Comprehending the occupying preference of manganese substitution in crystalline cement clinker phases: A theoretical study

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A B S T R A C T

Understanding the dopant behavior in cement clinker has been an important issue due to the increasing use of alternative fuels and secondary raw materials for cement manufacturing following the rising demand for reduction of CO_2 emissions and energy consumption. In this work, state-of-the-art *ab initio* calculations have been employed to systematically investigate manganese (Mn) doping mechanism in four dominant clinker phases. Corresponding experimental studies are incorporated to verify simulated results. A conspicuous preference of Mn for occupying the Fe site in ferrite is found based on formation energy analyses, which is in accord with our experiments and vast literatures. More in-depth analyses indicate the Mn doping mechanism follows the "electronic structure matching" principle, which influences the stability of doped structures by inducing localized coordination distortions. The work provides a fundamental perspective to investigate doped clinker, which facilitates the searching for other doping species, thereby designing steerable doping-enhanced cement.

1. Introduction

Since 1980s, associations and companies have been pursuing the program of developing refuse derived fuel (RDF) as a supplemental energy source for the Portland cement industry [1], which has been of great significance for energy conservation and industrial benefits [2–4]. However, unfamiliar ingredients may be incorporated into cement clinker system especially in underdeveloped countries where the waste collection and disposal systems are not well developed. The impacts of these extrinsic elements to the sintering technology and hydration reactivity of clinker should be investigated thoroughly and carefully.

On the other hand, to follow the rising demand for global CO_2 reduction the use of secondary raw materials is increasing continuously [5]. To date the employment of alternative raw materials is not only the most effective way to reduce CO_2 emission of cement production [5] but also one of the most widely used technologies for disposal of hazardous materials [6–9]. These applications have changed the cement manufacturing process and properties of products [5]. The knowledge of the new complex clinker compound is in urgent need. One of the important aspects lies in understanding the influence of extrinsic ions to cement clinker. Manganese is one of the major trace metals in ordinary Portland cement (OPC) [3,10–12], which is chiefly derived from

alternative fuels [3] and secondary raw feeds [13] during the combustion process of clinker production [14]. Zhenzhou Yang and coworkers investigated the trace elements partitioning behavior in the soil surrounding a cement plant using hazardous waste as raw materials. They find Mn can be considered as a non-volatile element, which is primarily incorporated into the clinker, compared with volatile elements like mercury [10]. The manganese rich Portland cement with the additive of silico-manganese slags or steel furnace slags was studied by Nath and Kumar [15], Altun and Yilmaz [16], et al. According to their investigations, manganese lowers the reactivity and strength of the cement at early stage without decaying long-term activation. However, systematic researches on the site preference of Mn ions and their stability in the compound clinker system are deficient. In addition, those trace metals including Mn are usually difficult to be detected experimentally due to their low contents in cement clinker. Furthermore, most macroscopic experiments are not satisfactory enough to obtain essential comprehension due to the complexity of cement chemistry. The fundamental understanding of clinker chemistry remains an important and challenging issue [5].

Due to recent advances in first-principles calculations, it is possible to obtain a fundamental perspective to experimental observations. E. Durgun et al. studied the influence of alloying on the properties of

cement clinkers using atomic simulations and explained the variation of reactivity of doped clinker phases as the result of charge transfer and localization [17–22]. In this work, we present the results of detailed calculations to clarify the mechanism of stability of Mn doping systems, as well as the site preference of Mn ions. This approach is validated by parallel experimental observations and can easily be extended to other extrinsic heavy metal ions doping in cement clinker phases as well.

2. Methodology

2.1. Computational method

Tricalcium silicate (Ca$_3$SiO$_5$:C$_3$S) is the dominant clinker phase used to make OPC, which has seven kinds of polymorphs including R, M3, M2, M1, T3, T2, and T1 [23–28]. It has been reported that all these polymorphs, except the T1 form, are not stable at room temperature unless doped with impurities [19,29,30]. Consequently, the pure form of these polymorphs, if employed, may features singularly high lattice energy, which results in an unrealistic defect formation energy according to Eq. (1). Therefore, the T1 phase is chosen in the present study. The T1 form belongs to the P-1 space group and it contains 162 atoms (90 O, 18 Si, and 54 Ca atoms) in the primitive cell.

Dicalcium silicate (Ca$_2$SiO$_5$:C$_2$S) is the second important component of OPC, which is known as its impure form, belite. C$_2$S also has various polymorphs, such as α, $\acute{\alpha}_H$, $\acute{\alpha}_L$, β, and γ polymorphs [31–35]. The β phase is chosen as the underlying matrix to investigate Mn doping since it is the main form of C$_2$S observed in OPC by experiments. β-C$_2$S belongs to the $P2_1/n$ space group. The primitive cell contains only 28 atoms (16 O, 4 Si, and 8 Ca atoms) with two kinds of Ca sites (Ca1 and Ca2) with different oxygen coordination, six-fold for Ca1 and 8-fold for Ca2.

Tricalcium aluminate (Ca$_3$Al$_2$O$_6$:C$_3$A) is also an important phase in OPC (constitutes 5–10%). It accounts for the early development of compressive strength of cement due to the highest rate of reactivity among four main clinker phases. Pure C$_3$A crystal belongs to the Pa-3 space group, constituted of cubic primitive cell with parameter a equals15.26 Å [36].

Tetracalcium aluminoferrite (Ca$_2$AlFeO$_5$:C$_4$AF), also called ferrite phase, is another prominent phase in OPC (constitutes 5–15%) with no constant stoichiometric ratio. In the solid solution series Ca$_2$(Al$_x$Fe$_{1-x}$)$_2$O$_5$, x is usually approximately equal to 0.5, namely, C$_4$AF. C$_4$AF belongs to the Ibm2 space group, and its primitive cell contains 36 atoms [37].

All the calculations in the present work are based on density functional theory (DFT). The Vienna *Ab initio* Simulation Package (VASP) [38,39] was employed for the geometry optimization of all constructed models and the electronic properties were calculated by Cambridge Sequential Total Energy Package (CASTEP) [40]. The exchange-correlation potential was approximated by the Perdew–Burke–Ernzerhof (PBE) within generalized gradient approximation (GGA) [41]. The projector augmented plane wave method (PAW) [42] was implemented in the calculation with a kinetic energy cutoff of 500 eV for the plane wave basis after tests with higher cutoff showing no discernible difference (more computational details see Supplementary data). To clarify the site preference of Mn doping in the four clinker phases, we constructed Mn-doped models of clinker crystals by atomic substitutions using Mn atoms replacing Si, Ca, Al, or Fe atoms. Fig. 1 illustrates the studied clinker phases and part of doped models using VESTA [43]. It is worth noting that there are more than one type of Ca atoms in T1-C$_3$S, β-C$_2$S, and C$_3$A. The Si and Al atoms in T1-C$_3$S and C$_3$A also have different types due to their chemical environment differences. Hence, these multifarious sites are taken into account carefully in this work, which can be found in Supplementary data.

Several previous studies have demonstrated that the interstitial defects are much more difficult to generate than the substitutional defects [44–47]. Therefore, only the latter is discussed in this paper.

The defect formation energies (ΔE) of all doping types are evaluated by following equation given by [48–51]:

$$\Delta E = \frac{1}{n}[E - E_0 + n\mu_0 - n\mu_i + q(E_F + E_{VBM})] \tag{1}$$

where E_0 is the total energy of pure clinker crystal and E is the energy of doped crystal. μ_i and μ_0 present the chemical potentials of the impurities (Mn) and substituted atoms (Si, Ca, Al, or Fe) respectively. n is the number of introduced Mn atoms in clinker phase, and q is the number of net electrons of the doped cell. E_{VBM} means the energy of the valence band maximum of the pure clinker crystal and E_F is the Fermi energy relative to E_{VBM} (details see Supplementary data). As the defect concentration in the studied four clinker phases are not the same, we use the normalized defect formation energy (ΔE^*) to eliminate the influence of defect contents:

$$\Delta E^* = \Delta E/\omega \tag{2}$$

where ω is the mass concentration of Mn dopants. Here, it should be emphasized that the charge balance is sometimes a concern related to the atomic substitution. For instance, assuming Fe, Ca, and Si atoms feature the Fe^{3+}, Ca^{2+}, and Si^{4+} oxidation states respectively, people introduce two Fe atoms by replacing one Si and one Ca atom simultaneously to keep the entire doped system neutral [18]. However, the manual charge compensation is not applied in this work due to the following two main reasons: On the one hand, previous studies suggest that Mn ions present variable oxidation states in clinker phases such as Mn^{2+}, Mn^{3+}, and Mn^{4+} [52–57], which makes the manual charge compensation much difficult. One the other hand, the hinge of this work is to accurately estimate the defect formation energies of Mn substitution. Thus, even though the Mn substitution for some species may cause a charged state, the influence of the net charge on the defect formation energy is fully taken into consideration as embodied in Eq. (1).

2.2. Experimental method

According to the common mineral composition of OPC clinker, the analytical grade Ca(OH)$_2$, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and MnO$_2$ were used as the raw materials for clinker synthesis. For the doped samples, Mn ions were introduced into the raw meal in the form of MnO$_2$ oxide with dosage of 0.5, 1.0, 2.0, and 3.0 wt%. The chemical composition of the reference (without MnO$_2$ doping) were measured by X-ray fluorescence analysis and the potential mineral composition was estimated by Bogue calculation [59] (Table 1). The specimens were homogenized and pressed at 100 kN into pellets (height = 10 mm, diameter = 25 mm) to obtain a regular clinkering process. Pellets were sintered at 1450 °C for 150 min before air quenching. The quenched clinker was ground until passing 200 mesh sieves. The Quanta FEG450 environmental scanning electron microscope (ESEM) and coupled energy dispersive X-ray spectroscopy (EDS) (15 kV, 60 Pa) were used to identify the morphology and element distributions in sintered clinker.

3. Results and discussion

The computed lattice parameters as well as the volume and density of supercell are checked after geometry optimization. They are in very good agreement with experimental data (Table 2).

3.1. Site preference of Mn doping

The calculated ΔE^* of atomic substitutions in cement clinker phases are presented in Table 3. A positive ΔE^* suggests that extra energy is needed to overcome the energy barrier of doping reactions. Oppositely, a negative ΔE^* implies a spontaneous process in the stabilization of host matrix by dopants. Therefore, the magnitude of ΔE^* points to the possibility and stability of defect formation. In general, as shown in