liu, S. The adsorption of a single water molecule on low-index C3S surfaces: A DFT approach. Appl. Surf. Sci. 2019, 471, 658–663. [CrossRef]

12. Manzano, H.; Durgun, E.; Qomi, M.J.A.; Ulm, F-J.; Pellenq, R.J.M.; Grossman, J.C. Impact of Chemical Impurities on the Crystalline Cement Clinker Phases Determined by Atomic Simulations. Cryst. Growth Des. 2011, 11, 2964–2972. [CrossRef]

13. Qi, C.; Spagnoli, D.; Fourie, A. DFT-D study of single water adsorption on low-index surfaces of calcium silicate phases in cement. Appl. Surf. Sci. 2020, 518, 146255. [CrossRef]

14. Zhang, Y.; Lu, X.; Song, D.; Liu, S. The adsorption of a single water molecule on low-index C3S surfaces: A DFT approach. Appl. Surf. Sci. 2019, 471, 658–663. [CrossRef]

15. Wang, Q.; Manzano, H.; Guo, Y.; López-Arbeloa, I.; Shen, X. Hydration Mechanism of Reactive and Passive Dicalcium Silicate Polymorphs from Molecular Simulations. Chem. A Appl. Mater. Interfaces 2015, 7, 14726–14733. [CrossRef][PubMed]

16. Durgun, E.; Manzano, H.; Pellenq, R.J.M.; Grossman, J.C. Understanding and Controlling the Reactivity of the Calcium Silicate phases from First Principles. Chem. Mater. 2012, 24, 1262–1267. [CrossRef]

17. Laanaiya, M.; Bouibes, A.; Zaoui, A. Understanding why Alite is responsible of the main mechanical characteristics in Portland cement. Cem. Concr. Res. 2019, 126, 105916. [CrossRef]

18. Dovál, M.; Palou, M.; Mojumdar, S.C. Hydration behavior of C2S and C2AS nanomaterials, synthetized by sol–gel method. J. Therm. Anal. Calorim. 2006, 86, 595–599. [CrossRef]

19. Thissen, P.; Natzek, C.; Giraudo, N.; Weidler, P.; Wöll, C. Hydration of Concrete: The First Steps. Chem. A Eur. J. 2018, 24, 8603–8608. [CrossRef]

20. Zhang, Y.; Lu, X.; He, Z.; Song, D. Molecular and dissociative adsorption of a single water molecule on a β-dicalcium silicate (100) surface explored by a DFT approach. J. Am. Ceram. Soc. 2017, 101, 2428–2437. [CrossRef]

21. Zhang, Y.; Lu, X.; Song, D.; Liu, S. The Adsorption Behavior of a Single and Multi-Water-Molecules on Tricalcium Silicate (111) Surface from DFT Calculations. J. Am. Ceram. Soc. 2018, 102, 2075–2083. [CrossRef]

22. Qi, C.; Liu, L.; He, J.; Chen, Q.; Yu, L.-J.; Liu, P.-F. Understanding Cement Hydration of Cemented Paste Backfill: DFT Study of Water Adsorption on Tricalcium Silicate (111) Surface. Minerals 2019, 9, 202. [CrossRef]

23. Wang, Q.; Manzano, H.; López-Arbeloa, I.; Shen, X. Water Adsorption on the β-Dicalcium Silicate Surface from DFT Simulations. Minerals 2018, 8, 386. [CrossRef]

24. Huang, J.; Wang, B.; Yu, Y.; Valenzano, L.; Bauchy, M.; Sant, G. Electronic Origin of Doping-Induced Enhancements of Reactivity: Case Study of Tricalcium Silicate. J. Phys. Chem. C 2015, 119, 25991–25999. [CrossRef]

25. Saritas, K.; Ataca, C.; Grossman, J.C. Predicting Electronic Structure in Tricalcium Silicate Phases with Impurities Using First-Principles. J. Phys. Chem. C 2015, 119, 5074–5079. [CrossRef]
26. Tao, Y.; Li, N.; Zhang, W.; Wang, F.; Hu, S. Understanding the zinc incorporation into silicate clinker during waste co-disposal of cement kiln: A density functional theory study. J. Clean. Prod. 2019, 232, 329–336. [CrossRef]
27. Tao, Y.; Zhang, W.; Shang, D.; Xia, Z.; Li, N.; Ching, W.-Y.; Wang, F.; Hu, S. Comprehending the occupying preference of manganese substitution in crystalline cement clinker phases: A theoretical study. Cem. Concr. Res. 2018, 109, 19–29. [CrossRef]
28. De Noirfontaine, M.-N.; Dunstetter, F.; Courtial, M.; Gasecki, G.; Signes-Frehel, M. Polymorphism of tricalcium silicate, the major compound of Portland cement clinker. Cem. Concr. Res. 2006, 36, 54–64. [CrossRef]
29. Fukuda, K.; Ito, S. Improvement in Reactivity and Grindability of Belite-Rich Cement by Remelting Reaction. J. Am. Ceram. Soc. 1999, 82, 2177–2180. [CrossRef] [PubMed]
30. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50. [CrossRef]
31. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B Condens. Matter Mater. Phys. 1996, 54, 11169–11186. [CrossRef]
32. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 1993, 47, 558–561. [CrossRef] [PubMed]
33. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868. [CrossRef] [PubMed]
34. Bader, R.F.W. A quantum theory of molecular structure and its applications. Chem. Rev. 1991, 91, 893–928. [CrossRef]
35. Tang, W.; Sanville, E.; Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. J. Phys. Condens. Matter 2009, 21, 084204. [CrossRef]
36. Mahmoodi, T.; Mansouri, M. Structural effects of substitutional impurities on MoO$_3$ bilayers: A first principles study. J. Korean Phys. Soc. 2016, 69, 1439–1444. [CrossRef]
37. Jost, K.H.; Ziemer, B.; Seydel, R. Redetermination of the structure of β-dicalcium silicate. Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1977, 33, 1696–1700. [CrossRef]
38. Tasker, P.W. The stability of ionic crystal surfaces. J. Phys. C Solid State Phys. 1979, 12, 4977–4984. [CrossRef]
39. Noguera, C. Polar oxide surfaces. J. Phys. Condens. Matter 2000, 12, R367–R410. [CrossRef]
40. Tao, Y.; Zhang, W.; Li, N.; Ching, W.-Y.; Wang, F.; Hu, S. Atomic-level insights into the influence of zinc incorporation on clinker hydration reactivity. Open Ceram. 2020, 1, 100004. [CrossRef]
41. Hewlett, P.C.; Liska, M. Lea’s Chemistry of Cement and Concrete; Butterworth-Heinemann: Oxford, UK, 2019.
42. Chan, C.-J.; Kriven, W.M.; Young, J.F. Analytical Electron Microscopic Studies of Doped Dicalcium Silicates. J. Am. Ceram. Soc. 1988, 71, 713–719. [CrossRef]