Morphology of calcium silicate hydrate (C-S-H) gel: a molecular dynamic study

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Due to its complexity at nanoscale, calcium silicate hydrate (C-S-H), the dominant binding phase in cement hydrates, is not yet completely understood. In this study, molecular dynamics was employed to simulate the hydration products at low and high calcium/silicon ratios. It was found that two morphologies of calcium silicate hydrate gels can be distinguished – a branched structure at low calcium/silicon ratios and an ellipsoid particle structure at high calcium/silicon ratios. Using virtual X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) techniques, the simulated structures were characterised, confirming that they show features of calcium silicate hydrate as revealed by experimental approaches. The short-range structures of calcium and silicon atoms and the distorted calcium tetrahedrons resemble the features of silicate glasses obtained from experiments, implying the amorphous nature of the local structure in calcium silicate hydrate gel. Furthermore, formation mechanisms for the two morphologies are proposed. In the hydration process, calcium ions play roles in depolymerising the silicate structure and preventing the amorphous network formation. Therefore, at low calcium/silicon ratios, the reaction is governed by silicate skeleton growth, but at high calcium/silicon ratio, aggregations of calcium ions and short silicate chains dominate.

Introduction

As cement material is so widely utilised all over the world, much research has been carried out on the intrinsic properties of cement paste (Li, 2011; Ma and Li, 2013; Ma et al., 2013). The shrinkage, creep and strength of cement pastes are significantly affected by the structure of calcium silicate hydrate (C-S-H) gel, which has thus been investigated and is regarded as an essential topic for cement-based materials. The multi-scale characteristics and complicated chemical composition of calcium silicate hydrate gel bring challenges in interpreting the morphology of the hydration product. At microscale, calcium silicate hydrate gels observed by scanning electron microscopy (SEM) do not distribute uniformly and exist in various morphologies, such as fibres, flakes, honeycombs and tightly assembled grains (Li, 2011). The diversity of the morphologies is caused by many factors, such as the water content, calcium/silicon ratio and hydration degree. High-resolution transmission electron microscopy (TEM) can distinguish the calcium silicate hydrate gel into inner products of foil morphology and outer products of a fibrillar structure (Groves, 1987). However, because calcium silicate hydrate gels cannot be directly observed at nanoscale, their molecular structure was only inferred by combining experimental and computational techniques.

Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) techniques have shown that the average calcium/silicon ratio of calcium silicate hydrate gel is 1.7 and its density is 2.6 g/cm³ (Allen et al., 2007). Based on these results and silicate chain information from nuclear magnetic resonance (NMR) testing (Cong and Kirkpatrick, 1996) and calcium silicate layer information from X-ray diffraction (XRD) tests, a realistic model of calcium silicate hydrate gel (Pellenq et al., 2009) was proposed with the assistance of molecular simulation. However, even though this realistic model can give a good interpretation on the atomic structures and mechanical properties of calcium silicate hydrate gel to within 1 nm, a gap still exists between the molecular scale and the microscale. Large-scale molecular simulation, constructing a colloid model from molecular level, could provide linkage between the two levels. Dolado et al. (2007, 2011) employed the silica formation reaction in the presence of calcium hydroxide (Ca(OH)₂) to simulate the cement hydration reaction. The simulation box included more than 60,000 atoms. A hydration product – a branched structure of size around 5 nm – was achieved after a 2.3 ns simulation and also identified with features of calcium silicate hydrate gels. It is noted, however, that because of simulation time limitations, the branch structure of calcium silicate hydrate may not be the final hydration product. In addition, when the...
Calcium/silicon ratio is 1.65, the single morphology cannot represent the colloid phases of calcium silicate hydrate gel at different calcium/silicon ratios.

In this work, to bridge the gap between calcium silicate hydrate gel at molecular level and microlevel, molecular dynamics was utilised to simulate the hydration process of more than 80,000 atoms within a 10 nm system. Calcium silicate hydrate phases with high and low calcium/silicon ratios of 1.75 and 1.00 were simulated to investigate the calcium/silicon influence on the morphology of the gel at mesoscale. Such simulation results can provide information on the dynamics and structural role of calcium and silicon in the hydration process. Hydration simulation can directly describe the colloid cluster formation mechanism, validating the theoretical and experimental models. The local structure of calcium and silicon, \( Q \) species evolution and cluster size development were analysed for a comprehensive prediction of the colloid structure of calcium silicate hydrate gel.

**Simulation methods**

**Reaction mechanism**

Cement hydration, the production process of calcium silicate hydrate gel, is based on the sol–gel reaction in the presence of calcium ions. The oligomerisation of silicate monomers follows the water-producing condensation reaction (Feuston and Garofalini, 1990)

\[
\text{Si(OH)}_4 + \text{Si(OH)}_4 \rightarrow (\text{HO})_3\text{SiOSi(OH)}_3 + \text{H}_2\text{O}
\]

As illustrated in Figure 1(a), the reaction leads to the linkage of silicic monomers to form a dimer structure and the dissociation of one water molecule. The polymerisation reaction produces a different silicate cluster. The different silicate products are defined as \( Q_n \), where \( n \) is the number of bridging oxygen atoms for an individual silicate tetrahedral and varies from 0 to 4. It is shown in Figure 1(b) that \( Q_n \) species represent different silicate structures – \( Q_0 \) is the isolated monomer, \( Q_1 \) and \( Q_2 \) are chains, and \( Q_3 \) and \( Q_4 \) reflect the interconnected structures.

**Potential model and simulation procedures**

The Feuston–Garofalini (FG) model, developed for the silica system (Feuston and Garofalini, 1990), was used for the current sol–gel reaction. The model contains three interaction potentials: the Born–Mayer–Huggins (BMH) potential, the Stillinger–Weber (SW) potential and the Rahman–Stillinger–Lemberg (RSL2) potential. The interaction among calcium (Ca) and silicon (Si), oxygen (O) and hydrogen (H) can be achieved from a previous study about calcium silicate hydrate (I) phases (Faucon et al., 1996).

Molecular dynamics simulations were performed using the Lammps package (Lammps, 2008) to study the calcium silicate cluster evolution at calcium/silicon ratios of 1.75 and 1.00. The initial configuration was obtained by adding silicic acid (\( \text{Si(OH)}_4 \)), calcium hydroxide (\( \text{Ca(OH)}_2 \)) and water (\( \text{H}_2\text{O} \)) molecules randomly in a box of size \( 10 \times 10 \times 10 \) nm to achieve an overall density of about 1.2 g/cm\(^3\). Detailed information of the simulation system is given in Table 1. It should be noted that around 100,000 atoms can provide stable and accurate statistical results.

These initial configurations were relaxed at 300 K for 100 ps to let the atoms diffuse to random positions. In order to increase the reaction rate, the system was heated for 100 ps, linearly increasing the temperature to 1800 K. The reactions were implemented at 1800 K for 10,000 ps, followed by a linearly decreasing temperature to 300 K for 1000 ps. Finally, the systems were maintained at temperature (1800–2500 K) simulation environment is normally preferred to accelerate the reaction rate (Dolado et al., 2007; Garofalini and Martin, 1994). In the current simulation, 1800 K was adopted as the simulation condition.
300 K and further equilibrated for 50 ps before a long production run for 500 ps. Atom coordination information was recorded every 1 ps for later analysis. A time step of $1 \times 10^{-3}$ ps was utilised.

**Results and discussion**

**Calcium silicate hydrate morphology**

During around 10 ns sol–gel reaction time in solution, calcium silicate clusters with different morphologies are segregated from the water solution. As shown in Figure 2(a), at a low calcium/silicon ratio of 1.00, the calcium silicate cluster grows across the simulation box with a branch size larger than 3.5 nm. More interestingly, the network phase, growing in radiated style, demonstrates amorphous features similar to the silica glass achieved from a sol–gel reaction (Feuston and Garofalini, 1990).

On the other hand, the cluster with a calcium/silicon ratio of 1.75 nucleates and develops into an ellipsoid particle with a diameter of approximately 5 nm, as shown in Figure 2(b). Due to the long simulation time, the hydration degree is supposed to be higher than that reported by Dolado et al. (2011), which can transform the structure to an egg-like particle. Compared with the amorphous network structure, the hydration product at the high calcium/silicon ratio demonstrates a more ordered state. In the current simulation, the egg-like phase and network phase indicate that the composition of the calcium silicate hydrate gel, especially the calcium/silicon ratio, is an important factor influencing the morphologies of calcium silicate hydrate gel at the nanoscale.

The simulated morphologies can give some theoretical understanding of microscale observations. The gel structure of cement hydrate has been investigated by TEM at microscale. Two types of calcium silicate hydrate phases can also be observed on TEM photographs at the scale of around 100 nm (Groves, 1987). It is widely accepted and experimentally confirmed that the inner product (IPs) and outer product (OPs) are distinguished in accordance with the density and geometry morphology (Richardson and Groves, 1993). As shown in Figure 3, the IP is aggregated by small globule particles packed in a relatively dense state with a maximum pore size of less than 10 nm. On the contrary, the OP has a fibril structure, with a large length/width ratio and large pores between the fibril structures. Microanalysis of cement hydrate composition has demonstrated that the calcium/silicon ratio of the IPs is larger than that of the OPs (Richardson, 2004). According to the simulation results presented in this study, ellipsoid particles with a high calcium/silicon ratio are more likely to assemble together to construct the high-density phase, while the network structure with a low calcium/silicon ratio may transform into the loose fibril morphology. Furthermore, Figures 3(b), 3(c) and 3(d) show the morphologies of...
synthesised gel at calcium/silicon ratios of 0.66, 1.50 and 2.00 respectively (Sasaki et al., 1996; Viallis-Terrisse et al., 2001). It can thus be concluded that, with increasing calcium/silicon ratios, the calcium silicate hydrate gel changes from a loose fibril-like morphology to dense granular-like particles.

At a calcium/silicon ratio of 1.75, quite close to the average value of the calcium silicate hydrate gel, the simulated colloid particle with a diameter of around 5 nm matches well with the globule particle proposed by Jennings (2000, 2008) and predicted from SANS (Allen et al., 2007). To further study the properties of the simulated gels, the clusters were characterised with results from various virtual experimental techniques.

Comparison with experimental data
Simulated SANS and XRD curves were produced to further identify the geometry and the crystalline arrangement of the hydrated products. As shown in Figure 4, the simulated scattering curve has a good agreement with that achieved from the SANS test. The slope of the curve changes from the region \(-2.51\) to \(-2.85\) to \(-3.83\) to \(-3.85\), when the scattering vector is between \(0.012\) nm\(^{-1}\) and \(0.016\) nm\(^{-1}\), corresponding to an average size of 5–8 nm. As shown in Figure 5, in the simulated diffraction curve, two XRD intensity peaks can be observed at \(-7^\circ\) and \(30^\circ\). The former corresponds to 1.0–1.4 nm spacing in the calcium silicate cluster. It should be noted that this peak is also present in the tobermorite and synthesised calcium silicate hydrate gels. The

![Figure 3. High-resolution TEM photograph for different morphologies of calcium silicate hydrate at microlevel: (a) inner product (IP) and outer product (OP) (Groves, 1987); (b) calcium/silicon ratio = 0.66 (Viallis-Terrisse et al., 2001); (c) calcium/silicon ratio = 1.50 (Viallis-Terrisse et al., 2001); (d) calcium/silicon ratio = 2.00 (Sasaki et al., 1996) ](image)
distance ranging from 0.9–1.4 nm is widely accepted as the interlayer space between calcium silicate sheets in calcium silicate hydrate analogues such as tobermorite and jennite (Hamid, 1981; Janika et al., 2001; Merlino et al., 2001). By identification with experimental results, it is confirmed that the simulated gels in this study follow the features of calcium silicate hydrate gels.

Glass nature of the calcium silicate hydrate gel

For bonded atoms, the relevant bond distances can be readily determined by the positions of the peaks in the corresponding radial distribution function (RDF). In calcium silicate hydrate gel systems, the Si–O bond distance shows a clear dependence on the calcium concentrations. Figure 6(a) shows the Si–O RDFs of calcium silicate hydrate gel with calcium/silicon ratios of 1:00 and 1:75. The position of the first peak shifts slightly from 0.162 nm to 0.160 nm as the calcium/silicon ratio increases from 0.1 nm to 0.175 nm. Note that the Si–O bond lengths resemble those in amorphous silica (i.e. 0.162 nm) (Cormack and Du, 2001; Du and Cormack, 2004; Mead and Mountjoy, 2006).

Two types of oxygen atoms are present in the calcium silicate hydrate gels, as shown in Figure 6(b). An oxygen atom that bridges two neighbouring silicon atoms is defined as a bridging oxygen atom (BO) and an oxygen atom that is bonded to only one silicon atom is defined as a non-bridging oxygen atom (NBO). Thus, the Si–O RDF can be further decomposed into Si–BO and Si–NBO RDFs, and the two components are plotted in Figure 6(b) for the case of calcium/silicon = 1:00. From Figure 6(b), a difference of 0.006–0.007 nm was observed between...
Si–BO and Si–NBO bond distances. Furthermore, due to the smaller shielding effect from the neighbouring silicon atoms, the NBOs may show more electronegativity than BOs. The presence of calcium atoms can depolymerise the silica networks by breaking Si–BO bonds and hence increase the number of Si–NBO bonds. Such an effect results in a decrease in the Si–O bond distance at a high calcium/silicon ratio.

Figure 7(a) shows the Ca–O RDFs obtained from simulations of the calcium silicate hydrate gel systems at calcium/silicon ratios of 1:00 and 1:75. For the calcium silicate hydrate gel with a calcium/silicon ratio of 1:00, the result shows that the Ca–O bond distance is between 0.236 and 0.242 nm. Previous experimental studies of calcium metasilicate (CaSiO$_3$) glass using XRD, extended X-ray absorption fine structure (EXAFS) and neutron diffraction (Mastelaro et al., 2000; Taniguchi et al., 1997) showed a value between 0.236 and 0.249 nm. This implies that the local environment of calcium atoms in calcium silicate hydrate gel is quite close to that in the amorphous silicate glass.

Two peaks located at approximately 0.24 nm and 0.3 nm were found in both of the Ca–O RDFS. It is instructive to further decompose each Ca–O RDF into Ca–NBO and Ca–BO parts. As shown in Figure 7(b) for the case calcium/silicon = 1:75, the NBOs contribute to the first peak and BOs to the second (much smaller) peak. Thus, the Ca–NBO and Ca–BO distances are 0.24 nm and 0.3 nm respectively.

Cluster formation mechanism
The local structure of the simulated calcium silicate hydrate gel has been discussed and shows the nature of calcium silicate glass in short-range order. In this section, the long-range order will be further investigated by discussing cluster development and Q species evolution at low and high calcium/silicon ratios respectively.

Cluster development at low calcium/silicon ratio
At a low calcium/silicon ratio, cluster evolution demonstrates the polymerisation process of silicic acid in the presence of calcium atoms. The silicon cluster is defined as those silicon atoms connected together by BOs and the minimum cluster is a dimer. Cluster evolution is characterised by a maximum cluster size and cluster numbers, which can be calculated by a recursive algorithm proposed in previous simulation (Rao and Gelb, 2004).

Three obvious stages – initial small cluster formation, cluster–cluster aggregation and large cluster densification – construct the whole process of hydration. In the initial stage, a dimer structure first forms and small chains randomly distribute in the water box, isolated by calcium atoms and water molecules. As shown in Figure 8(b), the number of small structures, dimers or long chains, widely increases in this period and reaches the peak value in the cluster number evolution (Figure 8(a)). Maximum cluster development has a low growth rate in this period because dimer formation is the dominant reaction and connections between different isolated silicate polymers have not widely occurred. The second period starts at around 1.3 ns and the cluster growth rate suddenly changes in the maximum cluster curve. During the cluster–cluster aggregate period, small clusters begin to aggregate with neighbouring ones and combine to form large clusters. Small clusters further aggregate and the density of the silicon clusters continues to increase. As shown in Figure 8(c), small clusters collide with nearby ones and the connection reaction between different clusters occurs widely. This leads to a rapid decrease in cluster number and an increase in maximum cluster size. At the beginning of the third stage, a newly formed large cluster size remains unchanged for more than 3 ns. This equilibrium period is also when the cluster transforms into energy preferable structures. Afterwards, the size of the large cluster continues to increase. Additionally, water molecules dissociating from the sol–gel reaction dissolve in the solution. Phase separation between calcium silicate clusters and water clusters can be observed in the final stage. Finally, a calcium silicate branch with a diameter of 3.5 nm is formed in the water environment, as illustrated in Figure 8(d).
Cluster evolution at high calcium/silicon ratio
As shown earlier, cluster development at a low calcium/silicon ratio is based on silicate chain skeleton growth resulting from the sol–gel reaction. With increasing calcium concentrations, the silicate chains are broken into short segments. At a high calcium/silicon ratio, cluster evolution is based on a different mechanism. Calcium atoms, associating with the NBOs in the silicon tetrahedral, play a role in bridging the isolated silicate polymer structure and construct the Si–Ca cluster. Due to the high diffusion rate, calcium atoms can bridge with NBO atoms quickly and, at the very beginning, small Si–O–Ca clusters form (Figure 9(a)). Meanwhile, in the local silicon-rich region, silicate chains can grow by the polymerisation reaction in a relatively slow mode. Therefore, the structure of the calcium silicate hydrate gel depends on the competition between the sol–gel reaction and the NBO–Ca association.

More than 95% of the Si–Ca aggregations finish within 3 ns, which is far quicker than the sol–gel cluster formation at low calcium concentrations. Silicate chains and calcium atoms initially nucleate into small clusters that are attributed to both sol–gel reaction and Ca–NBO association. Due to the large surface energy of the nanoscale colloid in water solution, unstable small
clusters, with a high kinetic potential, collide with their neighbours and merge together. In the merging period, branch structures are able to be produced, as shown in Figure 9(b). Such structures have also been observed by Dolado et al. (2011). However, a branch involving a large percentage of calcium and silicon in the system is just a temporary structure in the middle period of hydration. Because the network constructed by the Ca–NBO–Si bonds is much weaker than a skeleton consisting of...
Si–BO–Si bonds (Shahsavari et al., 2009) at low calcium/silicon ratios, the branch-like structure is likely to transform to a more stable morphology with a larger colloid size (Figure 9(c)). The continuous interaction between water and Ca–Si clusters can finally result in densification of the calcium silicate hydrate gel structures that are energetically stable ellipsoid particles (as shown in Figure 9(d)).

After 10 ns equilibrium time, the morphology of the calcium silicate hydrate gel at both high and low calcium/silicon ratio remained unchanged in the current simulation. However, it is worth noting that extending the simulation time can further enhance the hydration degree. Considering the periodic conditions of the simulation box, in a longer simulation run, for the low calcium/silicon ratio case, the network of the calcium silicate hydrate gel can grow into the fibril-like structure in a radiative manner. On the contrary, at high Ca/Si ratio, for a longer simulation run, isolated calcium silicate hydrate ellipsoids can aggregate together to form a relatively dense packing morphology.

The cluster formation mechanism for the calcium silicate hydrate gel also provides a molecular insight into curing conditions such as the temperature and the introduction of the mineral admixtures. The sol–gel reaction is based on the dimerisation reaction between silicate monomers and elevating the temperature can help accelerate the hydration degree. On the one hand, high temperatures help overcome the reaction energy barrier so that the monomers can de-proton and associate with each other more easily and, on the other, the mobility of the atoms is increased at high temperature so that they collide with each other more often and accelerate the reaction rate. NMR studies have also shown that a high curing temperature can enhance the polymerisation degree in calcium silicate hydrate gel (Brough et al., 1994).

Mineral admixtures also have a great influence on the morphology of calcium silicate hydrate gel. For example, adding silica fume to cement can introduce many silicate phases to the hydration process, reducing the calcium/silicon ratio. At a lower calcium/silicon ratio, the morphology of calcium silicate hydrate gel is based on silicate skeleton growth and a network structure is more likely to form. Other mineral phases can result in alumina and sodium atoms in the hydration products, which might have an influence on network formation. In future work, other ions in cement, such as Al\(^{3+}\) and Na\(^{+}\), will be added to the simulation system to explore their influence on the structure of hydration products at nanoscale.

**Connectivity factor Q evolutions**

Previous cluster analysis gives insights about the calcium silicate hydrate gel growth in respect of colloid development. In order to better interpret the change of intrinsic molecular structures, Q species evolution should be taken into consideration (Feuston and Garofalini, 1988). As shown in Figure 10, the Q\(_0\) species decreases monotonically and the growth rates of Q\(_1\) and Q\(_2\) are larger than those of Q\(_3\) and Q\(_4\). The evolution process indicates that the sol–gel reaction is the structural transformation from monomers to silicate chains, cross-linkage structures or networks.

The main difference in Q species between the high calcium/silicon phase and the low calcium/silicon phase is the percentage of Q\(_4\) species. At a low calcium/silicon ratio, Q\(_4\) species take up more than 30% of the whole gel, indicating that the long chain structures can interconnect with each other, which is similar to connected silicate chains in the tobermorite model of Merlino et al. (2001). Nevertheless, at a high calcium concentration, the network structure (Q\(_4\)) and the cross-branched structure (Q\(_3\)) almost disappear. The discrepancy in Q species composition mainly results from the de-polymerisation role of calcium atoms. On the one hand, to connect with a neighbouring silicate structure, silicate monomers have to compete with calcium atoms. However, as proposed in a previous calcium silicate glass simulation (Mead and Mountjoy, 2006), NBOs energetically prefer to connect the calcium atoms. Consequently, adding more calcium contributes to more Si–O–Ca bonds and decreases the amount of Si–O–Si bonds. On the other hand, with respect to dynamics, calcium atoms slow down the diffusion of silicon.
atoms. Thus, compared with calcium atoms, the restricted silicon atoms have less probability of colliding with nearby NBOs.

It should be noted that $Q_3$ and $Q_4$ species are the main structural discrepancy between the calcium silicate hydrate morphology at low and high calcium/silicon ratios. $Q_1$ and $Q_2$ species also have a great influence on the mechanical performance of the calcium silicate hydrate gel. A previous ab initio calculation (Shahsavari et al., 2009) showed that the presence of $Q_3$ species can improve the interlayer stiffness of tobermorite, a mineral analogue of calcium silicate hydrate gel (Merlino et al., 2001), by forming a hinge mechanism. The skeleton role of the silicate structure is based on the percentage of $Q_3$, and the binding energy of Si–O bonds is larger than that of Ca–O bonds. Therefore, the absence of $Q_3$ and $Q_4$ species in a composite with a high calcium concentration weakens the mechanical properties of the structure.

The mean chain length, $2(Q_1 + Q_2 + Q_3)/Q_1$, is an important structural factor used to estimate the connectivity of the silicate chains (Chen et al., 2004). Figure 11 shows that the mean silicate chain length decreases with increasing calcium/silicon ratio. The chain length in the simulated system is consistent with the trend as revealed in experiments, implying that the simulated calcium silicate hydrate gel can describe the inner silicate structure well.

The silicate chain length evolution as a function of calcium/silicon ratio is an important characteristic for the calcium silicate hydrate gel. Generally, nanostructure development depends mainly on the silicate skeleton evolution. At a low calcium/silicon ratio, cluster evolution is based on the growth of the silicate chains. Calcium atoms fill the cavities in the silicate deficient parts and do not influence the skeleton extension to network or branch structures. On the other hand, at a high calcium/silicon ratio, the cluster aggregation process results from the associations of calcium ions and isolated silicate composites. In this respect, a high calcium concentration prefers to form the crystalline calcium silicate hydrate phase, while a silicon-rich cluster favours amorphous gels. Therefore, from a low to a high calcium/silicon ratio, the morphology of the calcium silicate hydrate gel gradually transforms from an amorphous network structure to an ordered ellipsoid-like structure.

According to the previous discussion, the morphology of calcium silicate hydrate gel at nanoscale can be generally described. The molecular mechanism for cluster formation produces some ideas of how to optimise the structure of calcium silicate hydrate gel at nanoscale. At a low calcium/silicon ratio, even though the silicate skeleton, including $Q_1$ and $Q_4$ species, improves the stiffness of the structure to some extent, the fibril morphology, characterised by large nanoporosity, weakens its mechanical behaviour. On the contrary, despite no $Q_3$ species, the relatively dense and ordered morphology of calcium silicate hydrate gel at a high calcium/silicon ratio, with a low porosity, can maintain cohesive forces at a high level. Therefore, an ‘optimum’ nanostructure should attempt to reduce the nanoporosity and increase the percentage of $Q_3$ and $Q_4$ species. To obtain an ‘optimum morphology’, an appropriate calcium/silicon ratio, hydration temperature and the introduction of mineral admixtures should be comprehensively considered.

**Conclusion**

Two types of calcium silicate hydrate phases at the mesoscale – a branch structure and an ellipsoid particle structure – were produced by a molecular dynamics simulation. The discrepancy in morphology is mainly a result of the calcium/silicon ratio. The simulated high calcium/silicon ratio and low calcium/silicon ratio phases are quite similar to the inner and outer products respectively. In particular, it is valuable to note that the ellipsoid particle of around 5 nm size is consistent with Jennings’ model (Jennings, 2000, 2008) and SANS results (Allen et al., 2007). The simulation constructs a bridge between molecular and colloid morphologies and gives physical insights into the formation of colloid particles in the cement hydration process. Further density, composition, XRD and SANS tests confirm that the structural features of the simulated calcium silicate hydrate gels match the experimental results well. For the local structure, the bond length distributions of Si–O and Ca–O imply short-range disorder of the covalent and ionic connections inside the calcium silicate hydrate gel. The defective silicate network and distorted Ca–O octahedrons in the simulated calcium silicate hydrate gels resemble the amorphous nature of silicate glass.

In order to understand the hydration mechanisms of the two calcium silicate hydrate phases, the calcium silicate hydrate gel evolution was analysed in terms of cluster growth and $Q$ species evolution. At a calcium/silicon ratio of 1:00, calcium silicate hydrate gel growth is based on the silicate skeleton growth, which is more likely to form an amorphous network and extends in a radiative mode. On the contrary, at a calcium/silicon ratio...
of 1.75, calcium atoms de-polymerise the network formation of the silicate structures and the branch structure ($Q_3$) is not likely to form. The cluster nucleates to an ellipsoid structure. Calcium and silicon influence the cluster morphologies in different ways: the former contributes to an ordered structure while the latter increases the amorphous state of the structure. Furthermore, a wide range of calcium/silicon ratios should be taken into consideration to observe morphology evolution; this study is currently ongoing. Other ions rich in cement (e.g. Al$^{3+}$ and Na$^+$) will also be added to the simulation system to explore their influence on the structure of hydration products at mesoscale.

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