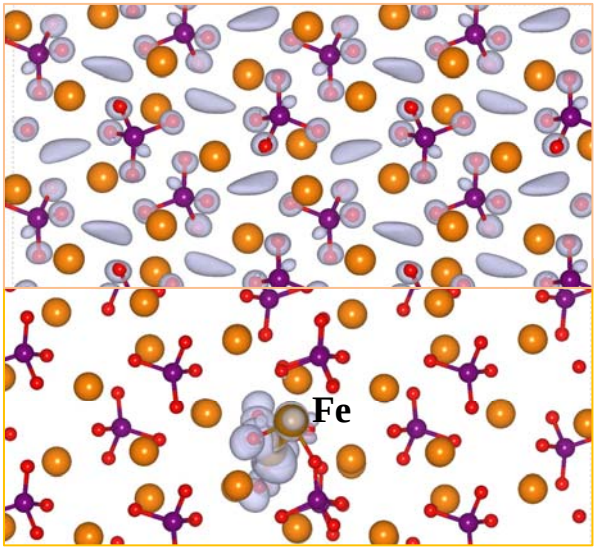
Clinker: When Impurities Matter

Problem

One of the key questions to control clinker reactivity rates is the role of impurities. In fact, commercial clinker crystals are far from chemically pure, due to the high heterogeneity of the raw materials, clays, shales, limestone etc. As a consequence, guest ions (Al, Fe, Mg, Na) in different concentrations are commonly present in commercial clinker. These impurities are known to affect the clinker reactivity. They can accelerate or slow down the reactions, and in some cases they can bring the reaction to a halt. Yet at present, a systematic understanding of the effect of impurities is lacking. Progress on this front is critical to overcome experimental limitations and to optimize clinker charactersitics. Moreover, an understanding of the role of guest ions on the clinker crystal structures may also help to design new possible chemical substitutions that allow a rational engineering of clinker dissolution rates, which can ultimately translate into higher strength development. This appears to be one bottleneck for the implementation of strategies to lower greenhouse gases, such as high belite content cements or high SCM content blended cements.



Spatial location of pure belite (Top) and Fe-substitute belite (Bottom) Valence Band Minimum (blue clouds). These areas represent the most reactive spots under nucleophilic attack.

Approach

We employ a combination of classical force field (FF) and quantum mechanical (QM) atomic computational methods to study in great detail the physical-chemical changes of alite (C_3S) and belite (C_2S) when Mg^{2+}, Al^{3+} and Fe^{3+} guest ions are incorporated into their structure. By FF methods, we first study the preferential substitution sites, the structural rearrangement necessary to accommodate the guest ions, and the impact on elastic properties. Then, the conduction band maximum (CBM) and valence band minimum (VBM) are computed by QM methods. The CBM and VBM represent the most reactive areas under electrophilic and nucleophilic chemical attack respectively, and their spatial location gives us a great deal of insight into the impact of impurities on reactivity.

Findings

The key initial finding of this research is the clear difference in impact of light elements versus heavy elements. Heavy elements such as Fe, Zn or Ge as guest ions localize the CBM and VBM, and thus decrease the number of available reactive sites. In contrast, light elements such as Be, B or F, which do not localize CBM and VBM, are good candidates as impurities to accelerate the dissolution of alite and belite.

Impact

This research highlights the critical role of guest ions on available reactive sites in alite and belite. The novel understanding of the role of impurities on reactivity opens the possibility for designing new doped clinker phases with a higher reaction rate, and hence, earlier strength development. Engineering the reactivity of belitic cements could thus become a reality through an appropriate choice of impurities.

More

Research presented by Dr. Hegoi Manzano, Post-doctoral Fellow in the CSHub, in collaboration with Drs. J. Grossman, E. Durgun and R. Pellenq.

This research was carried out by the CSHub@MIT with sponsorship provided by the Portland Cement Association (PCA) and the Ready Mixed Concrete (RMC) Research & Education Foundation. The CSHub@MIT is solely responsible for content. For more information, write to CSHub@mit.edu.