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Intermolecular dynamics of ultraconfined interlayer water in tobermorite: influence on mechanical performance

Nilanjan Mitra, Prodip Kumar Sarkar and Dipak Prasad

Ultraconfined interlayer water within the tobermorite molecular structure is responsible for changes in the uniaxial tensile and compressive response of the family of tobermorites: 9 Å, 11 Å and 14 Å. These confined interlayer water molecules are engaged in solvation of cations and anions within the tobermorite structure, which has been demonstrated through the intermolecular vibrational spectra and hydrogen bond lifetime of the water molecules. This study demonstrates that instead of ionization of water molecules (as proposed in an earlier study), breaking of hydrogen bonds of water is more plausible leading to solvation of ions within the molecular structure of tobermorite. A schematic of the coordinate covalent bonds between the water molecules and the cations and anions of the tobermorite structure has been proposed in this study.

Introduction

Tobermorite is a naturally occurring mineral that usually exists in three different states: tobermorite 9 Å, 11 Å and 14 Å. These numbers represent the interlayer distances in between the calcium silicate layers that are usually filled up with water molecules. The difference between these molecular structures is typically in the water molecules present in the interlayers. It should be noted that tobermorite is considered to be an analog to the calcium silicate hydrate structure with the difference being in the Ca/Si ratio. Usually, for the naturally occurring tobermorite, we have a Ca/Si ratio of 0.67 to 1.0, whereas for the calcium silicate hydrate (CSH) compound, the primary compound of cement hydrates, we have a Ca/Si ratio of 1.2 to 2.3, which is also dependent on the water cement ratio of the mix. In other words, the CSH system can be considered as a defective tobermorite structure.

In a previous study, it was postulated that water dissociates into ions that eventually contribute to the increase in the strength of the CSH compound (modelled as a tobermorite structure). The REAX model was used for water and it was argued that water dissociates into H⁺ and OH⁻ ions that eventually react with calcium and/or silicate ions in the CSH structure. It should be realized at this point that a significant amount of energy is required to break the covalent bond of water so as to result in ionization into H⁺, H₂O⁺ and OH⁻ ions (56.8 kJ mol⁻¹), which cannot be provided in the system at ambient temperature and pressure during the process of hydration of cement. It is true that the hydration reaction of cement is exothermic but even an increase in temperature (by around 200 °C) is not sufficient to provide the required energy for ionization of water. Instead, it can be postulated that the calcium and silicate ions (within the molecular structure of tobermorites) are solvated by the confined water molecules within the tobermorite structure. This solvation mechanism of calcium and silicate ions in water (ultraconfined in the interlayers of the tobermorite structure) can be understood through intermolecular dynamics of the ultraconfined water molecules. Typically, in solvation studies of cationic and anionic ions, the hydrogen bonds of the water molecules are broken and there results a formation of dative (or coordinate) covalent bonds between the cationic and/or anionic ion and the water molecule. It can easily be argued that it is much easier to break hydrogen bonding of water (having an energy of 0.3286 eV) rather than to break the covalent bonding of water resulting in ionisation (having an energy of 56.8 kJ mol⁻¹ or 0.5887 eV).

Since it can easily be established (by comparison of the two energies of breaking of covalent bonds and hydrogen bonds for water molecules) that there is no dissociation of water in the ultraconfined spaces, there is no requirement of the introduction of a potential for water that is able to dissociate (the REAX model for water). Standard or conventional potentials (that do not allow dissociation) can easily be applied to the system to understand the dynamics of the molecules. It should be noted that inclusion of models for water that are able to demonstrate dissociation (REAX) comes with an extra cost of computational resource requirements.
It is therefore hypothesized that the presence of confined water molecules eventually leads to the formation of dative (or coordinate) covalent bonds with cationic and/or anionic ions (in the tobermorite structure), which is primarily responsible for the stability of the different structures of tobermorite and also influences the mechanical performance of these molecular structures. The manuscript demonstrates changes in the hydrogen bond dynamics with an increase in interlayer water in different forms of tobermorite. Eventually, it also relates how the changes in the water layer affect the mechanical performance of the different tobermorites thereby offering a plausible explanation of the effect of hydrogen bonding of the ultraconfined interlayer water (which is also engaged in solvation of ions within the tobermorite structure) on the mechanical performance of the tobermorite.

In this regard, it should be mentioned that hydration of C₃S resulting in the formation of CSH (a tobermorite like structure) has been discussed in the literature, however, the study does not perform a detailed analysis of water molecules and their bond dynamics with other cations and anions as has been done in this study for the case of different phases of tobermorite. The role played by water molecules for other minerals such as gypsum (along with its different anhydrous phases) has also been highlighted by authors in a previous work. Commenting on the Ca²⁺ ion dynamics, which is expected to play a crucial role in the molecular structure of CSH, it has been mentioned in the literature that aluminates can adsorb onto hydroxylated C₃S mainly through strong ionic interactions between aluminate and calcium ions on the surface of silicate thereby retarding the hydration kinetics of C₃S. Previous literature also mentions that Ca²⁺ ions form some covalent bonds within the C₆A molecule. Therefore, based on the discussed literature, it can be said that CSH hydrates are ionic-covalent compounds.

It should also be mentioned that there are a few literature reports that argue that CSH should not be taken to be a disordered phase of tobermorite/jennite having a C/S ratio, but instead the total bond order density should be evaluated properly. Hence, the crystal structures are different from each other due to their characteristic basal spacing (9 Å, 11 Å, and 14 Å) and degree of hydration. It has been demonstrated in earlier studies that the hydration of cement eventually leads to coexistence of all of these different phases of tobermorite within the mix. The crystal structure of tobermorite 11 Å is monoclinic and it belongs to the space group B11m having a Ca/Si ratio of 0.66, whereas the selected structure of tobermorite 14 Å is also monoclinic with a space group B11b but having a Ca/Si ratio of 0.83. The adopted atomic structure of tobermorite 9 Å has a triclinic unit cell with space group C1 and a Ca/Si ratio of 0.8. The detail unit cell parameters of all the three phases are given in Table 1. It should be noted that tobermorite 14 Å has the maximum water content followed by tobermorite 11 Å. Both these tobermorite structures are composed of continuous silicon dioxide chains stretched along the Y direction where the silicate tetrahedra are linked to each other and also coordinated to the Ca ions. These particular arrangements of atoms within the crystal create calcium silicate parallel layers that are then separated by the presence of water molecules within the inter-layer space (ref. Fig. 1b and c). The difference between these two phases is that in the case of tobermorite 11 Å, the parallel silicate chains are connected to each other with the help of bridging tetrahedra at a regular interval (ref. Fig. 1b), whereas no interconnections occur for the parallel silicate chains of tobermorite 14 Å. In both cases, the layers run perpendicular to the coordinate direction Z. In the case of tobermorite 9 Å, the layers are slightly inclined to Z and the structure does not contain any water molecule within it (ref. Fig. 1a).

Interactions of different atoms give an important input to study the dynamic evolution of any molecular system. Proper mathematical expression is necessary to calculate the energy accurately and therefore computation of the interaction coefficients needs special attention such that it can mimic the experimental results or the available results computed with the help of density functional theory (DFT). The hydrated phases of cement have been studied utilizing the CSH-FF potential, which has been developed by improving the ClayFF potential form. The potential has been utilized to study the deformation behavior of tobermorite under uniaxial loading. The potential parameters have been decided based on the results of DFT calculations and the fitting parameters, which enables an accurate calculation of lattice parameters and elastic constants of tobermorite 11 Å. During the parameterization of CSH-FF, the interaction between different atoms has been taken as nonbonded interactions (electrostatic and van der Waals) except for the interactions of oxygen and hydrogen in hydroxyl groups and water molecules, which are modeled as a harmonic potential. In this context, it should be noted that the continuous silicate chains of tobermorite are made of ionic-covalent Si–O atoms, but this

### Simulation methodology

The tobermorite mineral has been studied extensively as a natural analogue of CSH formed due to the hydration of portland cement. The crystal structures of tobermorite 9 Å, 11 Å and 14 Å have been

<table>
<thead>
<tr>
<th>Name</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobe 9 Å³</td>
<td>11.156</td>
<td>7.303</td>
<td>9.566</td>
<td>101.08</td>
<td>92.83</td>
<td>89.98</td>
</tr>
<tr>
<td>Tobe 11 Å³</td>
<td>6.735</td>
<td>7.385</td>
<td>22.487</td>
<td>90</td>
<td>90</td>
<td>123.25</td>
</tr>
<tr>
<td>Tobe 14 Å³</td>
<td>6.735</td>
<td>7.425</td>
<td>27.987</td>
<td>90</td>
<td>90</td>
<td>123.25</td>
</tr>
</tbody>
</table>
Interaction is considered in the CSH-FF model as only a non-bonded interaction (considering only the ionic contribution). It should be realized that ionic interactions are directionally independent, whereas the covalent interactions are directionally dependent, which helps to maintain the alignment of silicate chains within the structure. It has been mentioned in the literature that the polarity of chemical bonds influences the structure and reactivity of a chemical bond, which needs to be incorporated into the force-field through parameterization to make the model more consistent and physically realistic. The possible strength of a covalent bond is dependent on the atomization energies/electro affinities of the elements. Since the ratio of covalent bonding to that of ionic bonding is well described for silicates by the IFF force-field compared to that of CSH-FF, the interface force field has been chosen in this study to represent the tobermorite structures.

In this particular study, the INTERFACE force field (IFF) has been adopted where the ionic-covalent bonds can be modeled effectively. The model considers the covalent interactions of Si–O and H–O through a higher order harmonic potential and the interactions of Ca with all other atoms as well as the ionic contribution of the Si–O bonds are modeled as nonbonded interactions. The IFF can efficiently reproduce both the cell parameters and elastic constants in comparison to the CSH-FF.

In addition to that, the covalent connections between the atoms govern a directional dependency of the molecular arrangement during the simulation, which is generally ignored for the case of CSH-FF. The IFF has been tested against the computation of several physical and chemical properties like surface/interface properties, vibration spectra etc. The force field can be utilized by employing several energy expressions like the PCFF (polymer consistent force field), COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies), CVFF (Consistent Valence force field), OPLS-AA (Optimized Potentials for Liquid Simulations-all atom) etc. and by using their respective coefficients; but, for this manuscript, the PCFF energy expression has been used. The energy expression is composed of a harmonic form of both bonds, angle interactions (which together constitute a bonded energy part) and the nonbonded energy as the sum of Coulombic electrostatic and van der Waals interactions (modeled as 9-6 Lennard-Jones potential) (refer to eqn (1)). The particular potential can effectively reproduce the crystal lattice parameters like cell parameters, density and many other physical and chemical properties like thermal properties, surface/interface properties, vibration spectra etc. The parameters in the LJ expression are mentioned for interactions between the same atom types and a sixth power combination rule is prescribed to compute the interactions between different atom types.

The lattice parameters of the unit cells used in this study are summarized and given in Table 1. The simulation box for different structures has been created by replicating the unit cell in three mutually perpendicular directions. For tobermorite 9 Å, the unit cell has been replicated by 5 × 8 × 6 times along X, Y and Z directions, respectively, where replication multipliers are 8 × 7 × 2 for both tobermorite 11 Å and 14 Å. The total box dimensions for tobermorite 9 Å are 55.78 Å × 58.42 Å × 57.39 Å (no. atoms = 15360), whereas for tobermorite 11 Å and tobermorite 14 Å, the adopted box sizes are 53.88 Å × 51.69 Å × 44.97 Å (no. atoms = 9856) and 53.88 Å × 51.97 Å × 55.97 Å (no. atoms = 11648), respectively. Energy minimization has been performed for all the three structures using the conjugate gradient method to ensure initial minimum energy configurations. The configurations are then equilibrated for 100 ps with a time step of 0.2 fs using the NPT ensemble to bring the initial system to room temperature (298 K) and pressure 1 atm. The Nose–Hoover thermostat and the barostat are used during the equilibration.
The stress–strain behavior for compression is very similar to the tensile response except in the order. Here, the peak stress for tobermorite 11 Å is 18.5 GPa at a strain level of 0.11, which is also the largest within the family and also the failure nature is brittle. The strength of tobermorite 14 Å and 9 Å has been observed to be 7.7 GPa and 5 GPa, both of which occur around a strain value of 0.18.

The reason for this anomalous response of high strength in tension and compression for tobermorite 11 Å compared to that of tobermorite 9 Å and tobermorite 14 Å can be traced to their molecular structures. The parallel silicate chains are interconnected to each other by bridging tetrahedra at regular intervals for tobermorite 11 Å, whereas for tobermorite 14 Å, the chains run parallel without any interlink. The confined water molecules are also observed in between the parallel silicate chains for tobermorite 11 Å with no calcium ions near it. This suggests that coordinate covalent bonding can occur between the oxygen atom of the silicate chains and the hydrogen atom of the water molecules. On the other hand, for tobermorite 14 Å, calcium ions are present in between the silicate chains where there are also water molecules. Therefore, coordinate
covalent bonding between the calcium ions and oxygen of the water molecules can easily form. In this regard, it should be mentioned that the possibility of formation of coordinate covalent bonds between water and calcium and silicate ions of the CSH structure (which is a defective tobermorite structure) and its effect on unaxial tension of the material have been discussed in previous literature.\textsuperscript{27} However, the dynamics of confined water and the hydrogen bond lifetime estimation were not presented in the earlier manuscript as have been presented in this work.

**Intermolecular dynamics of ultraconfined interlayer water engaged in solvation of ions within the tobermorite structures**

It has been mentioned earlier in the manuscript that water in ultraconfined form is present in the interlayer regimes of the tobermorite structure. This ultraconfined water is also engaged in the solvation of the cations and anions in the tobermorite structure. Typically, water exhibits different peaks corresponding to intermolecular as well as intramolecular vibrations. The intramolecular vibrations are typically captured in the infrared domain with H–O–H bending and O–H stretching associated with 1643 cm\(^{-1}\) and 3404 cm\(^{-1}\), respectively. The libration motions associated with the rotation of the molecules about various axes are obtained at 500–1000 cm\(^{-1}\). A water molecule is connected to 4 other water molecules through hydrogen bonding, which are typically associated with O⋯O⋯O bending (occurring at 50–60 cm\(^{-1}\)) and O⋯O stretching modes (occurring at 175–200 cm\(^{-1}\)).\textsuperscript{41–45} All the above wavenumbers have been determined experimentally for bulk water at ambient temperature and pressure and it is anticipated that a blue or red shift of these wavenumbers would occur under the application of load or when the water is constrained (such as the presence of intermolecular water in a molecule structure) or in solvation of any ions or salts takes place. It has been mentioned in the literature\textsuperscript{11} that changes in the water structure associated with the addition of salts (due to solvation of salts in water) are similar to that occurring due to the application of pressure in the order of 100 MPa.

Obviously, the determination of interatomic potential governs the hydrogen bond behavior. In order to investigate the behavior of INTERFACE potential in its ability to identify hydrogen bonding of water, a sample of bulk liquid water is modeled and analyzed using the INTERFACE potential after equilibrating the structure. Initially, 100 molecules are created inside an amorphous cell that is subjected to energy minimization at 0 K. Now, in order to generate a larger system, this cell is replicated to \(2 \times 2 \times 2\) in all three orthogonal directions. This system is again subjected to energy minimization followed by equilibration at 298 K under canonical (NVT) conditions for 200 ps. Furthermore, the temperature equilibrated system is subjected to pressure equilibration using the isothermal–isobaric (NPT) integration scheme for 200 ps under ambient temperature and pressure conditions. All simulations were performed using a timestep of 0.5 fs and the Nose–Hoover thermostat and barostat algorithm.\textsuperscript{46–48} Final density of the bulk system under ambient conditions was obtained as 1.029 gm cc\(^{-1}\).

In order to obtain the absorbtion spectra of the water molecules, it is necessary to determine the velocity auto correlation function (VACF) for individual oxygen and/or hydrogen atoms, which has been estimated based on the following formulae\textsuperscript{49,50}

\[
C_V(t) = \frac{\langle \vec{v}(t) \cdot \vec{v}(t+\tau) \rangle}{\langle \vec{v}(t) \cdot \vec{v}(t) \rangle}
\]

where \(\vec{v}(\tau)\) denotes the velocity vector of an atom at a particular instant of time \(\tau\), while \(t\) is the autocorrelation time. For the calculation of the VACF, all three orthogonal velocity components of all the atoms within the molecule are stored up to 2 ps at an interval of 1 fs. The power spectrum is calculated as the cosine Fourier transform of the velocity autocorrelation function (VACF).

\[
I(\omega) = \int_0^\infty C_V(t) \cos(\omega t) dt
\]

The power spectra of the entire water molecule are presented in Fig. 3, which demonstrates that the INTERFACE potential is able to capture well almost all the vibrational spectral peak lines with reasonable accuracy. For comparison, the sample of pristine water was also analysed using the TIP4P flexible model, which is one of the most widely used models for water. The experimentally observed vibrational spectra are represented as line diagrams indicating the peak positions. It can be observed that the INTERFACE potential is able to capture well the O⋯O⋯O bending mode at 50–60 cm\(^{-1}\). However, the interface potential is unable to capture the O⋯O stretching modes explicitly, as could be done by using the TIP4P model. With regards to the libration modes, we also observe a blueshift in wavenumbers for the IFF potential compared to that of TIP4P and experimental observations. With regards to O–H stretching and H–O–H bending, we observe a blueshift in response for the IFF potential compared to that of the TIP4P and the experimental results. However, it should be noted that our interest lies in the intramolecular dynamics part (which contributes to solvation dynamics) and not other parts and therefore we restrict our discussion to wavenumbers within 0–1000 cm\(^{-1}\).

In order to identify differences of intramolecular dynamics of the confined water in the two tobermorite structures, which is also engaged in the solvation of cations and anions, the VACF plot of oxygen atoms is presented in Fig. 4. It can be observed that bulk water modeled using the INTERFACE potential shows a negligible dip in response in comparison to that of the TIP4P
model. It should be noted that these dips in response indicate different kinds of relative motions of oxygen atoms. The first minimum in $C_V$ corresponds to the backscattering of the atoms, i.e. the to and fro motion of oxygen atoms in O···O vibration. Similarly, a second dip corresponds to the movement of oxygen atoms resulting in O···O···O bending modes. Two dips in response can be observed for confined water in tobermorite 11 Å signifying the presence of two relative motions of the oxygen atoms. However, it should be noted that these dips in response observed for the confined water in the tobermorite 11 Å structure are significantly different from the response as demonstrated by TIP4P for bulk water both in terms of the dip amplitude as well as the peak (trough) position. On the contrary, confined water in tobermorite 14 Å shows only one dip. The probable reason behind this phenomenon is the presence of an extra water layer between calcium silicate sheets in tobermorite 14 Å. Based on the position of interlayer water in tobermorite 14 Å, water can form hydrogen bonding with the calcium ions as well as the silicate layers, which eventually results in restraining the overall movement of water molecules thereby forcing the merging of the two dips. For the case of tobermorite 11 Å, water can only form hydrogen bonds with silicate layers and not with calcium ions therefore it is less restrained compared to water in tobermorite 14 Å.

Fig. 5 shows the velocity autocorrelation for the movement of hydrogen atoms. It should be noted that TIP4Pr represents the TIP4P rigid model of water whereas TIP4Pf represents the flexible TIP4P model for bulk water. The undulations in the curves arise due to intramolecular vibrations while the overall shape of the curve responds to intermolecular vibrations. Clearly, using the TIP4P rigid model for bulk water, these undulations are missing showing only two dips. The first dip arises due to librational modes and the second dip is due to hydrogen bond stretching. Confinement of water causes a similar kind of effect where two dips eventually merge for confined water in tobermorite 11 Å and 14 Å. The effect of this merging of dips and thereby constraining of individual motions of the hydrogen atoms are reflected in the spectral diagram for water (refer Fig. 3). For the case of bulk water, one obtains distinct peaks at 50–60 cm$^{-1}$, 500–700 cm$^{-1}$ for TIP4P and at 50–60 cm$^{-1}$, 300–400 cm$^{-1}$ for the INTERFACE potential; however, for the confined water in tobermorite crystals (11 and 14 Å) merged peaks are observed in between these two wavenumber peak regions.

Apart from the observance of absorption peaks, hydrogen bond lifetime is estimated for confined water in tobermorite 11 Å and tobermorite 14 Å. It can be quite expected that the lifetime would be significantly different compared to that of bulk water for this ultraconfined water that is also engaged in solvation of cations and anions within the tobermorite structure. Existence of hydrogen bonds depends on certain factors like distance between the donor and the acceptor oxygen atoms ($R_{OH}$), distance between hydrogen and acceptor oxygen atoms ($R_{OHO}$), and the angle subtended by the hydrogen and the acceptor oxygen atoms at the donor oxygen atom ($\phi_{OHH}$). The hydrogen bond is likely to exist if $R_{OH} \leq 2.5$, $R_{HOO} \leq 2.45$ and $\phi_{OHH} \leq 30^\circ$. The above stated criterion has been adopted from the literature.$^{53,54}$ The lifetime of the hydrogen bond formed between the water molecules is evaluated in two different manners, $S_{HB}$ and $C_{HB}$. Here, $S_{HB}$ indicates the actual lifetime of continuously existing hydrogen bonds (without considering breaking and reformation) while $C_{HB}$ provides the overall lifetime, which includes breaking and reformation of hydrogen bonds.

$$f(t) = \begin{cases} 1 & \text{if the H-bond exists at time } t \\ 0 & \text{else} \end{cases}$$

(4)

$$g(t) = \begin{cases} 1 & \text{if the H-bond continuously exists from 0 to time } t \\ 0 & \text{else} \end{cases}$$

(5)

$C_{HB}(t)$ and $S_{HB}(t)$ are then defined as

$$C_{HB}(t) = \frac{\langle f(t)f(t+t) \rangle}{\langle f(t) \rangle}$$

(6)

$$S_{HB}(t) = \frac{\langle f(t)g(t+t) \rangle}{\langle f(t) \rangle}$$

(7)

Both continuous ($S_{HB}$) and intermittent ($C_{HB}$) hydrogen bond lifetimes show an identical pattern for bulk water, and confined water in tobermorite 11 Å and tobermorite 14 Å (refer Fig. 6). Confined water in tobermorite demonstrates a more stable hydrogen bond lifetime compared to that of bulk water. It should be realized that this stability in hydrogen bond lifetime is not only because of the confinement but also due to the solvation of ions by confined water (which eventually restrains the motion of the water molecules). Since confined
water in tobermorite 14 Å is able to form more coordinate covalent bonds with both cations and anions, the stability of the hydrogen bonds of confined water in the tobermorite 14 Å structure is more than that in the tobermorite 11 Å structure.

Discussion

It can be observed that the breaking of hydrogen bonds of water molecules to form coordinate covalent bonds with the cations and anions of the tobermorite structure is different for the tobermorite 11 Å and 14 Å structures. Based on the position of the water molecules and associated cations or anions, a schematic can be presented with regards to the solvation of these ions with the confined water molecules. Fig. 7a demonstrates a schematic representation of solvation in the tobermorite 11 Å structure in which water molecules are only accessible by the silicate chains. Fig. 7b represents a schematic representation of solvation of the tobermorite 14 Å structure in which the water molecules are accessible to the Ca²⁺ ions. It should be noted that in the tobermorite 14 Å structure, there is also a possibility of solvation of silicate chains as in tobermorite 11 Å.

Conclusion

The primary difference in the molecular structure of tobermorite 9 Å, 11 Å and 14 Å is in the presence of confined interlayer water molecules, which engage in the solvation of cations and anions in the tobermorite structures. The presence of these water molecules eventually results in changes in the mechanical response of these structures in uniaxial tension and compression. It should be noted that ionization of water molecules (as postulated in a previous study) is not realistic since it requires a significant amount of energy to break the covalent bond of water; instead, the hydrogen bond of water can be broken much more easily resulting in solvation of cations and anions within the tobermorite structure. These confined water molecules also engaged in solvation of cations and anions of the tobermorite structure demonstrate differences in intermolecular vibrational spectra as well as hydrogen bond lifetimes. It is observed that the confined water in tobermorites has much more stable hydrogen bonds than bulk water.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


