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Cementitious materials have material, geometric features ranging from molecular/nano, micro-, meso- and macro scales. Features and changes in material chemistry/nano scale influence the hydration process, formed micro scale morphology, associated properties and behavior at engineering length scales. In the present paper, effect of material ion exchange on mechanical stiffness properties of nano level hydrated cement paste constituent - calcium silicate hydrate (C-S-H) based on its material chemistry structure are studied following a molecular dynamics (MD) computational modeling methodology. Calcium ions are replaced with Magnesium ions in traditional C-S-H Jennite crystal structure of the hydrated cement constituent. Traditional C-S-H Jennite structure, and Magnesium modified structures obtained by calcium exchange of magnesium are used in the MD based material modeling analysis. Extensive modeling analysis established optimal computational MD modeling parameters and molecular material sizes employed. The present study clearly shows the influence of material chemistry due to Magnesium ion exchange in CSH-Jennite with predicted elastic modulus that changes with the level of Magnesium in CSH-Jennite material chemistry structure.

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COMPUTATIONAL MATERIAL MODELING OF HYDRATED CEMENT PASTE CALCIUM SILICATE HYDRATE (C-S-H) CHEMISTRY STRUCTURE — INFLUENCE OF MAGNESIUM ION EXCHANGE ON MECHANICAL STIFFNESS: C-S-H JENNITE

RAM V. MOHAN¹, WAYNE D. HODO², BABATUNDE ADEBIYI¹, JOHN RIVAS¹,
AND AHMED MOHAMED¹

¹Department of Nanoengineering, North Carolina A&T State University
2907 E Lee Street, Greensboro, NC 27401, USA
rvmohan@ncat.edu; <http://jsnn.ncat.uncg.edu>

²U. S. Army Engineer and Research Development Center
3907 Halls Ferry Road, Vicksburg, MS 39180, USA
Wayne.D.Hodo@usace.army.mil; <http://www.erd.c.usace.army.mil>

Key words: Material Chemistry, Calcium Silicate Hydrate, Magnesium Ion Exchange, Mechanical Stiffness Modulus

Abstract. Cementitious materials have material, geometric features ranging from molecular/nano, micro-, meso- and macro scales. Features and changes in material chemistry/nano scale influence the hydration process, formed micro scale morphology, associated properties and behavior at engineering length scales. In the present paper, effect of material ion exchange on mechanical stiffness properties of nano level hydrated cement paste constituent - calcium silicate hydrate (C-S-H) based on its material chemistry structure are studied following a molecular dynamics (MD) computational modeling methodology. Calcium ions are replaced with Magnesium ions in traditional C-S-H Jennite crystal structure of the hydrated cement constituent. Traditional C-S-H Jennite structure, and Magnesium modified structures obtained by calcium exchange of magnesium are used in the MD based material modeling analysis. Extensive modeling analysis established optimal computational MD modeling parameters and molecular material sizes employed. The present study clearly shows the influence of material chemistry due to Magnesium ion exchange in CSH-Jennite with predicted elastic modulus that changes with the level of Magnesium in CSH-Jennite material chemistry structure.

1 INTRODUCTION

Cementitious materials have material, geometric features ranging from molecular/nano, micro-, meso- and macro scales. Features and changes in material chemistry/nano scale influence the hydration process, formed micro scale morphology, associated properties and behavior at engineering length scales. Cement paste is made by combining dry Portland cement and water. The process of making cement paste is referred to as hydration, during which, there is loss of workability, solidification and hardening. The hydration of the different clinker phases results in different hydration product phases, which makes up the cement paste.

The hydrated cement phases include; calcium silicate hydrate (C-S-H), calcium aluminum hydrate (C-A-H) and calcium hydroxide (C-H) ^[1,2]. In cement paste, four levels of scales have been identified^[3] i.e. molecular /nano-scale level determined by the material chemistry features, micro-scale with microstructural morphology features, meso-scale and macro-scale. Distinct length scales and features are based on the requirement that each scale should be separated from the next scale by at least one order of length magnitude, which is also stated in the literature as a prerequisite for the application of continuum micromechanics^[1, 2]. As a result of the multi-scale nature of cement paste, the properties and material composition of the macro and engineering scale cement can be controlled or affected by the molecular level. A potential ability to alter and manipulate the chemistry level structure of hydrated component of traditional C-S-H, a structure predominantly influenced by calcium - a major constituent of the cement paste at the fundamental material chemistry level - will imply that the elastic and deformation properties of the paste would be impacted. Figure 1 shows the different levels of scale associated with cementitious materials.

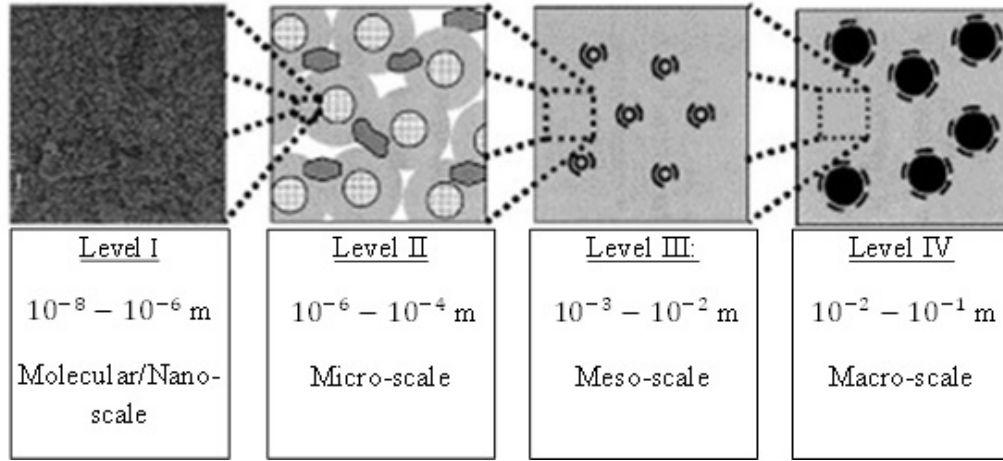


Figure 1: Schematic of multi-scale structure of cement based materials [3]

Traditional cement paste is primarily calcium-based, but there is interest in the engineering community for alternate formulations of cement; which may provide tailored properties for specific applications, could utilize local, and cheaper materials. Another factor influencing the alternate forms cement cited in the literature is the need to reduce the energy required to produce the clinker phase, and the carbon foot print of the cement industry^[1]. Hence there have been efforts to look for alternate cement formulations that are not calcium-based, might be cheaper, and have the potential for reducing carbon footprint in the manufacturing stage of calcium based cement. Several forms of cement formulations has been sought, for instance, other forms of belitic cements are sought by trial and error to improve the reactivity of the clinker phase. Some additional approaches that have been used trying to improve the properties of cement-based materials include thermal processing^[4,5] and addition of new chemical compounds and ions ^[4,5,6]. Most common types of ionic substitution which has been used in cement include; Mg^{2+} for Ca^{2+} , 2Al^{3+} and 2Fe^{3+} for 3Ca^{2+} , and 2Ca^{2+} for Si^{4+} ^[6,7]. The present work investigates the influence of replacement of calcium ion with magnesium ion in the material chemistry level of C-S-H with a focus on mechanical stiffness determined via

computational material modeling.

Several studies have focused on different aspects of cement material improvement. Hegoi and co-workers^[6] studied the effects of the presence of chemical substitution on the physicochemical properties of cement clinker phases - alite and belite. They incorporated Mg^{2+} , Al^{3+} and Fe^{3+} into the structure using classical forcefield methods and reported that the crystallographic site within the unit cell is equally probable for Mg, Al and Fe substitution. It has also been reported that Mg incorporation does not change the electronic structure appreciably compared to Al and Fe incorporation^[6], and that there are no preferential substitution for any calcium sites, when Mg^{2+} , Al^{3+} and Fe^{3+} were incorporated. The main focus of their research was on the reactivity of the clinker phase for reduced energy production.

As discussed in the literature, Mg provides a feasible incorporation option in cement paste. In a study of the hydration process of cement, Stephan and co-workers^[7], provided analytical evidences that in low concentrations, Mg^{2+} does not change the hydration process of calcium trisilicate (C_3S) – a component of cement, although the reactivity may increase with weight percent and with cement age. Also, because of the relative availability and the ionic similarities to Calcium, Mg can be considered as a potential candidate for ionic replacement. Additionally, with the replacement of Ca by Mg, a lower temperature for processing the clinker phase can be achieved.

The focus of this paper is to understand the influence of the effects of the exchange of Calcium ion with Magnesium ions in hydrated cement material chemistry structure based on the mechanical stiffness properties of the modified material chemistry configuration using computational material modeling and simulations. Different computational simulation methods have been employed in the past to study heterogeneous materials. Manzano et al^[6] used a combination of forcefield and DFT atomistic simulations, while others have used ab initio methods to study the structure of C-S-H^[8,9]. There are also prior studies on the mechanical behavior of heterogeneous materials using multi-scale modeling, and studies to understand cement hydration with finite element modeling, as well as temperature dependency of the microstructure of cement hydrates^[3,10,11] reported in the literature. The present paper presents and discusses results from our work on material chemistry modeling to understand the effect of Calcium ion substitution with Magnesium on chemistry level structure of C-S-H on the predicted mechanical stiffness.

2 MATERIAL CHEMISTRY LEVEL MODELING OF C-S-H

Material chemistry level modeling following the principles and techniques commonly grouped under Computational Material Science is one of the key facilitator of material science that is experiencing fast growth pace and forms the basis of the present work^[13]. The major hydrated component of cement paste C-S-H gel is responsible for the load bearing attributes and strength of cement, and has a complex material chemistry^[14]. The molecular structural representations of C-S-H gel are still inconclusive with several structural representations cited in literature^[15]. These include:

- Wollastonite group which comprises of Foshagite ($Ca_4(Si_3O_9)(OH)_2$)^[16], Hillebrandite ($Ca_2(SiO_3)(OH)_2$)^[17], Xonotlite ($Ca_6Si_6O_{17}(OH)_2$)^[18], Okenite ($[Ca_8(Si_6O_{16})(Si_6O_{15})_2(H_2O)_6]^{4-}[Ca_2(H_2O)_9] \cdot 3H_2O$)^[19], and others that are compiled by

Richardson^[15].

- Tobermorite group which comprises of Clinotobermorite^c ($\text{Ca}_5\text{Si}_6\text{O}_{17}\cdot 5\text{H}_2\text{O}$), Clinotobermorite^d ($\text{Ca}_5\text{Si}_6\text{O}_{17}\cdot 5\text{H}_2\text{O}$), Clinotobermorite 9 Å^c ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$), Clinotobermorite 9 Å^d ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$)^[20,21], anomalous and normal Tobermorite 11 Å^o ($\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ respectively)^[22,23] and Tobermorite 14 Å^[24].
- Jennite group comprising Jennite and Metajennite ($\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6\cdot 8\text{H}_2\text{O}$). A complete composition and crystal information for most of the C-S-H and other related phases have been tabulated by Richardson^[15].

From various material chemistry molecular structures of C-S-H, Tobermorite 14 Å and Jennite structures are traditionally accepted, widely used, and adapted material molecular structural representation of C-S-H cement paste^[2,14,15,25,26]. In the present paper, the structural configuration of C-S-H Jennite is employed to study and understand the influence of material chemistry changes due to Magnesium replacement.

Jennite is a representative mineral form of calcium silicate hydrate (C-S-H). It has a chemical formula of $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6\cdot 8(\text{H}_2\text{O})$ ^[15,24,25]. The molecular/chemistry level structure of C-S-H Jennite is defined by a triclinic unit cell of dimensions $a = 10.6 \text{ Å}$, $b = 7.3 \text{ Å}$, $c = 10.9 \text{ Å}$, and angles $\alpha = 101.3^\circ$, $\beta = 97.0^\circ$, $\gamma = 109.7^\circ$. In Figure 2 a crystal of C-S-H Jennite, consisting of 64 unit cells in a $4\times 4\times 4$ arrangement, is illustrated. The molecular structure of C-S-H Jennite is layered, formed by sheets of calcium oxide connected to short silica chains, three silica monomers¹ long, that are not connected to each other. The calcium oxide sheets are linked to each other by additional calcium octahedral sites. The layers containing the calcium octahedral sites connecting the calcium oxide sheets also contain most of the free water molecules in the structure^[25,27].

The atomic positions of the initial unit cell of C-S-H Jennite were obtained from American Mineralogist Crystal Structure Database (AMCSD), which corresponds to the C-S-H Jennite structure defined by Bonaccorsi *et al.*^[25]. The molecular dynamics modeling analysis was performed using the molecular dynamics analysis code Accelrys Material Studio[®], employing the Discover module with the associated atom interaction energy represented by COMPASS force field^[28].

Material chemistry molecular models of C-S-H are employed based on a Molecular Dynamics (MD) modeling methodology to understand the influence of Magnesium ion exchange are based on a 64 unit cell configuration shown in Figure 2. The material molecular chemistry system size of 64 unit cells and other MD modeling parameters were determined after a careful study^[29]. Other MD simulation analysis parameters employed were a dynamic analysis time of 200 ps; periodic boundary conditions applied to the molecular system, temperature and pressure control based on Nose Thermostat and Parinello Barostat, with a time integration time step of 1 fs (femto second) following a Velocity-Verlet method.

¹ A silica monomer is a single SiO_2 unit.

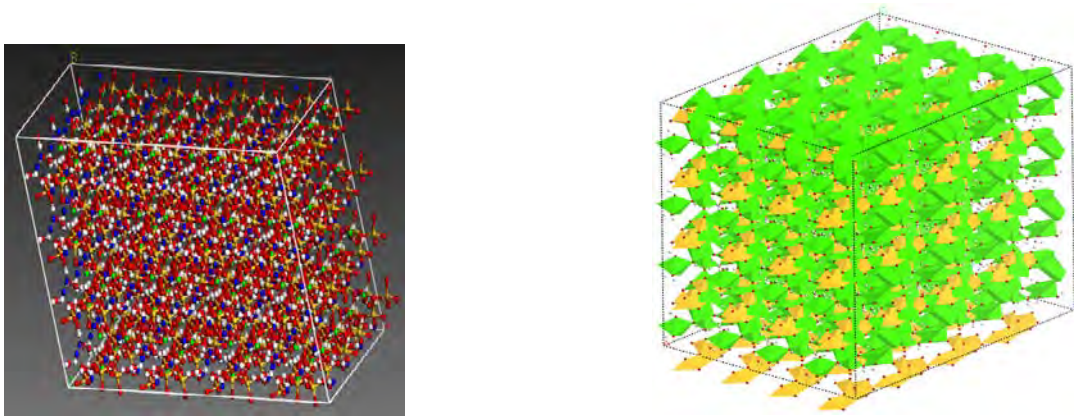


Figure 2: Molecular structure of nanoscale C-S-H Jennite. Both full 3D atomic structure and configuration with Calcium Oxide molecules represented in green and SiO_2 molecules represented in yellow are shown

2.1 Magnesium Ion Exchange in C-S-H Jennite

The relevance and applicability of Magnesium ion exchange in hydrated cement C-S-H structure was discussed earlier. Following this, Magnesium (Mg) ion exchange in traditional C-S-H Jennite was obtained by replacing the Calcium (Ca) ions in the molecular structure of Jennite C-S-H structure with magnesium ions. The unit cell configuration of C-S-H Jennite consists of 9 calcium ions. The magnesium modified C-S-H Jennite structure based on a same crystal configuration is obtained by replacing one or more calcium atoms by magnesium atoms. The different magnesium modified C-S-H Jennite structures, and their corresponding magnesium percentage based on calcium and magnesium molar mass considered in the present work are tabulated in Table 1^[29].

Table 1: Number and percentage of Mg in ion exchange in one unit cell C-S-H Jennite configuration

Structure	Ca atoms	Mg atoms	Magnesium percentage by weight
J0	9	0	0.0
J1	8	1	7.0
J2	7	2	14.8
J3	6	3	23.0
J4	5	4	32.7
J5	4	5	43.0
J6	3	6	54.8
J7	2	7	68.0
J8	1	8	82.9
J9	0	9	100.0

Different unit cell configurations of traditional and magnesium modified C-S-H Jennite as noted above was replicated to create a 64 unit cell configuration in a $4 \times 4 \times 4$ arrangement. Figure 3 shows the material chemistry molecular structures of 64 unit cell C-S-H structures created and analyzed in the present work. MD dynamic analysis was performed to obtain

associated Virial stresses, potential energy of the system and elastic stiffness matrix. The time average values of the molecular dynamic analysis after reaching a stable energy configuration were employed in determining these physical parameters.

2.2 Predicted Mechanical Stiffness Properties from Material Chemistry Structure

Mechanical stiffness properties (Bulk, Shear, and Young's Modulus) were determined from the elastic constants obtained from the second derivative of potential energy of the material chemistry molecular system. This is defined by equation 1.

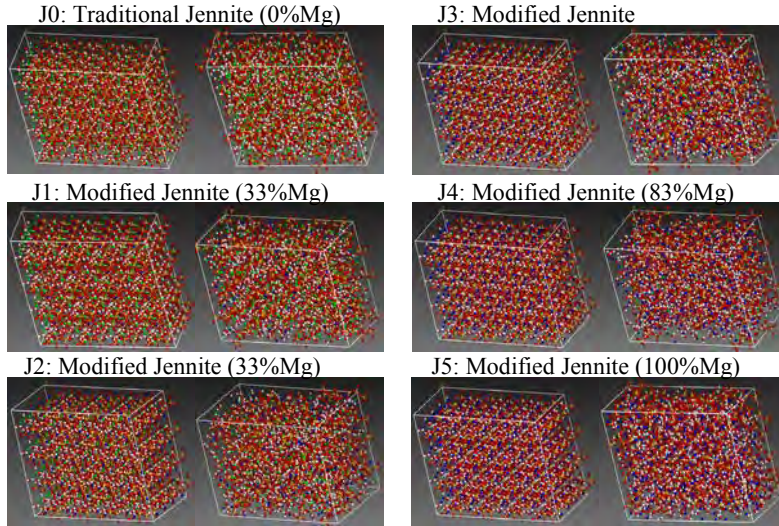


Figure 3: Material chemistry structures (initial on left; final after MD analysis) of traditional and Mg-modified C-S-H Jennite

$$C_{ij} = \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} \quad (1)$$

Here, ϵ_i , ϵ_j are lattice strain components, U is potential energy, V is simulation cell volume. The 6×6 elastic stiffness matrix, C can be obtained from the above relation.

$$C_{ij} = \begin{pmatrix} C_{11} & \cdots & C_{16} \\ \vdots & \ddots & \vdots \\ C_{61} & \cdots & C_{66} \end{pmatrix} \quad (2)$$

Elastic compliance matrix, $S = C^{-1}$ can also be obtained.

$$S_{ij} = \begin{pmatrix} S_{11} & \cdots & S_{16} \\ \vdots & \ddots & \vdots \\ S_{61} & \cdots & S_{66} \end{pmatrix} \quad (3)$$

Hence the mechanical stiffness properties for the homogeneous stiffness modulus can be predicted following Voight, Reuss or Hill average elastic stiffness relations from the elastic and compliance matrix coefficients as^[30]:

$$K_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31})} \quad (4)$$

$$K_V = \frac{(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})}{9} \quad (5)$$

$$K_H = \frac{(K_V + K_R)}{2} \quad (6)$$

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66})} \quad (7)$$

$$G_V = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})}{15} \quad (8)$$

$$G_H = \frac{(G_V + G_R)}{2} \quad (9)$$

$$E = 2G(1 + \nu) \quad (10)$$

where; K_R = Reuss bulk modulus, K_V = Voight bulk modulus, K_H = Hill average bulk modulus, G_R = Reuss shear modulus, G_V = Voight shear modulus, G_H = Hill average shear modulus, E = Young's Modulus, and C_{ij} and S_{ij} are the components of the stiffness and compliance matrix respectively^[30,31].

3 RESULTS AND DISCUSSIONS

The MD analysis methodology and predictive mechanical stiffness values from the potential energy as defined in section 2 were obtained for traditional and different Mg-modified C-S-H material chemistry configurations listed in Table 1. Figure 4 shows the change in the total energy for traditional and Mg-modified C-S-H Jennite configurations. The variation of normalized total energy is shown in Figure 4.

The predicted elastic modulus (Hill average) values for traditional and Mg-modified C-S-H Jennite material chemistry structures are shown in Figure 5. A sharp increase in the predicted elastic modulus is observed for the Mg-modified C-S-H Jennite structure at 33% Mg structure followed by a reduction in predicted elastic modulus values as the percentage of Mg modification further increases. Clearly, these results show that predicted elastic modulus have an impact with variations as shown in Figure 5. A Magnesium ion percentage of 33% is noticed to provide the highest increase in the predicted elastic modulus in Mg-Ion modified C-S-H compared to traditional C-S-H material chemistry structure.

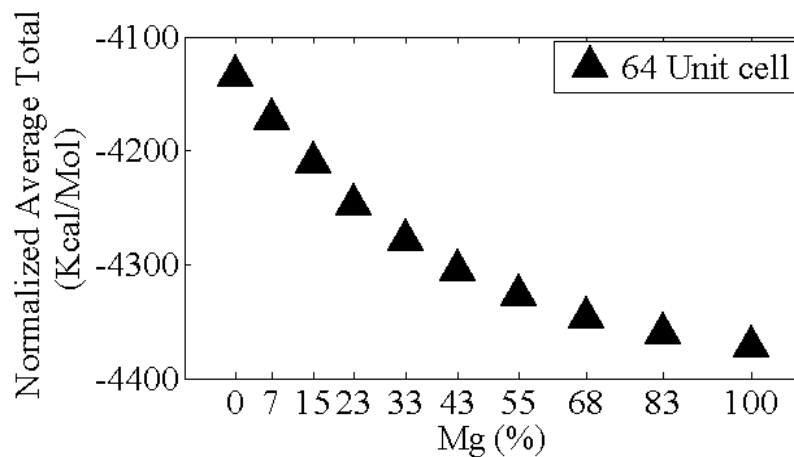


Figure 4: Change in total energy per mole for traditional and Mg-modified C-S-H Jennite

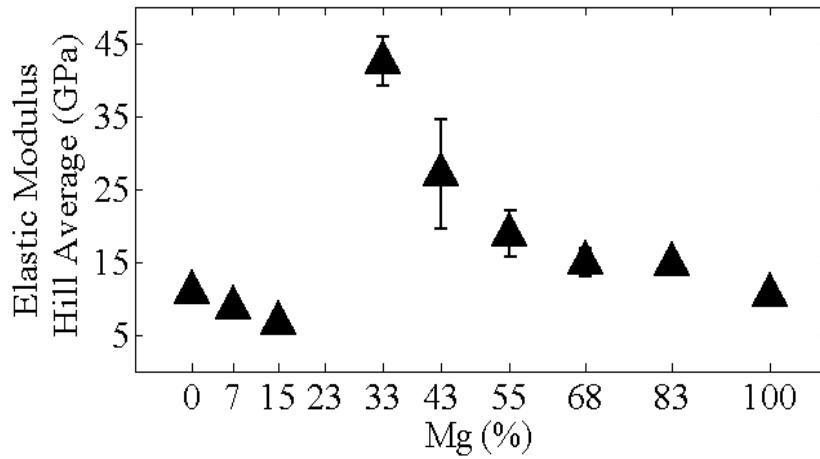


Figure 5: Predicted elastic modulus (Hill average) for traditional and Mg-modified C-S-H Jennite

The corresponding variation in the predicted bulk and shear modulus for various Mg-modified C-S-H Jennite material chemistry structures is shown in Figure 6. Again in both cases, present results indicate that there is a positive impact with increased bulk and shear modulus values until a Magnesium ion exchange of about 33%.

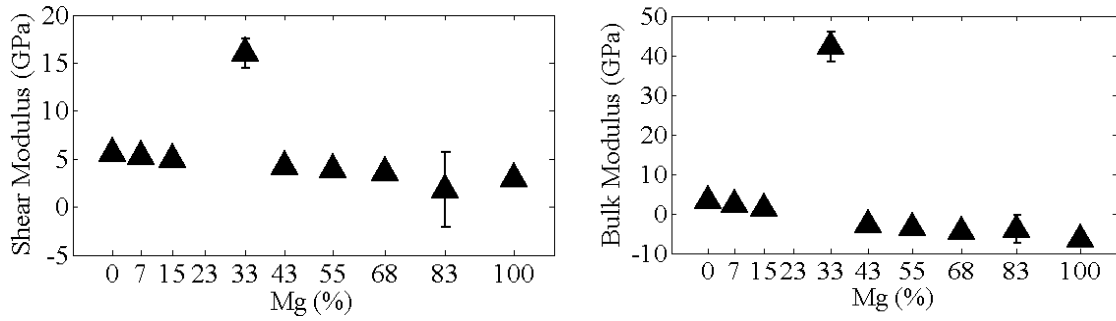


Figure 6: Predicted shear and bulk modulus (Hill average) for traditional and Mg-modified C-S-H Jennite

4 CONCLUSIONS

Material chemistry and modifications influence the evolving behavior of complex, hierarchical materials such as cement where material chemistry changes influence the hydration process, altering the microstructure and finally the engineering scale properties. In this paper, mechanical stiffness properties based on elastic modulus predictively obtained from traditional and Mg-modified showed that material chemistry does influence structural material stiffness modulus properties, and varies as the amount of Mg inclusion increases. These predicted material properties are based on molecular dynamics based material modeling with material chemistry structures; and thus provides an effective computational methodology to understand the expected variations due to material chemistry changes such as due to Magnesium ion exchange of C-S-H Jennite discussed in the present paper. Results from our current analysis is presented and further investigations are needed to explain some of the non-physical computational model values noted in the predicted values of bulk modulus that are

based on mechanics based approximations following the compliance matrix definitions in MD simulation analysis.

Engineering scale properties of interest are the stress-strain deformation behavior and effective prediction of estimated stress-strain behavior due to material chemistry changes, such as those discussed due to magnesium exchange in C-S-H Jennite are also of interest. Our work and results from such material chemistry level modeling will be highlighted in the presentation and will be discussed in future publications.

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