

Ceramic Expansion by Water Layers on Magnesium Oxide: AB Initio Study

Aqeel M. Ali¹, Ali H. Al-Mowali^{2,*}

¹Department of Physics, College of Science, University of Basrah, Basrah, Iraq

²Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

*Corresponding author: ali_almoali@yahoo.com

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Abstract MgO hydration is an expansive process. It is used in cement to compensate for shrinkage, but it can be harmful at higher concentrations. First-principles calculations have been used to investigate the electronic properties of the steps of the hydration of MgO using the general gradient approximation GGA functional method within density functional method (DFT). The energy bands along high symmetry directions, energy of hydration and energy of dissociation cut through various planes are presented. The first principles band structure calculations reported here were carried out using Perdew, Burke and Ernzerhof (PBE) method. The calculations have been applied to investigate water adsorption on the (001, 110, 111 and 210) surfaces of MgO crystal. The hydrated MgO surfaces show a similar band structure that of brucite material. Both molecular adsorption and dissociative adsorption have been found to occur. The MgO surfaces have different tendency to interact with water molecules, and they differ in susceptibility disintegration of expansion. The results show that the safest surface is (001) group, while the harmful surfaces are (210) and (111) groups.

Keywords: ceramic, DFT, MgO hydration, brucite, band structure

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1. Introduction

The hydration of magnesium oxide provides an interesting example for studying the surface structure and chemical reactions of ceramic oxides [1,2,3]. Its simple crystallographic and electronic structure makes MgO (periclase) a prototype for investigating the ceramic hydration [4,5,6,7]. The final product of MgO hydration is Mg(OH)₂, brucite, which is a layered mineral of hexagonal symmetry with the crystallographic space group *P3m1* [8]. The MgO hydration increases the solid volume by a factor of 2.2 Figure 1 [9,10,11]. The long-term expansion produced by periclase hydration compensates in part for the thermal and autogenous shrinkage in concrete [12,13]. Much research has been carried out to achieve shrinkage-compensating cement by increasing the amount of MgO and determining the proper hydration conditions. Due to the heat produced by cement hydration, the temperature in an uncooled mass of concrete may reach more than 50 °C [14,15,16].

Although there is a great deal of theoretical and experimental data on the interaction of water with MgO, less information are available for the change in its band structure and the potential which felt by the electrons. In view of the wide range of applications, an understanding of the hydration process of MgO at an atomic and nanometer scale is desirable. This paper describes the

quantum-mechanical modeling of the magnesia hydration on a scale ranging from the atom to the nanometer cluster.

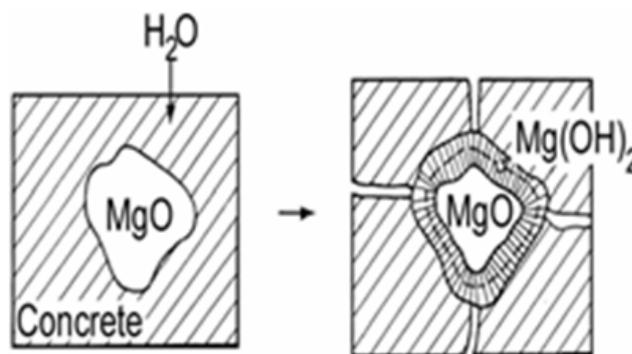


Figure 1. Schem of MgO hydration with volume expansion in concrete

2. Computational Method

The calculations are performed by density-functional theory (DFT) using ADF (Amsterdam Density Functional simulation package), version 2012.01 [17]. The exchange-correlation contribution to the total energy is modeled using the general gradient approximation GGA functional of Perdew, Burke and Ernzerhof PBE [18]. All computations carried out using full double zeta basis set. For the hydration of MgO or dehydration of Mg(OH)₂, there is an epitaxial relationship between (111) surface of

MgO and (0001) surface of $\text{Mg}(\text{OH})_2$. Therefore, the hydration of MgO is studied on the (111, 001, 110 and 210) surfaces of MgO, which eventually forms (0001) surface of $\text{Mg}(\text{OH})_2$. The surfaces of MgO are modeled using the slab supercell approach. Each supercell is modeled in a slab periodic mode with eight atomic layers plus the adsorbed species with the vacuum space of 11 Å.

The water/solid interaction energies have been calculated using the equation.

$$E_{hvd} = 1/n [E(2H_2O/MgO) - nE(H_2O) - E(MgO)]$$

where $E(2H_2O/MgO)$ is the energy of the film after the addition of (n) water molecules at the equilibrium binding distance, $E(H_2O)$ is the energy of an isolated water molecule and $E(MgO)$ is the energy of the clean film. The obtained energy was then divided by (n) in order to get the hydroxylation (hydration) energy per water molecule.

3. Results and Discussions

The band structure of electrons in a crystal depends on the form of a potential function which the electrons are affected by its field. The different potentials made different band structures of valence and conduction bands, so the type of crystal depends on the kind of band structure. We studied the band structure of brucite $\text{Mg}(\text{OH})_2$ and hydrated MgO (001, 110, 111 and 210) surfaces to explain the relationship between hydrated MgO surfaces and $\text{Mg}(\text{OH})_2$ crystal.

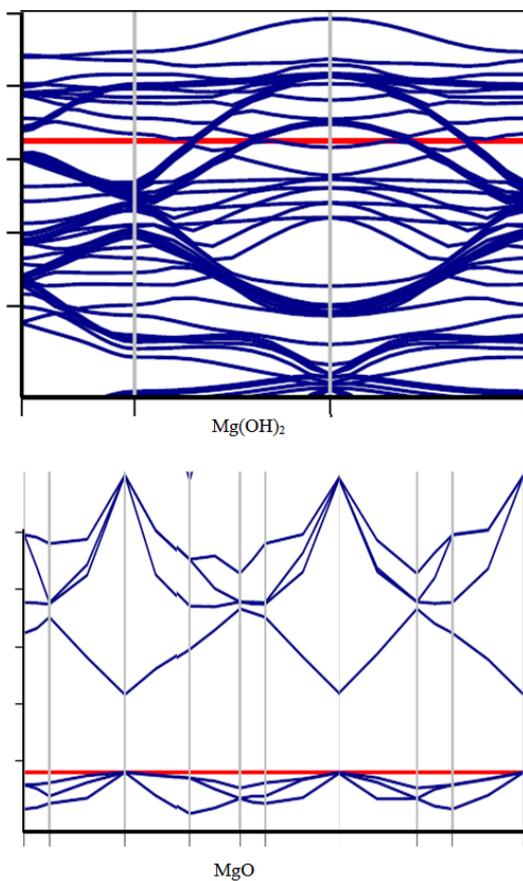


Figure 2. The band structure of (a) $\text{Mg}(\text{OH})_2$ and (b) MgO

Figure 2, shows the band structure of $\text{Mg}(\text{OH})_2$ which depends on the type of potential energy that is felt by

electrons. The valence and conduction bands are cross each other and both of them pass the Fermi energy level (red line). While, the MgO crystals have separated valence band and conduction band by an energy gap. The field of potential in MgO crystal is induced by ionic bonding of positive charged Mg^{+2} ions and negative charged O^{-2} ions. $\text{Mg}(\text{OH})_2$ has the same ionic bonds between Mg^{+2} and O^{-2} ions in addition to the dipolar bonding of OH pairs between every two layers.

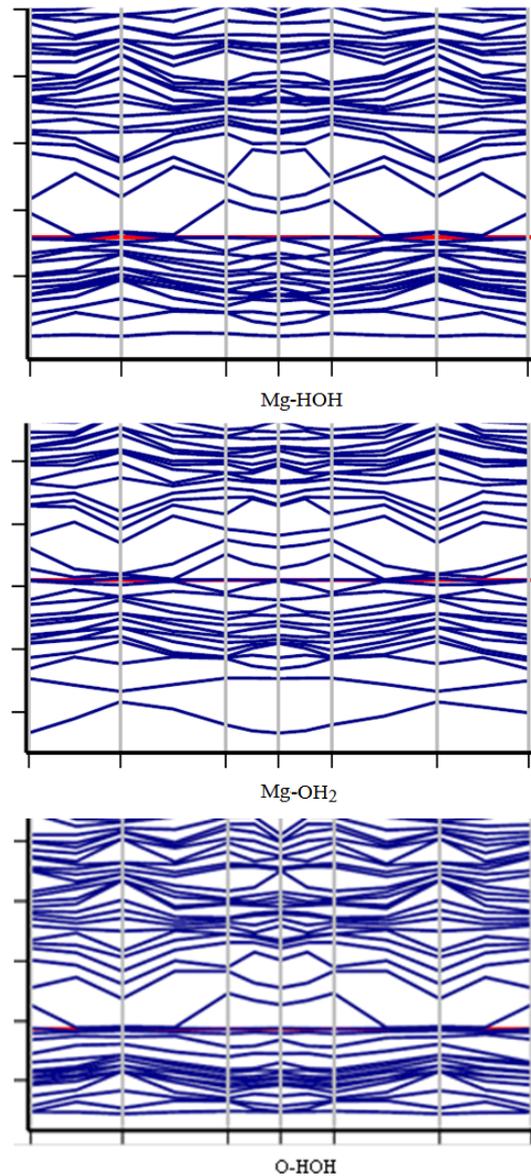


Figure 3. The band structure of hydrated (001) MgO surface in different cases of interactions of H_2O molecules with Mg- or O-atom of crystal

After the adsorption of water on MgO surfaces, the situation is completely changed due to the presence of adsorbed species. Figure 3, presents the valence and conduction bands of MgO (001) surface at three kinds of hydration cases. First, H_2O molecule interacts with Mg-atom via one of its H-atom, second, the interaction is done via O-atom of water with Mg-atom and third, the oxygen atom of MgO crystal surface interacts with H-atom of a water molecule. All of these cases present meeting states of valence and conduction bands at Fermi energy level, and the lowest band of empty electron states passes the Fermi energy. The potential inside the hydrated MgO crystal of these interaction cases approaches to the

potential of a brucite crystal, and thus water molecules induce primary changes in the interior potential of MgO crystal. The other MgO surfaces have the same changes in potential energy which may be induced by water molecules.

The energy of formation of these three interaction cases which may occur for all four surfaces is studied to identify the more probable interaction cases. The results for different cases of interactions are shown in three tables (Table 1, Table 2 and Table 3). We calculated the dissociation energy of double layers of pure and hydrated MgO crystals (E_{dis} and $E_{h_{dis}}$). Also we estimated the energy of hydration E_{hyd} and the total energy of hydration and dissociation (hydrated MgO) $E_{hyd+dis}$. For unhydrated MgO crystal, the ionic bonds are strong and a dissociation of a layer is unexpected (unstable system), with the exception of (210) surface which has a negative value of E_{dis} . This means that the MgO layers in (210) surface are unstable and it may be released by heating above the room temperature (0.025 eV). The hydration and dissociation energies depend strongly on the surface type and the kind of interaction. The (001) surface is unreactive to interact with water molecules because of its high energy of hydration and dissociation. High reactivity appeared by (111) surface to adsorb H_2O molecules and it dissociated as layer by layer. Also, the (110) surface had a moderate reactivity. The (210) surface has a good reactivity, but it only reacts in a good manner in which Mg interacted with O of water.

Table 1. The interaction parameters of all Mg-atoms of MgO surfaces with H-atom of water molecules. Energy of dissociation E_{dis} (pure MgO), energy of hydration E_{hyd} and dissociation $E_{h_{dis}}$ and sum of them $E_{hyd+dis}$

Surface Mg-HOH	E_{dis}	E_{hyd}	$E_{h_{dis}}$	$E_{hyd+dis}$
001	Unstable	100.908	-18.214	82.694
111	Unstable	3.594	-136.024	-132.430
110	Unstable	5.067	-0.0001	5.067
210	-0.035	2.552	0.000	2.552

Table 2. The interaction parameters of all Mg-atoms of MgO surfaces with O-atom of water molecules. Energy of dissociation E_{dis} (pure MgO), energy of hydration E_{hyd} and dissociation $E_{h_{dis}}$ and sum of them $E_{hyd+dis}$

Surface Mg -OH ₂	E_{dis}	E_{hyd}	$E_{h_{dis}}$	$E_{hyd+dis}$
001	Unstable	73.015	29.866	102.881
111	Unstable	368.07	-159.53	208.542
110	Unstable	2.613	-0.0001	2.613
210	-0.035	-6.651	0.0002	-6.651

Table 3. The interaction parameters of all O-atoms of MgO surfaces with H-atom of water molecules. Energy of dissociation E_{dis} (pure MgO), energy of hydration E_{hyd} and dissociation $E_{h_{dis}}$ and sum of them $E_{hyd+dis}$

Surface O-HOH	E_{dis}	E_{hyd}	$E_{h_{dis}}$	$E_{hyd+dis}$
001	Unstable	30.060	0.021	30.082
111	Unstable	-174.341	-0.252	-174.593
110	Unstable	70.329	-0.0001	70.329
210	-0.035	32.865	0.0002	32.865

4. Conclusions

An ab initio quantum mechanical treatment of defect free (0 0 1), (1 1 0), (1 1 0) and (2 1 0) eight-layer films of the alkaline earth oxide, MgO, and the interaction with water molecule using supercell model at DFT levels of ab initio theory led to the following conclusions: The stability of the surfaces is high toward decomposing, except the (210) which has tendency for decomposing by some heat treatment. The water/solid interaction energies increase in the order, Mg-O < Mg-H < O-H, whatever the considered film, and in the order, (2 1 0) < (1 1 1) < (1 1 0) < (0 0 1), whatever the considered oxide. The unstable (210) surface is the more reactive among others that interact via Mg-atom and O-atom of water molecule. The more reactive one is (111) surface for H-atom of water molecule to adsorb on Mg or O atoms.

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