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Study on the Structural Model of Calcium Silicate Hydrate based on Computer Simulation

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Abstract. Calcium Silicate Hydrate (C-S-H) is the main hydration product of Portland cement, it has an important impact on the properties of cement and causes a wide range of study. In recent years, superplasticizer, of which the main component is organic macromolecules, has become an important component in preparation for high performance concrete. Molecular dynamics simulation of cement hydration products were summarized, the simulation of hydration process of cement paste and the formation of microstructure were introduced and model of calcium silicate hydrate mixed with superplasticizer were studied in this paper.

Keywords: Calcium silicate hydrate(C-S-H), Molecular dynamics, Model, Computer simulation

1. Introduction

With high strength and high performance concrete materials technology are increasingly becoming one of the main directions, various engineering materials with excellent properties have played a great role in the development of national economy by adding a certain amount of organic molecules compounds to Portland cement[1,2]. On the other hand, material science research is undergoing a transition from macro to micro research, from equilibrium to non-equilibrium study, from qualitative to quantitative change. Current computer simulation technology has become the third key component to solve practical problems of materials science in addition to theory and experiment. Since Grudemo's[3] seminal work on the composition and structure of calcium silicate hydrate in the 50s of the last century, Taylor [4,5], Grutezk [6], Wieker [7], Viechland[8] and other scholars have conducted further studies and achieved fruitful research results. But until the mid-nineties of the last century, have scholars [9,10] conducted a preliminary study on computer simulation of its structure (at atomic level), and there were no followed results found in the report. Combined with development trend of cement concrete technology and materials science, it is of great significance for the technology development of cement and concrete to carry out studies on impact of organic macromolecules on the structure of calcium silicate hydrate and simulate the structure of calcium silicate hydrate using computer simulation technology.

2. Application of Computer Simulation in Researches on Cement-based Materials

Computer simulation is of great significance in study of modern materials, it can not only compare and verify the calculated conclusions with the conclusions of theoretical calculation and experimental results to discuss the nature of the problem, but also can divide up factors whose causal relationships can not be

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identified in the experiment into individual factors and then look for regulars. According to the characteristics of simulation, simulated/model can be divided into different types, which are shown in Table1.

Table 1: The category of simulation/models according to their characteristics

Basis of the classification	The category of models
Spatial scale	Macroscopic, mesoscopic, microscopic, nanoscopic
Space latitude	One-dimensional, two-dimensional, three-dimensional
Spatial dispersion	Continuum, atomic theory
Predictive features	Deterministic, random, statistical
Descriptive characteristics	First principles, phenomenological, empirical
Path correlation	Dynamic, empirical

2.1. Introduction of Computer Simulation Method

The starting point of Molecular Dynamics (MD) system is the deterministic microscopic description of the physical system (position and velocity). It studies time and temperature dependent properties in the science system, so it can handle non-equilibrium problems. In recent years, the abinitio molecular dynamics and first principles molecular dynamics simulations combined with other calculation method occured. Under the variation of the unknown issues, Monte Carlo (MC) method establishes a statistical model which consistent with Boltzmann (Boltzmann) distribution to control particle motion according to the statistical laws of the physical phenomenon itself or random sequence generated by computer, then conducted a number of statistical tests in accordance with the model to make some statistical parameters the solution to questions [11]. Cellular Automata (CA) is a kind of grid dynamic model, in which time, space and states are discrete, spatial interaction and temporal causality are localized [12]. It has a direct inspection for local interactions and then achieves the overall behavior led by this effect by means of computer simulation and gets their configuration changes. So it's very suitable for dynamic simulation of complex systems.

2.2. Molecular Dynamics Simulation of Cement Hydration Products

The mid-90s of last century, Faucon [9, 10] simulated the structure of hydrated calcium silicate with the Ca/Si ratio between 0.66 and 0.83, he inputted Tobermorite structure of 0.9 nm found by Hamid, and simulated the cause of instability of structure of the calcium silicate hydrate, fracture mechanism silicate chain and the effect on structure after replacing silicon with cation (Al^{3+}) using isovolumic method molecular dynamics. The results show that: with the Ca/Si ratio increases, the bridge silicon-oxygen tetrahedron becomes unstable, but the chain will not break; if water molecules exist in the structure, the chain break between bridge silicon-oxygen tetrahedron and non-bridge silicon-oxygen tetrahedron and form two Q1, meanwhile water molecules are decomposed and are connected to the two new Q1 to ensure the four-coordination of silicon. If Al replaces silicate in bridge silicon-oxygen tetrahedron, the chain does not break up and replace, if Al replaces silicate in non-bridge silicon-oxygen tetrahedron in the participation of water molecules, the chain break between bridge silicon-oxygen tetrahedron and non-bridge silicon-oxygen tetrahedron.

2.3. Simulation of Hydration Process of Cement paste and the Formation of Microstructure

In the mid-80s of last century, Wittmann[13] conducted original work on two-dimensional numerical simulation of the structure and properties of concrete. They have built a simple model, and use the model to simulate the shape and distribution of aggregate. They then calculated thermal conductivity, elastic modulus and other physical properties of concrete using the finite element simulation. Subsequently, Jennings [14] completed three-dimensional model of hydration and formation of microstructure of C3S according to Jennings, and later developed a series of consecutive model, such as HYDRASM, HYMOSTRUC, DuCOM, SPACE and so on. In the nineties, combined with random walk algorithm, digital image and cellular automata model, the first generation of NIST (National Institute of Standard and Technology) hydration

model of cement paste--three-dimensional model of cement hydration and the structure (CEMHYD3D)[15] was generated, normally it was regarded as the typical representation of digital image-based model. Three-dimensional model of cement hydration and the structure is different from the continuous based model, it doesn't regard the spatial distribution of spherical cement particles in the reference elements as a starting point, but make the spatial distribution of pixels which represent the various phases of cement minerals as a starting point. A series of Cellular Automata rules are applied for the direct operation of pixels which express the micro-structure in simulation, so it studies the whole system at sub-particle level.

3. Structural Models of C-S-H

Calcium Silicate Hydrate is the main hydration product of Portland cement, the composition of cement has been an important part in scientific research, the main structure model of C-S-H are as follows.

3.1. Models of Tobermrite and Jennite

According to crystallographic characteristics and chemical measurement, calcium silicate hydrate can be divided into two phases: tobermrite-C-S-H (I) and jennite-C-S-H (II). Both of them are two-layer silicon-oxygen tetrahedron chain "clip" a layer of calcium oxide layer and the general formula of its ideal composition are Ca4(Si6O18H4)·2H2O (Ca/Si=0.66) and Ca8(Si6O18H4)·6H2O (Ca/Si=1.33). Taking into account of dehydration, two hydrogen lost in structure, in order to balance the charge, calcium would enter the layer, the general formula of the two mentioned above changed into Ca5(Si6O18H2)·8H2O (Ca/Si=0.83), and Ca9(Si6O18H2)·6H2O (Ca/Si=1.5). In both structures, the silicon-oxygen tetrahedron chain extended, and the two non-bridge oxygen silicon-oxygen tetrahedron which coordinate with calcium are located below, however, the third silicon-oxygen tetrahedron which connects the two silicon-oxygen tetrahedron is the bridge silicate-oxygen tetrahedron located above. As is shown in Figure 1, in tobermrite, two of the non-bridge oxygen in non-bridge silicon-oxygen tetrahedron coordinate with calcium, while only one non-bridge oxygen coordinate with calcium in jennite. Structures of C-S-H (I) and C-S-H (II) are similar to tobermrite and jennite, only some of the silicon-oxygen tetrahedron in the silicon-oxygen tetrahedron chain leaned or rotated, or even missing part of the bridge silicon-oxygen tetrahedron and resulted in multiple dimer, which is shown in Figure 1.

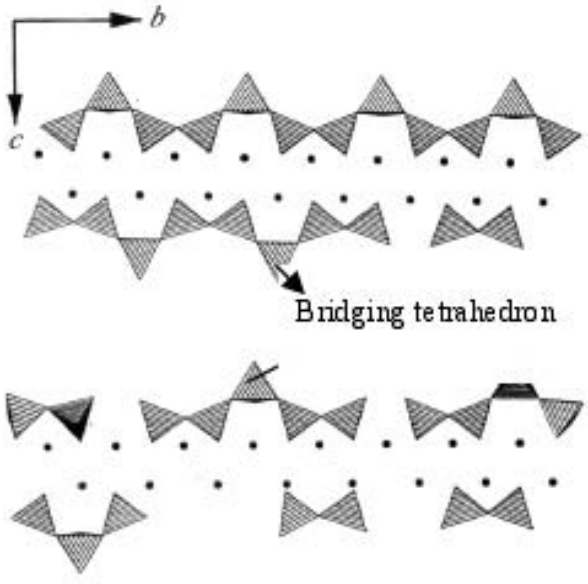

Fig. 1：Models of defect structural for C-S-H (· denotes CaO layers)

3.2. Models of Calcium-rich and Silicon-rich

According to Ca/Si ratio, C-S-H can be divided into silicon-rich C-S-H (Ca/Si=0.65~1.0) and calcium-rich C-S-H (Ca/Si=1.1~1.3). Tested by NMR analysis shows: in silicon- rich C-S-H ,Q1/Q2≈0.15±0.05, and is almost constant value, but there is no Q3, which indicates that silicon-oxygen tetrahedron long-chain exists in the structure, its structure is similar to 1.4nm tobermrite; In calcium-rich C-S-H, Q1/Q2 fluctuates between 1.0 to 1.5, it means that there exist approximately 50% dimer and 50% triple-repeat silicon-oxygen

tetrahedron chains and thus its structure is different from tobermrite and jennite, so we can infer that the structure of such calcium silicate hydrate is groups-like silicate structure, the general formula should be Ca4Si2O7(OH)·H2O.

3.3. Models of Solid Solution

The model maintains that CH dissolved in the C-S-H to form solid solution from the viewpoint of thermodynamics, a description of its structure tends to sandwich-like structure, which means tobermrite layer lies in the middle of CH layer.

3.4. Models of Intermediate Structure

The model maintains that in the range of 1.0~10 nm, C-S-H should have short-range order, nano-crystals and partial order structure. In the context of nano-crystals (less than 5 nm), composition of C-S-H is stable; in the context of short-range order (less than 1 nm), structure and composition of C-S-H are variable; as the amorphous form, composition of C-S-H changed greatly. Calcium silicate hydrate has a "sandwich"-like layered structure, that means a layer of calcium oxide is clipped in two layer of silicon-oxygen tetrahedron. Two kinds of inter action mechanism exist between C-S-H and the organic components: one is the role of physical and chemical surface (adsorption); the other is that the organic molecules intercalate into the layers, in this reaction additives consumption is greater than adsorption. According to intercalation reaction mechanism, organic molecules clip into C-S-H layer to form ion-typed cross-linked structure shown in Figure 2, which inevitably affects the specific surface area of C-S-H, and how it affects will depend on the arrangement of organic groups and the nature of inorganic metal ions on functional group. In general, effects of intercalation reaction on specific surface area are as follows: blocking hole effect (organic groups plug holes to reduce the specific surface area) and the open hole effect (macromolecules and hydrated metal ions distracted silicon-oxygen tetrahedron layer, two-dimensional porous network structure with micropore and mesopore formed in intercalation reaction to increase surface area).

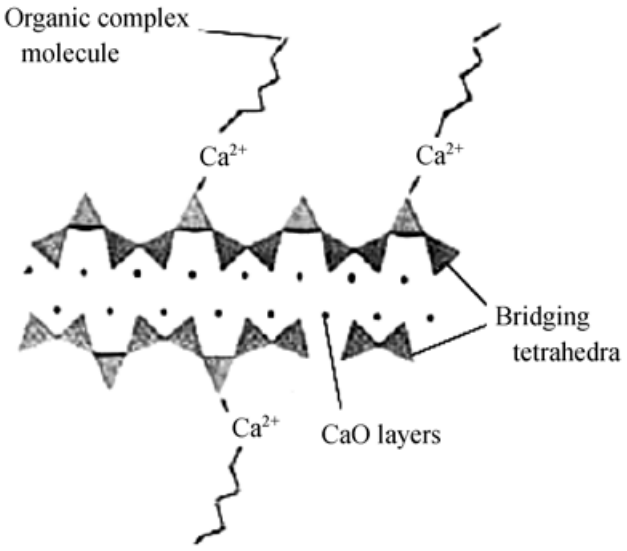

Fig. 2：Structure of C-S-H contained the organic molecule

4. Conclusions and Outlook

Computer simulation is of great significance in study of modern materials, it can not only compare and verify the calculated conclusions with the conclusions of theoretical calculation and experimental results to discuss the nature of the problem, but also can divide up factors whose causal relationships can not be identified in the experiment into individual factors and then look for regulars.

Cement paste, cement mortar and concrete, etc. is extremely complex whether in chemistry or structure. But rapid development of computer science and technology making the simulation of cement (or single-phase minerals) hydration and formation of paste microstructure increasingly become a reality. Calcium

Silicate Hydrate is the main hydration product of Portland cement, the composition of cement has been an important part in scientific research, the main structure model of C-S-H are as follows: models of tobermrite and jennite; models of calcium-rich and silicon-rich; models of solid solution and models of intermediate structure.

Combined with development trend of cement concrete technology and materials science, it is of great significance for the technology development of cement and concrete to carry out studies on impact of organic macromolecules on the structure of calcium silicate hydrate and simulate the structure of calcium silicate hydrate using computer simulation technology.

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