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MOLECULAR DYNAMICS MODELING OF HYDRATED CALCIUM-SILICATE-HYDRATE (CSH) CEMENT MOLECULAR STRUCTURE

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Abstract

Multi-scale modeling of complex material systems requires starting from fundamental building blocks to capture the scale relevant features through associated computational models. In this paper, molecular dynamics (MD) modeling is employed to predict mechanical properties of key hydrated cement constituent calcium-silicate-hydrate (CSH) at the molecular, nanometer scale level. Due to complexity, still unknown molecular configuration of CSH, a representative configuration widely accepted in the field of mineral Jennite is employed. A detailed study on effect of increasing MD simulation cell size shows good convergence. MD experiments were conducted to study predicted mechanical properties of CSH Jennite at higher thermodynamic pressure state conditions. Static higher thermodynamic pressure state was followed by MD analysis of increasing dynamic pressure states over very short time periods to emulate shock wave propagation at the molecular scale. The associated equation of state curve (EOS) for pressure – specific volume under isothermal conditions is presented and discussed.

Key words: *Molecular Dynamics, Calcium silicate hydrate, Mechanical properties*

1. INTRODUCTION

1.1 Cementitious materials. Concrete, one of the most used materials in the world is a mixture of cement, water, fine and coarse aggregate, and is an excellent example of highly heterogeneous material system. Cement paste consisting of starting configuration of dry cement powder and water mixture by itself is a complex, multi-scale material system. Though commonly used over the years, cementitious materials are one of the complex material systems in terms of material morphology and structure than most materials, for example, crystalline materials. In addition, cementitious materials undergo chemical and morphological changes gaining strength during the transient hydration process. Hydration in cement is a very complex process creating complex microstructures and the associated molecular structures that vary. A fundamental understanding can be gained through nano to continuum multi-scale level modeling for the behavior and properties of both hydrated and un-hydrated cement constituents at the atomistic length scale to further explore their role and the manifested effects at larger length scales. Building upon this, this paper focuses on the modeling of key cement genome molecular hydrated Calcium-Silicate-Hydrate (CSH) to obtain their predictive mechanical properties and study the influence of static high pressures, and dynamic high pressure effects emulating shock wave propagation on the CSH structure via molecular dynamics (MD) modeling. Present molecular dynamics modeling analysis provide a fundamental understanding of the high pressure molecular structural behavior of the hydrated CSH.

Portland cement in the powder form consists of four different major constituents: Tricalcium silicate (C_3S), Di-Calcium silicate (C_2S), Tri-Calcium aluminate (C_3A), and Tetra calcium aluminoferrite (C_4AF) [1]. Different mixture percentage of these constituents produce different types of Portland cement which is the most common used cement [2].Cement and water mixture (cement paste) is the binder for the concrete, Hydration of cement is the chemical reaction between cement compounds and water, which cause that hardens the cement. The hydration process is highly complex and produces complicated products that control the strength. The most important hydrated cement product is Calcium Silicate Hydrate (CSH). Due to the complexity of CSH, molecular structure of CSH has not been resolved yet. Other naturally occurring minerals Jennite [3] and Tobermorite14 [4] molecular structures are the closest representation of CSH crystal, accepted in the field. Following a Materials By Design paradigm, mechanical properties such as Elastic modulus(E)[5], Bulk Modulus(K)[6], Shear modulus (G)[7], and Poisson's ratio[8] for material systems can be obtained through molecular dynamics modeling of the molecular material structures. These mechanical property predictions based on the CSH Jennite molecular structure via MD modeling and understanding the behavior of hydrated CSH Jennite structure is the focus of the present paper.

1.2 Computational power and Atomic scale. Recently, computational modeling is playing an important role in science and engineering of materials. Computational models by definition are mathematical representation of a phenomenon for a system. Scientists and engineers are now using computational models to investigate and predict future system properties under different thermo physical conditions. Computational models along with both experimental investigations and analytical theory are the three corners of the processing-structure-property triangle when it is too hard to conduct experiments. Due to the rapid growth of Computational Materials Science (CMS) in the field of materials research [9], and because of the need to understand the scale size of the associated material genome molecular structures, researchers and engineers are challenged to dig deeper than macro and micro scale levels. Computational simulations at the molecular/nano scale level enable to study the behavior of materials at the molecular, material genome level. This is critical not only to predict but also improve the mechanical properties through appropriate material additives and molecular structural changes. Molecular Dynamics modeling is an effective methodology for such analysis at the molecular, nano scale level and is the computational methodology employed.

This paper employs MD analysis to predict the mechanical properties (Young's modulus, Shear Modulus, Bulk modulus, and Poisson's ratio) of CSH Jennite molecular structure. To confirm the finite size of the computational cell in MD analysis does not introduce any computational artifacts, a detailed study on the effect of increasing the molecular dynamic simulation cell size on the predicted mechanical properties of CSH Jennite was completed and discussed. This is followed by MD computational experiments to study predicted mechanical properties of CSH Jennite at higher thermodynamic pressure state conditions. Details of the analysis and results are presented and discussed. Static higher thermodynamic pressure state was followed by MD analysis of increasing dynamic pressure states over very short time periods to emulate shock wave propagation at the molecular scale. The associated equation of state curve (EOS) for pressure – specific volume under isothermal conditions is presented and discussed.

2. METHODOLOGY

Accelrys Materials Studio is a suite of molecular dynamics modeling software, that is used in advanced modeling of various materials (polymers, nanotubes, catalysts, metals, ceramics, etc.) [10]. Molecular Dynamics modeling is a computer simulation of atoms and molecules interacting with each other. MD method was discovered in the late 1950s and early 1960s by Alder and Wainwright [11]. At the present time, MD is applied in modeling materials science and biomolecules, because it can study

and investigate the structure and behavior of the interacting atoms at any molecular system. The methodology is based on transient dynamics analysis of atoms represented by system of particles based on classical Newtonian mechanics. The transient dynamic atomistic configurations under varying thermodynamic state conditions is coupled with statistical mechanics to obtain the predicted, thermo-physical properties as well as molecular level behavior of material systems based on the atomistic positions and velocities. The associated Newton's equation of motion can be represented by:

$$Fi = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 r_i}{dt^2}$$

where (m_i, v_i, r_i) are atom mass, velocities, position respectively, F is associated force, defined as the gradient of the potential energy representing the bonded and non-bonded energy associated with the material's molecular configuration.

The total potential energy for the material system varies for different molecular types because of the change of associated molecular parameters and atoms. The potential energy of the CSH Jennite molecular structure is determined using a COMPASS force field in the present work. The functional form of the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) contains three major terms, which are Bond terms, Non-bond terms, and Cross terms[12]. Bond terms include bond stretch, angel bending, angel rotation, and out of plane angel terms, associated with molecular configuration of the CSH Jennite structure. Figure 1 presents the bonded atom interaction components in the COMPASS force field/potential energy definition for CSH Jennite. These include bond stretching, angle bending, torsion, and out of plane rotation. Non-Bonded energies include Vander Waals and electrostatic energy as shown in figure 2.

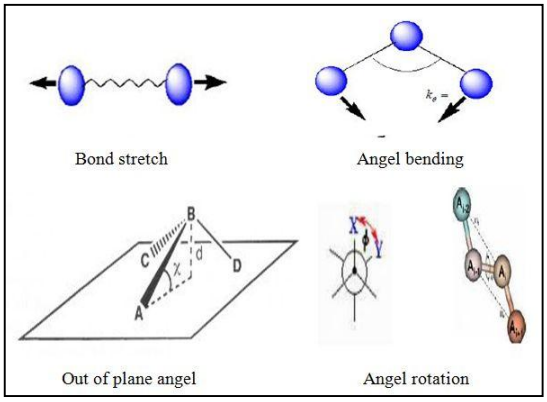

Figure 1 COMPASS Atom Bond Interaction Energy Components

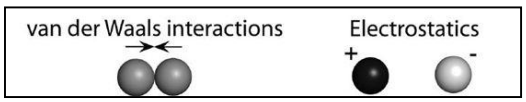

Figure 2 COMPASS Non-bond Energy Components

In addition, cross terms are important for predicting the vibration frequencies and structural variation, and include the combination of internal coordinates like Bond-bond, Bond-angel, and Bond-torsion.

2.2 Molecular dynamics. Molecular dynamics (MD) is a combination of molecular modeling, computer simulation, and statistics mechanics [13]. MD simulation consists of three steps, energy minimization, dynamic simulation, and calculation of the mechanical properties [14-16].

2.2.1 Energy minimization is to find the stable structure configurations, which corresponds to lowest energy for the molecular system. Some of the methods that can be used in the static minimization are: steepest descents, conjugate gradient, Newton-Raphson, and simplex method. Steepest descents and conjugate gradient methods are Gradient methods, which depends on the direction of the first derivative, and indicates where the minimum lies. Molecular Dynamics applications use the so called smart minimization method. Smart minimization is a combination of the Gradient and Hessian methods. For systems less than 200 atoms, starting with the steepest descent method, followed by the Conjugate Gradient method and ends with a Newton method. For systems larger than 200 atoms, starting with the steepest descent, followed by the Conjugate Gradient method[10]. This is employed in the present work.

2.2.2 Dynamic simulation. The dynamics of atom motion based on initial velocities that are based on the temperature conditions are determined by solving Newton's equation of motion. The time dependent atom configuration at each time step forms the trajectory with molecular configuration at each time step forming the possible phase state configuration of the molecular system following the principles of statistical mechanics. Time integration algorithms are used to integrate the equation of motion. Some of the time integration methods are Euler Method, 2nd order Runge-Kutta Method (RK2) or sometimes it is called Modified Euler Method, 4th order Runge-Kutta Method (RK4), Verlet algorithm, Velocity Verlet algorithm, and Predictor-Corrector Methods. However, the most commonly used time integration algorithms in molecular dynamics are Verlet algorithm and Predictor Corrector algorithms. The present work employed Velocity-Verlet algorithm. The time dynamic trajectory consisting of several snapshots of atomic positions and velocities of CSH Jennite molecular structure are used for the predictive mechanical property determination in conjunction with Ergodic Hypothesis linking the time average from classical mechanics and phase averages in statistical mechanics.

2.2.3 Mechanical properties Determination. Elastic constants can be determined by the following equation based on the associated potential energy of the molecular system.

$$C_{ij} = \frac{1}{V}\frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j}$$

where $\varepsilon_i, \varepsilon_j$lattice strain components, U is potential energy, and V is the MD molecular cell volume. The above equation can be used to obtain the Elastic stiffness matrix (C) and the Elastic compliance matrix (S) (the inverse of C) can be determined. Elastic modulus (E) can be computed from Elastic compliance matrix (S)

$$E_x = S_{11}^{-1}, E_y = S_{22}^{-1}, E_z = S_{33}^{-1}$$

Bulk modulus (K) can be computed using Reuss, Voight, and Hill definitions from the elastic stiffness matrix.

$$K_{Hill} = \frac{1}{2}(K_{Voight} + K_{reuss})$$
$$K_{Voight} = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2(C_{11} + C_{13} + C_{23}))$$
$$K_{reuss} = \frac{1}{9}(S_{11} + S_{22} + S_{33} + 2(S_{11} + S_{13} + S_{23}))^{-1}$$

Shear modulus (G) can be computed using Reuss, Voight, and Hill definitions from the elastic stiffness matrix.

$$G_{Hill} = \frac{1}{2}(G_{Voight} + G_{reuss})$$
$$G_{Voight} = \frac{1}{15}(C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - C_{12} - C_{13} - C_{23})$$
$$G_{\mathrm{Re}uss} = \frac{15}{4(S_{11} + S_{22} + S_{33} - S_{12} - S_{13} - S_{23}) + 3(S_{44} + S_{55} + S_{66})}$$

Poisson's Ratio (ν) which is the ratio of lateral to longitudinal strain can be computed from the following equation:

$$\nu = \frac{3K - 2G}{6K + 2G}$$

2.3 Periodic boundary condition (PBC). The use of the PBC in MD analysis mathematically helps in predicting the properties of Bulk system employing smaller molecular configurations.

2.4 Ensemble. Ensemble is a collection of points over time satisfying the same macroscopic or thermodynamics properties used in the MD analysis. Common ensembles in MD are: Micro-canonical Ensemble (NVE), Canonical Ensemble (NVT), and ISOBARIC-ISOTHERMAL Ensemble (NPT). NVE is a fixed number of atoms, fixed volume, and fixed energy. NVE is not recommended for equilibration, but it is good for exploring constant energy configuration. In NVE there is no control on pressure or temperature. NVT is a fixed number of atoms, fixed volume, and fixed temperature. NVT is good when pressure is not a major factor, and when the MD simulation is conducted in a vacuum without periodic boundary conditions. MD analysis employs temperature controlling methods such as Velocity scaling, Berendsen, Anderson, Langevin dynamics, and Nose-Hover. NPT is a fixed number of atoms, fixed pressure, and fixed temperature. NPT is good when correct pressure, volume, and densities are important during the MD analysis. Pressure control is achieved via Parrinello[17], Berendsen, and Anderson control methods commonly used in MD.

2.5 Time step. Time step is one of the important parameters in MD simulations, because the right choice of the time step value will lead to stable and accurate results. Time step should be around one tenth of the shortest period of motion of the atoms. A time step of 1 *fs* (femto second) is employed in most of the MD analysis in the present work.

3. ANALYSIS DETAILS

Based on the above discussions, a summary of the parameters employed in the present work for the MD analysis is presented in Table 1.

MD Parameters	Value/Method
Super cell sizes	(1a) x (1b) x (1c)
Molecular tools	Discover
Minimization method	Smart minimization
Force field	Compass
Ensemble	NPT
Temperature	298k (25°C)
Temperature control	Anderson/Nose
Pressure	(0.0001) GPa
Pressure control	Parrinello/Berendsen
Time step	1 Femto second (fs)
Dynamic time	100 Pico second (ps)
Cut off distance	12.5 nm
PBC	on

Table 1 Simulation run parameters.

To confirm the finite size of the computational cell in MD analysis does not introduce any computational artifacts, a detailed study on the effect of increasing the molecular dynamic simulation cell size on the predicted mechanical properties of CSH Jennite was studied. This was achieved by changing the cell dimensions one, two, and three unit cell were used (1a-3a) x (1b-3b) x (1c-3c), with increasing number of atoms for the CSH-Jennite molecular configuration.

MD computational experiments to study predicted mechanical properties of CSH Jennite at higher thermodynamic pressure state conditions were completed by changing the pressure to different static pressure thermodynamic state pressure values in the range of 0.0001 GPa – 3 GPa (atmospheric pressure – 3 GPa).

MD analysis of the increasing dynamic pressure states over very short time periods to emulate shock wave propagation at the molecular cell was achieved by: For dynamically pressure increase, the super cell used was (4x4x4) with a total of 4352 atoms. Ramping of pressure increment by 0.1GPa form 0.0001-5.0001 GPa (atmospheric pressure to 5.0001 GPa); Each pressure increment has two dynamic run steps, first step is based on NPT ensemble for 500 *fs* to obtain a stable corresponding thermodynamic pressure state of the CSH molecular system followed another NPT by 10000 *fs* to for the dynamic analysis. The average equilibrium pressure and corresponding specific volume values after each iteration were obtained. This is used to obtain the associated equation of state (EOS) of pressure – specific volume under isothermal conditions. MD modeling methodology followed here allows one to determine this EOS for a material system (demonstrated here for CSH Jennite) computationally without a need for any experiments.

4. RESULTS AND DISCUSIONS

Results from the prior discussed MD experiments are presented next. These are organized and divided into four parts: 1. MD mechanical property predictions for CSH Jennite and comparisons with literature data; 2. Effect of increasing MD cell sizes with increased number of atoms employed in the MD analysis for CSH Jennite; MD computational experiment results for the predicted mechanical properties at higher static thermodynamic pressure states; 4. Equation of State for pressure – specific volume obtained computationally from MD analysis for increasing dynamic pressure states over very short time periods to emulate shock wave propagation of CSH Jennite at the molecular scale level.

4.1 MD Mechanical Property Predictions for CSH Jennite. Table 2 presents a comparison of the mechanical properties obtained from the present MD analysis and available results from literature at atmospheric pressure for CSH Jennite molecular structure.

Mechanical Properties	Current	Ref.[14] MD	Ref.[18] Nanoindentation
Tensile (GPa)	69	82	66
Bulk (GPa)	70	78	43
Shear (GPa)	26	31	26
Poisson's Ratio	0.34	0.33	0.24

Table 2 MD Mechanical Property Predictions for CSH Jennite and Comparisons

Molecular Dynamics predicted mechanical properties for CSH Jennite are in concurrence with prior MD analysis results at atmospheric pressure, and corroborate well with nano-indentation based averaged experimental values. It is to be noted that in nano scale material systems, material properties are scale dependent with molecular configuration of CSH Jennite at a nano scale level while nano-indentation is generally based on a much large length scale at several orders of molecular scale structure. The initial and final molecular configuration of CSH Jennite structure from the molecular dynamics analysis is shown in Figure 3.

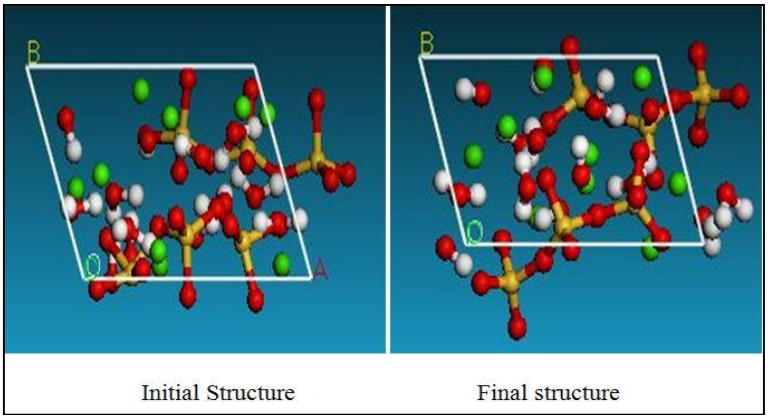

Figure 3 Initial and Final CSH Jennite structure from MD Analysis

4.2 Effect of Increasing MD Cell Size. As discussed earlier, a comparison of Jennite mechanical properties, namely Tensile modulus, Shear modulus, Bulk modulus and Poisson's ratio using different MD computational cell sizes (1x1x1, 2x2x2, and 3x3x3) of the unit cell at atmospheric pressure. Table 3 presents the predicted mechanical properties obtained at different MD cell sizes.

size	1x1x1	2x2x2	3x3x3
Tensile (GPa)	68.51	67.36	67.68
Bulk (GPa)	70.47	73.10	72.00
Shear (GPa)	25.60	25.02	25.19
Poisson's Ratio	0.3380	0.3464	0.3433

Table 3 MD Property Predictions for CSH Jennite Structure at Various Cell Sizes

From Table 3 it can be seen that the effect of increasing cell size on the Elastic modulus (E) is very minimal with convergence reached with increased cell dimensions. A difference of about 2.8% in tensile modulus, 4.3% in Bulk modulus (K); 4% in Shear modulus (G) is 4.0%, and 2.5% on the Poisson's ratio. A snapshot of molecular structure from the simulations is shown in figure 4.

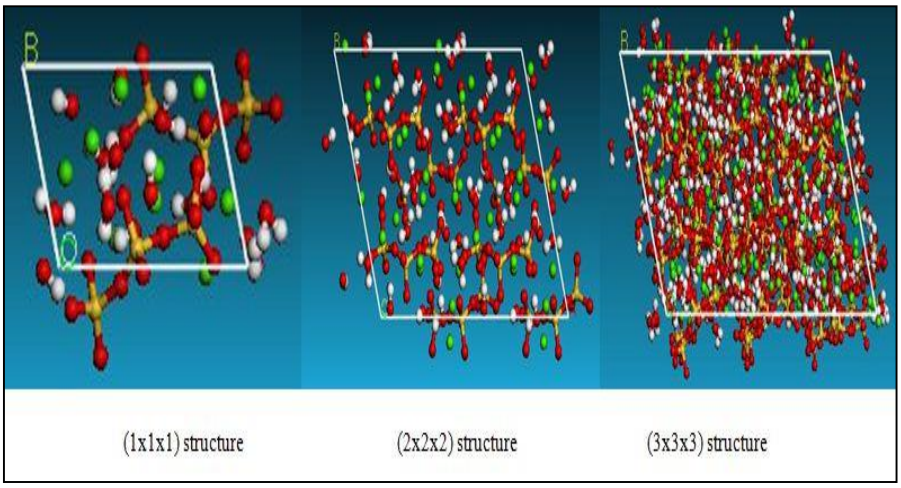

Figure 4 CSH Jennite Molecular Structure at Different MD Cell Sizes

4.3 MD Predicted Property Values at Higher Thermodynamic Pressure. Table 4 presents the MD predicted mechanical properties at various static, thermodynamic pressure tastes. Mechanical properties Elastic, Bulk, and Shear modulus decreased with the increase of pressure values from 0.0001 to 3.0 (GPa). Clearly, these molecular dynamics modeling analysis provide a means to obtain the associated predictive mechanical modulus properties and their associated pressure derivatives that are difficult to obtain experimentally.

Pressure (GPa)	Elastic	Bulk	Shear	Poisson
0.0001	68.51	70.47	25.6	0.338
0.001	60.22	69.75	22.2	0.3561
0.01	61.47	73.32	22.59	0.3603
0.05	63.98	69.83	23.75	0.3473
0.1	56.72	69.82	20.78	0.3646
0.2	60.28	65.55	22.38	0.3467
0.4	52.54	67.72	19.16	0.3707
0.6	62.53	66.49	23.27	0.3433
0.8	57.41	57.86	21.51	0.3346
1.0	56.16	60.95	20.86	0.3464
1.5	64.12	68.73	23.84	0.3445
2.0	70.86	65.32	26.86	0.3192
3.0	42.69	46.34	15.85	0.3465

Table 2 CSH Jennite structure MD mechanical predictions at various pressures

Figure 6 presents the variation in the MD mechanical property predictions at various thermodynamic state pressure conditions for CSH Jennite. Results showed three different regimes based on the static pressure range. In the initial pressure increase region of (0.0001-1.0) GPa, predictive mechanical properties (E, K, and G) decrease with the increase of pressure. In the range of pressure values (1.0-2.0) GPa, mechanical properties increases with the increase of pressure, while in the (2.0-3.0) GPa range, mechanical properties decreases with the increase of pressure.

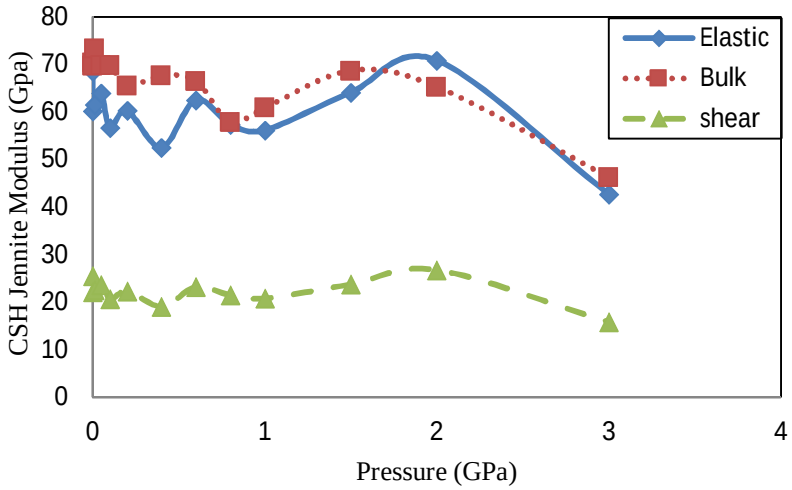

Figure 5 CSH Jennite MD Predicted Mechanical Properties – Pressure Variation

Figure 6 presents the CSH Jennite structure after the dynamic analysis under different thermodynamic state pressure conditions. Increasing pressure states has a significant effect on the structure configuration, which can be seen in the locations of atoms and the dimensions of the lattice.

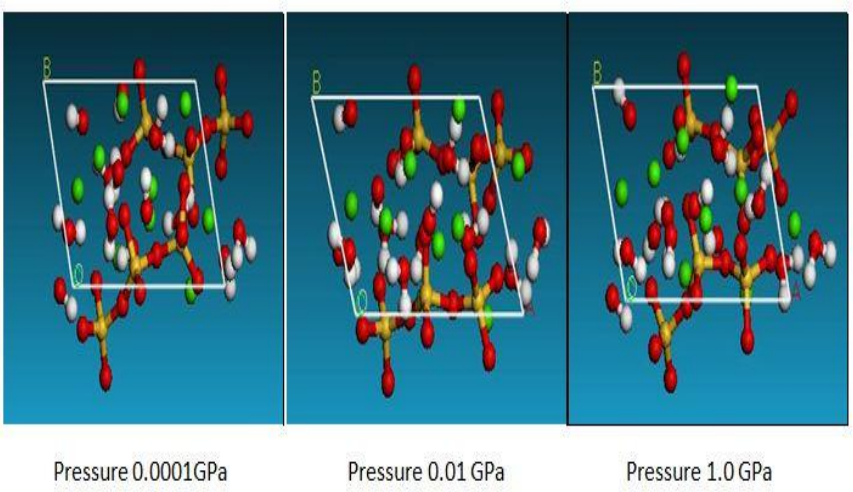

Figure 6 Jennite structure under different pressure values

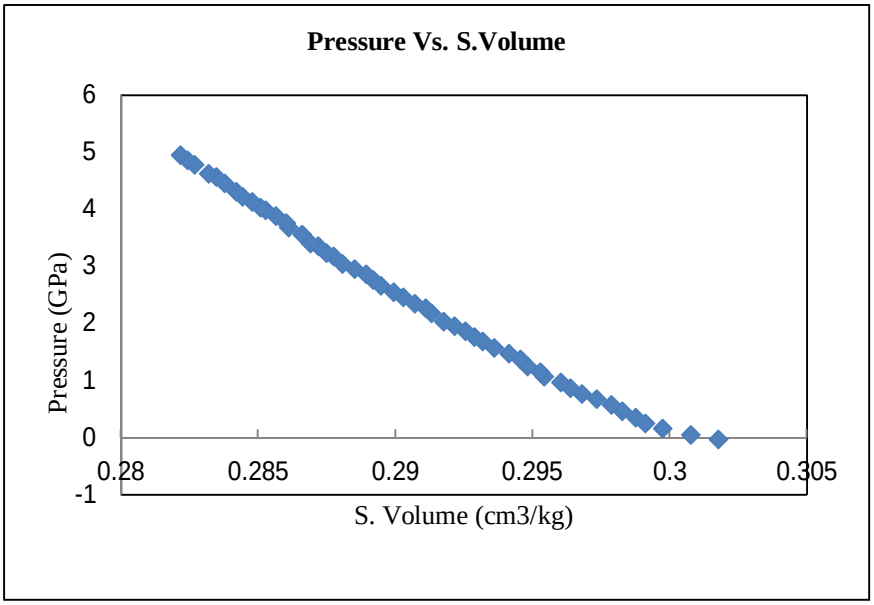

Figure 7 Pressure – specific volume EOS for CSH Jennite molecular structure

4.4 Isothermal EOS for pressure – specific volume in CSH. As discussed earlier, Equation of State for pressure – specific volume obtained computationally from MD analysis for increasing dynamic pressure states over very short time periods to emulate shock wave propagation of CSH Jennite is presented in figure 7. Isothermal pressure - specific volume equation of state (EOS) was developed using molecular dynamic simulation by dynamically changing the pressure as discussed earlier and obtaining the corresponding specific volume[19]. Current equation of state relating the pressure –

specific volume curve following the MD analysis discussed earlier is presented in figure 7. The results presented are a first step in obtaining the Hugoniot state curve for CSH Jennite structure directly via molecular dynamic analysis.

5. CONCLUDING REMARKS

Clearly, molecular dynamics modeling analysis provide an effective means for fundamental understanding of the high pressure molecular structural behavior of CSH Jennite structure; a means to obtain the associated predictive mechanical modulus properties and their associated EOS states required for the understanding of dynamical material behavior that exist in shock loading conditions.

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