C-S-H GLOBULE CLUSTERING ON NANO-SCALE SIMULATED BY THE DISCRETE ELEMENT METHOD FOR PORE STRUCTURE EXPLORATION

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Introduction
The pore structure of cement-based materials plays an important role in understanding the transport phenomena that are usually connected to the durability performance of these materials [1]. To assess the pore structure of hydrated cement, several computer-based models have been developed to simulate the hydration process in the last few decades. The vector approach, used in HYMOSTRUC [2], SPACE [3], μic [4], “Extended Integrated Particle Kinetics Model” (XIPKM) [5] assumes cement grains to be spherical. In these models, the major reaction products (calcium silicate hydrate, C-S-H) are assumed to partly replace hydrated grains (CSH-in) and the rest precipitate evenly on the surface of cement particles (CSH-out). As the volume of the reaction products exceeds that of the reactants, particles grow in size outwards and invade pore space as hydration progresses in time. However, pore size distribution, porosity of hydrated cement evaluated using the double random multiple tree structuring (DRaMuTS) method developed by Le [6] leads to an overestimation of several orders of magnitude compared to experimental data.

To determine the influencing factors which affect porosity estimation, Scrivener [7] investigated the effect of particle shape, flocculation, nucleating clusters and surface roughness on the pore-sizes in the simulated microstructure. Although most parameters considered by Scrivener have some effect on the simulations, the surface roughness is the one with the most significant influence. It is explained that the structure of C-S-H is actually very porous and non-homogenous itself, hence there is not a distinct boundary of C-S-H precipitated onto the particles’ surface and pore space.

Modelling of C-S-H
Based on scattering measurements and sorption isotherms experiments, Jennings developed a colloidal model-II (CM-II) [8] by introducing the concept of non-spherical globules, as schematically shown in Figure 1, which is closer to a realistic situation compared to CM-I [9] earlier. As a consequence, nano-pores exist in the gel-like structure in contrast to homogenous substance currently accepted. On the basis of Jennings’ model, many researches have been carried out in past decade. A multi-technique investigation performed by Constantinides and Ulm [10] suggests the existence of two C-S-H structures with different characteristic values of the indentation modulus under different cured temperatures. These two types of C-S-H are classified as low-density (LD) and high-density (HD) according to different packing densities (around 64% and 74%), which correspond to the CSH-out and CSH-in in the precipitation model, respectively (as shown in Figure 2). Similar to the precipitation model, LD C-S-H is assumed to grow outwards, while HD C-S-H grows in an opposite direction. So far, the authors just concentrated on CSH-out, which is more porous, CSH-in is assumed to be nonporous. Its deposition during hydration is assumed to leave the volume of the hydrating particle unchanged. Only tricalcium silicate (C₃S) as the most important cement compound is considered so far. Hydration neither involves the globules to grow in size on the hydrating surface nor in free space. Instead, they are increasing in numbers invading the available space until the reaction between grains and water terminates. However, there may be a slight structural difference in CSH-out close to a cement grain and further away in pore space. Anyhow, the relatively large pores detected in the current approach will be subdivided into smaller ones, and the pore network can be expected more realistic.

A rough estimation is made to determine the number of globules necessary for representing the structure of LD C-S-H properly. According to Bentz’s [11], the chemical equilibrium reaction during hydration can be expressed in relative volume ratios of water and hydration products to reactants by:

\[ 1.0V_{\text{CS}} + 1.34V_H \rightleftharpoons 1.521V_{\text{CS}} + 0.610V_{\text{CH}} \]  \hspace{1cm} (1)

Considering that a diameter range of Portland cement grains employed in simulations is usually 3-30 μm, 10 μm is selected for evaluating roughly the total number of globules. Hundreds of millions of nano-particles would be required to represent CSH-out during hydration simulation. Obviously, this approach is not feasible for the hydrated system containing thousands or even more grains.
To overcome this limitation, another assumption is made. Instead of packing the entire available pore space with LD C-S-H nanoparticles, only a representative volume element (RVE) shown in Figure 3 is selected, which should be large enough to represent the whole system. Although the RVE selected has not a regular shape, it can be considered as a box when the included angle α is small enough. The globules are added continuously into the RVE to reach the required packing density as hydration continues. As C₃S dissolves and reacts with free water, globules probably nucleate at the place near the cement grains’ surface at first and then spread to the pore space further away. This means that a density gradient may develop in the LD C-S-H system. In general, the packing density decreases as the distance from grain surface increases, as illustrated in Figure 3.

Fig. 1: a) CM-II proposed by Jennings, taken from Ref. [8]; b) Illustration of globule in CM-II.

**CM-II**: colloidal model-II.

Particle packing in LD C-S-H on the nano-scale

The Discrete Element Method (DEM) has been proven an effective tool to investigate granular materials. Herewith, the advanced DEM system HADES will be employed to obtain the representative volume element of LD C-S-H by packing globules in the near future. HD C-S-H is neglected here by assuming that there are no pores in it, as a consequence, the original cement particle keeps unchangeable in volume during hydration. Although CM-II reveals that globules should be something like a brick or a disk, which has been further verified by Chiang [13] by small-angle neutron scattering, spherical particles with diameter 5 nm suggested by CM-I can still be chosen as a starting point. The main reason is that the overlap detection

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*Fig. 2: Hydration products represented by HD and LD C-S-H, the right image is taken from Ref. [12]*
between non-spherical particles becomes more complicated and will result in increased calculation efforts. As a result of hydration, the contact area of LD C-S-H between neighbouring grain surfaces should be considered when choosing a suitable RVE, as illustrated in Figure 4. LD C-S-H close to the grain surfaces (left part and right part) has higher density compared to the middle part. A new algorithm will be necessary to model such structure by DEM.

In the DEM model, the physical description of interparticle forces is an important factor when designing a new algorithm. Although the hydration mechanism is not fully understood at present, Wittmann’s research provides a possible solution to obtain a reasonable description of forces between particles in cement paste [14]. By assuming that hardened cement paste can be looked upon as a colloidal system for its large specific surface, Wittmann subdivided the total complex interaction into two attractive components, the Van der Waals forces and the capillary pressure, and two repulsive components, the double layer repulsion and the structural force. Alternatively, contact forces together with friction forces between colliding particles which are based on Hertz contact law can be employed in contrast to the structural force, which is still very difficult to identify mathematically. The gravity force can be ignored as it is too small to consider in the nanometer range. Specifically, contact forces including “static” elastic forces and “dynamic” viscous forces are calculated according to Hertz-Mindlin law [15]. As the most commonly used theory for describing the forces
in a colloidal system, DLVO-theory (Derjaguin-Landau-Verwey-Overbeek) is employed to represent Van der Waals forces and electric double-layer forces, see [16-17] for more details. For the last item, capillary forces can be calculated using Fisher’s approach [18], viscous forces caused by fluid (water) between particles are solved on the basis of the computational model developed by Adams [19] and Goldman [20]. It is expected that a realistic pore network can be simulated once a proper RVE of LD C-S-H is obtained.

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**REFERENCES:**


