

A Brownian Dynamic study on the formation of cementitious Calcium-Silicate-Hydrate (C-S-H) nanostructure

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The Calcium Silicate Hydrate (C-S-H) gel is the most important hydration product present in cementitious materials. Thanks to recent advanced nanoindentation experiments [1,2], there is now evidence that in terms of its mechanical properties the C-S-H gel can present itself either in a low stiffness and Low Density variety (called LD C-S-H gel) or in a variety with a high stiffness and High Density (called HD C-S-H gel). This dissimilar bearing capacity is indeed much more pronounced in their resistance to osteoporosis-like degradation processes. Along their life-service, cementitious materials, akin to human bones, may lose calcium (the so called calcium leaching). This is a slow and long-term process, but it leads to a significant loss of strength/stiffness and impermeability, reduces the concrete's capacity to passivate the steel and ultimately causes the material to become significantly stress sensitive, which may eventually impair the structural integrity.

The existence of two dissimilar varieties of C-S-H gel fits well with the current colloidal conception of the C-S-H gel, i.e. the Jennings model (see figure) [3,4]. According to this model ~5nm sized globular Basic Building Blocks (BBB) exist and pack themselves together to form LD and HD C-S-H forms depending on ad-hoc packing factors (see figure 1). Although this ad-hoc model has rationalized much of the information available at this scale it is clear that this description is an oversimplification. In fact, several nagging questions persist. On the one hand, numerous TEM and SEM analysis have shown that C-S-H gel effectively presents itself in two varieties, but not in globular ones. It is usual for TEM microscopists to differentiate between the morphologies close to the cement grains (called Inner Product) with respect to those found in the outer free space (called Outer Product (OP)) (figure 2)[5]. As can be seen from the annexed figure the Inner product (IP) turns to be dense and made of tiny globular-like particles, whereas the Outer Product is loose (or at least looser than the IP) and made of strands of aligned particles. These dissimilar morphologies can not be easily accounted for by the Jennings model. On the other hand, the Jennings model neglects the underlying chemistry by assuming a granular nature for the assemblage of C-S-H particles. Under this assumption the aggregation of the basic C-S-H particles (or BBBs) is merely described as coming from isotropic Hard Sphere (HS) aggregations [6,7]. It is clear that OP morphologies can not be explained in such terms. By the contrary, it is fair to assume that they require both directional long-range interactions to "align" the particles and short range forces to bond the particles.

In this scenario, the employment of computational means to describe the aggregation of nanoparticles is appealing. Aggregating systems can be considered from two different viewpoints. Either we speak of concentration fluctuations of individual particles governed by inter-particle forces derived from a potential (MD simulation) or we speak of aggregates, which form and break-up continuously i.e. the approach developed in BCD simulations. Both techniques are strictly equivalent but the main advantage of BCD simulations is that they are able to monitor the kinetics, the dynamics and the statics over longer time and for bigger systems compared with classical MD simulations. In this study we have studied the relaxation of the system by cooperative cluster motion and also the effect and bond rigidity. With our computational scheme we have monitored gel formation, phase separation, glass formation, crystallization, etc.. It is clear that this computational framework can help us to achieve a better understanding of the colloidal behavior of the C-S-H nanoparticles. This knowledge might allow us in a future to control the aggregation in order to improve the cohesion in cementitious materials.

References

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Figures

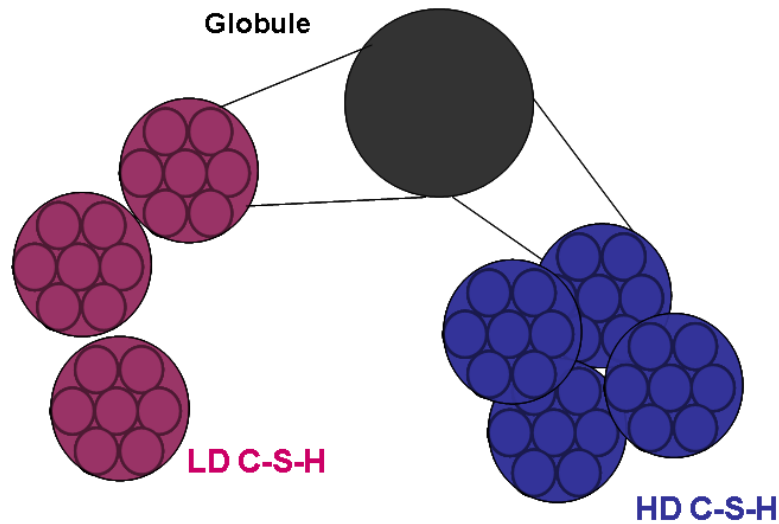


Figure 1: Schematic representation of the colloidal model I of Jennings

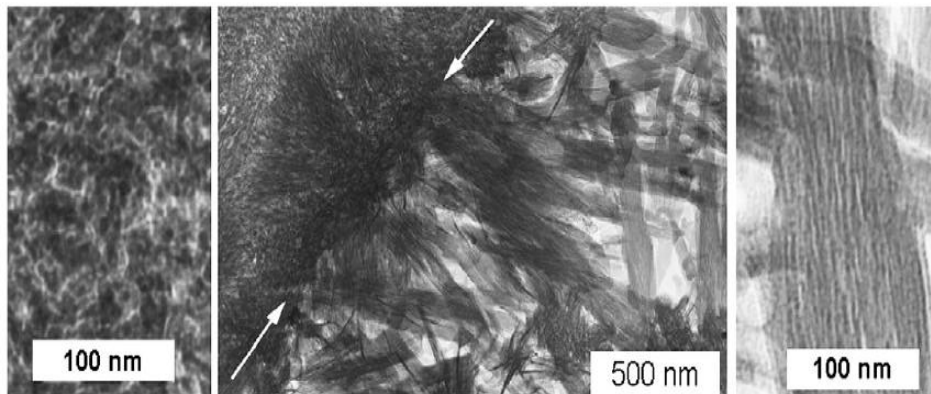


Figure 2: TEM picture of the structure of the C-S-H gel .On the left the inner product and on the right the outer product. [5]