

Modeling C_3S impurities using Cluster Expansion

PROBLEM

With the aim of lowering the energy requirements in the production of cement clinkers, prior work has focused on increasing the reactivity of belite (C_2S), constituting 15-30% of normal cement clinkers. Engineering the dominant phase, alite (C_3S), that makes up 50-70% of portland cement clinker has received comparatively less attention due to its inherently high reactivity and higher production temperature relative to C_2S . Yet, if the reactivity of C_3S could be increased even further, it might be possible to reduce the total amount required in cement clinkers, resulting in lower energy consumption and CO_2 emissions.

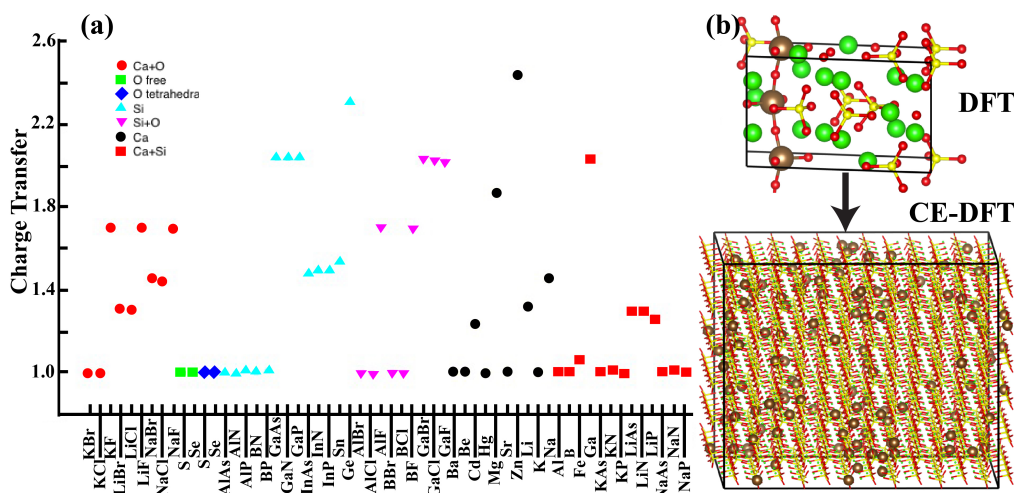


Fig. 1 (a): Variation of charge transfer with 58 different impurities for the M3 polymorph of alite. Values between 1 and 4 could lead to enhanced reactivity. The inset shows which atoms of C_3S are substituted with impurities. Depending on the atomic weight of impurity defects, impurity concentration in the simulation cell varies between 1-13 wt%. (b) Periodic doping of Al in the unit cell of alite calculated with DFT is shown in upper figure, while the lower figure shows how Al impurities distributed with experimental concentrations in a large supercell simulated at 300 K with the cluster expansion method. Ca, Al, Si and O atoms are represented by green, brown, yellow and red, respectively.

Exploring the chemical, physical, and mechanical properties of C_3S with different impurities at varying concentrations, employing the same types of simulations we previously carried out for C_2S , is the subject of this investigation.

APPROACH

First-principles fully quantum mechanical analytical techniques are applied to the modeling of impurities in C_3S . Density Functional Theory (DFT) calculations are very accurate, but computationally very demanding. Large numbers of atoms in the simulation cell cannot be modeled efficiently due to computer processing constraints. This study consists of two stages. In the first stage, we examine how crystal structure defects from single impurities (dopant, vacancy, etc.) might affect the reactivity of C_3S in a small simulation cell where the

concentration of the impurity is higher than in a naturally occurring material. In the second stage, we implemented a new method, Cluster Expansion (CE-DFT), where accurate DFT calculations can be used as training sets to model large realistic supercells using statistical analysis. Multiple impurities with different concentrations in the same simulation cell can then be modeled.

FINDINGS

Figure 1(a) shows the variation of charge transfer for different impurities. Although this is a bulk quantity, it is qualitatively related to reactivity. As a result of the charge transfer between ionic oxygen atoms and impurity defects, our simulations indicate that the reactivity of C_3S could be manipulated. Using the cluster expansion method (CE-DFT), it is shown that the impurity distribution in the crystal is not homogeneous and clustering of impurities can occur at elevated temperatures, which can affect the electronic properties significantly. In the case of aluminum as shown in Figure 1(b), due to clustering of impurities the reactivity of C_3S is enhanced significantly. By controlling the concentrations and temperature, one can also have a better understanding of impurity-impurity interactions in realistic cement clinkers.

IMPACT

This is the first study where very accurate DFT calculations are applied to large supercells of clinker using the cluster expansion method. Simulations can be carried out at varying concentrations with many different impurities including the effects of temperature in the same simulation cell, and the reactivity can be inferred from the charge localization. With this method, we are one step closer to modeling realistic cement clinkers. Engineering the reactivity of not only C_3S , but also the C_2S phase can be simulated using such an approach.