Machine Learned Interatomic Potential for Low-CO2 Cement Compounds

Chloé Andrieux-Amadeï [†], Luis Lorenzana[†], Ethan Ritz[††]

Ritz Lab, Department of Engineering
[†]Harvey Mudd College, [††]University of Toronto

Introduction and Background

Cement production is responsible for over 8% of global CO_2 emissions, created during the chemical reaction to create clinker (cement pebbles that will then be ground down to powder) and by burned fossil fuels to heat the high-temperature kilns for these reactions. Ye'elimite is a form of Calcium Sulfoaluminate (CSA) cement that can be synthesized at 150˚C lower than conventional cement, creating a 25-35% decrease in fuel emissions. Ye'elimite is currently being used in Carbonatable Calcium Silicate Cement (CCSC) clinker mixtures in China for large-scale pre-cast molds [1]. CCSC cements require CO_2 gas to cure, limiting on-site curing capabilities, but creating a potential for carbon neutral cement production. This project seeks to computationally characterize the structure of Ye'elimite and establish a model to further test differing compositions and hydration mechanics.

Methods and Computational Approach

This research employs density functional theory (DFT) to determine the crystal cell structure of Ye'elimite, which is essential for studying unit cell parameters. Calculations were performed using VASP, a software efficient for converging complex crystal structures. Once optimized cells were created with DFT, these were then utilized to train models in molecular dynamics (MD) simulations. These MD models used a specific training process to create Machine Learned Interatomic Potentials (MLIP) in accordance with [2]. The MLIP models allowed the accuracy of 0 K DFT calculations to support dynamic MD simulations at finite temperature. The MLIP models were then subject to specific temperature fluctuations to attempt to validate the presence of Ye'elimite solid phase changes. This approach will then allow the alteration of the base Ye'elimite structure to allow the study of different compositions, and later facilitate the study of hydration mechanics with the addition of water.

Ye'elimite

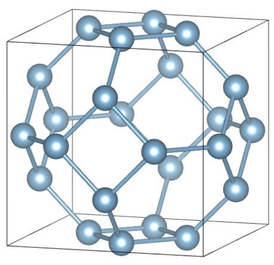


Figure 1: CSA cements are characterized by aluminium arranged in a sodalite cage.

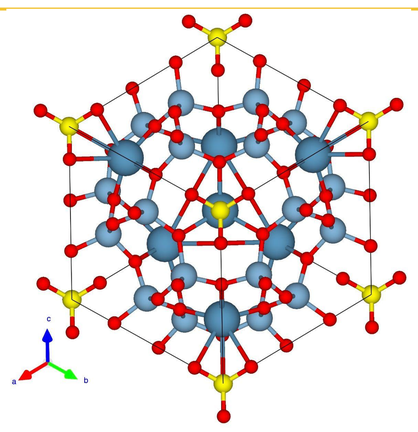


Figure 2: Converged Unit Cell of Cubic Ye'elimite in VESTA

Ye'elimite ($Ca_4[Al_6O_{12}]SO_4$) has two distinct solid phases. Under 750 K, its structure is orthorhombic with a unit cell described by 3 different side lengths (Figure 3). Ye'elimite boasts faster hydration mechanics than traditional cements, particularly in its cubic phase (Figure 2). This presents incentive to find atomic substitutions (dopants) that stabilize the cubic phase at lower temperatures to minimize required heating during production. For example, Ye'elimite's structure can accommodate substitutions such as: Ca → Na or Sr, Al → Si or Fe, and P → S. The goal is to understand the effect of each dopant such that the structure can be optimized for cost of environmental impact with minimal effect on the mechanical properties.

My research explored a model with an Al → Fe substitution to the aluminium sodalite cage in cubic Ye'elimite (Figure 4). Experimental evidence corroborates that this substitution can alter the phase transition temperature [3]. Matching the established experimental trends is the first step in confirmation that our model properly captures the dynamics of the system.

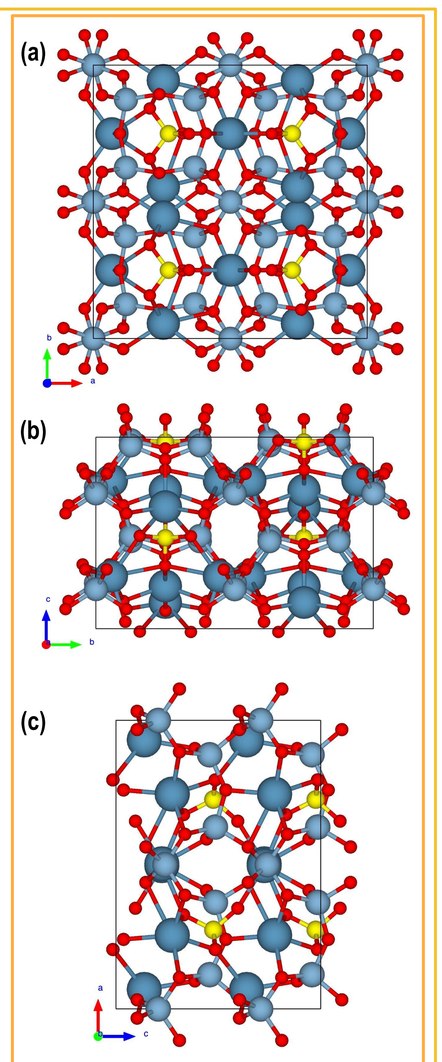


Figure 3(a-c): Converged Unit Cell of Orthorhombic Ye'elimite in VESTA

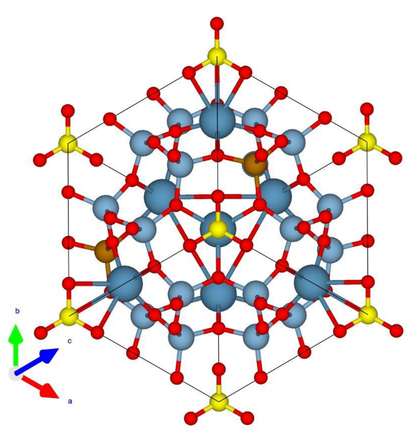


Figure 4: Converged Unit Cell of Iron-Doped Cubic Ye'elimite in VESTA

Elastic Constants

My research this summer focused on created converged cells of cubic and orthorhombic ye'elimite to establish baseline unit cell sizes and accurate computational models. Utilizing these cells and DFT, they could be stretched in particular ways to fully characterize the elastic tensor matrices of these materials.

C_{11}	C_{12}	C_{13}	0	0	0
C_{12}	C_{22}	C_{23}	0	0	0
C_{13}	C_{23}	C_{33}	0	0	0
0	0	0	C_{44}	0	0
0	0	0	0	C_{55}	0
0	0	0	0	0	C_{66}

Figure 5: Elastic constant tensor for orthorhombic Ye'elimite

For Cubic ye'elimite, given its symmetry, its matrix is entirely characterized by C11 (commonly referred to as Young's Modulus), C12 (Poisson's ratio), and C44 (Shear Modulus), as the other constants are defined by symmetry. To establish these values, known distortions from -2% to 2% were applied to the unit cell parameters. DFT relaxations were then run on these distorted cells, and the results were fit to produce the constants. A bulk modulus can then be derived from the tensor and was found to be 89.6 GPa for the cubic phase.

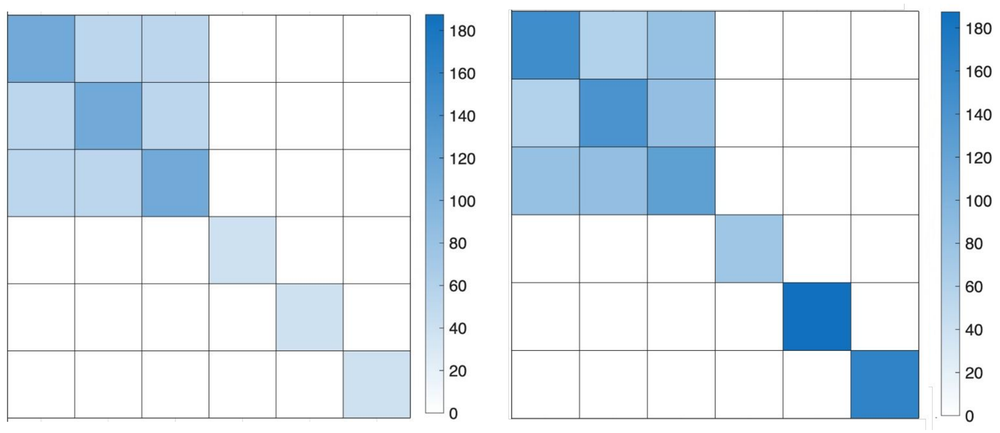


Figure 6: Visual representation of the elastic constant tensor results (GPa) from each distortion for cubic Ye'elimite (left), and orthorhombic ye'elimite (right)

For the orthorhombic structure, more of the constants are unique due to lower symmetry. These constants can be used to indicate the presence of a phase transition. As MD simulations are heated or cooled through the phase transition temperature, we can track the change of the elastic constants and determine the temperature at which the structure changes phases. We see large changes in the shear constants (C44, C55, and C66), meaning these are likely the best candidates for tracking the phase transitions.

Future work

The next step will be to ensure that the MD run utilizing the MLIP potential is stable and accurate throughout the entire temperature range of interest. We can iteratively improve the MLIP model by running DFT calculations on atomic configurations in which the MLIP model has low confidence. Once it is validated over a temperature range large enough to see the phase transition in pure Ye'elimite, further models for doped Ye'elimite will be created to test if the phase transition occurs at a different temperature. Subsequently, the iron percentage will be increased for different models to confirm how this affects the phase transition temperature. Once the models are completed, then surfaces can be created and water molecules added to them. This will allow us to explore the hydration mechanics. We hope to then continue to explore differing substitution elements to explore their effects on hydration mechanics and the phase transition.

References

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[2] E. Podryabinkin, K. Garifullin, A. Shapeev, and I. Novikov, "MLIP-3: Active learning on atomic environments with moment tensor potentials," The Journal of Chemical Physics, vol. 159, no. 8, Aug. 2023. doi:10.1063/5.0155887

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