Molecular Dynamics Simulation on Structure and Characteristics of Cement Hydration Products

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***Abstract*—Structure and characteristics of cement hydration products were studied by means of molecular dynamics simulation. Stable structure of cement hydration products was obtained by using energy minimization theory, and layered structure which water filling in was in good agreement with the literature. Through simulation and calculation of the stability system, X-ray Diffraction (XRD) diagram, radial distribution function (RDF), the interatomic distances and coordination number were obtained. The results show that, the majority of cement hydration products are amorphous CSH gel. Molecular dynamics simulation provides new means for further study on the structure and characteristics of cement hydration products.**

***Index Terms*—cement hydration products; molecular dynamics simulation; radial distribution function**

I. INTRODUCTION

Properties of cement hydration products have important impact on its performance. However, the complexity of hydration, non-conformance of a large number of manual operation, non-comparability of test results, and the ambiguity of the inherent law have become barriers to study on cement hydration. Hydration is complex, heterogeneous, and heterogeneous chemical reaction [1], which requires us to use multi-level approach to simulate the microstructure of hydration products of cement-based materials [2].

In the mid-80s of last century, Wittmann [3] conducted original work of two-dimensional numerical simulation on the structure and properties of concrete. They established a simple model to simulate the shape and distribution of concrete aggregates, and used finite element analysis to calculate thermal conductivity, elastic modulus and other physical properties of concrete. Subsequently, Jennings [4] completed the establishment of three-dimensional model on C3S hydration and formation of microstructure. According to Jennings, HYDRASM, HYMOSTRUC [5,6], DuCOM, SPACE [7,8] were developed later. In the 90s, the first generation of NIST (National Institute of Standard and Technology) hydration model of cement paste--three-dimensional model of cement hydration and structure (CEMHYD3D) [9-12]was established through combination of random walk algorithm, digital image, and cellular automata model, it's typical representative of the digital image-based model.

Predecessors have done a lot of creative work on cement hydration, but cement hydration mechanism and structure of hydration products they didn't understand thoroughly. In recent years, as the continuous development of computer technology and the theory, molecular simulation has become the trend of study on cement hydration products, which made the researches on nanometer scale come true. Molecular dynamics simulation method is used in this paper to study the composition of cement hydration products, structural characteristics and microscopic structural information so as to obtain precise information on the cement hydration products.

II. EXPERIMENTAL

A. Simulation Experiment

Materials Studio software provided by Accelrys company was used. Universal force field was chosen, Amorphous Cell Tools module was used for establishment of the model, and energy minimization and simulated calculation were conducted. Energy minimization calculations were realized through different iterated steps, the steps until energy will not decrease were chosen as the steps for calculation of energy minimization. Long-range electrostatic interactions were calculated by method of Ewald sum, van der Waals effects was treated by atomic sum, and the cutoff radius of van der Waals forces was 12Å. According to three-dimensional periodic boundary conditions, simulation box was used repeatedly to simulate the macroscopic system in three directions.

The study models were established based on structure of amorphous calcium silicate hydrate [13]: the initial system is orthorhombic, a = 11.7 nm, b = 12.8 nm, c = 23.675nm, $\alpha = \beta = \gamma = 90^\circ$, c varies with water content in interlayer. In Amorphous Cell Tools module, the simulation system density is 2.45g/cm^3, which is in good

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agreement with the density of cement hydration products. Based on the chemical formula of cement hydration products, atoms were inputted according to the proportion, so that the atoms could fill in the unit cell freely and randomly, while the structure of the final stable system was obtained according to energy minimization. Calculations were conducted at 300K using NVT canonical ensemble and the NVE micro-canonical ensemble to census structure and dynamics information of the system. In the calculation, steps were 10,000, step length was 1fs, simulation time was 10ps, XRD, RDF and other structural characteristics were obtained and analyzed and was used to judge the correctness of the structure.

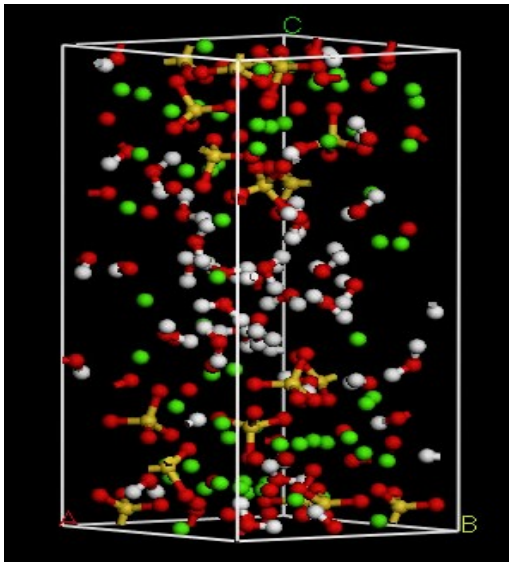

Fig1. The molecular model of cement hydration product:s the green spheres are calcium ions, respectively; yellow and red spheres are silicon and oxygen atoms in silica tetrahedral, respectively; the white spheres are hydrogen ions

B. Universal Force Field

Universal force field is for the molecular mechanics and dynamic simulation for the entire periodic table of elements, force field parameters are calculated based on element, the hybrid and chemical combination of elements, and combined with the charge balance. The force field parameters are rely on hybrid of atomic bonding radius, hybrid angle, van der Waals parameters, torsion and bond angle plane bending barrier and the effective nuclear charge number[14].

For the system to be studied, the basic model of UFF molecular field was employed in Universal force field, the energy function consists of two parts: bonding interaction energy and non-bond interaction energy. Bonding interactions consists of energy of bond stretching, angle bending, dihedral angle torsion and bond angle plane bending, non-bond interaction consists of electrostatic effect and the van der Waals energy components, the expression of major energy are as follows.

$$E = E_R + E_\theta + E_W + E_\phi + E_{VDW} + E_{ei} \quad (1)$$

For the bond stretching energy E_R, Harmonic form was used, K_{ij} is force constant; r_{ij} is the standard bond length.

$$E_R = 1/2 * K_{ij}\left(r - r_{ij}\right)^2 \quad (2)$$

For the coordinates environment of linear systems, triangular plane, plane square, and octahedral, angle bending energy E_θ can be expressed.

$$E_\theta = K_{ijk} \Big/ n^2\left[1 - \cos(n\theta)\right] \quad (3)$$

Bond angle plane bending energy E_W and dihedral angle torsion energy E_Φ are expressed in formula(4)and (5), K_{ijkl} is the force constant , X_{ijkl} is angle of plane IL and the IJK.

$$E_W = K_{ijkl}\left(C_0 + C_1 \cos W_{ijkl} + C_2 \cos 2W_{ijkl}\right) \quad (4)$$

$$E_\phi = (1/2)V_\phi\left[1 - \cos n\phi_0 \cos n\phi_0\right] \quad (5)$$

van der Waals interactions and electrostatic interactions were expressed by Lennard-Jones function and the Coulomb force respectively, in the formula(6), D_{ij} is dissociation energy; X_{ij} is bond length for the VDW, D_{ij} and X_{ij} could been obtained from parameters of atom in the same nuclear through chemical combination. In the formula (7), Q_i and Q_j represent the charge of electronic unit; R_{ij} is the distance; ε is dielectric constant.

$$E_{VDW} = D_{ij}\left\{-2\left[X_{ij} \Big/ X\right]^6 + \left[X_{ij} \Big/ X\right]^{12}\right\} \quad (6)$$

$$E_{ei} = 3320637\left(Q_i Q_j \Big/ \varepsilon R_{ij}\right) \quad (7)$$

C. Black Box Theory

The so-called "black box" [15], means all unknown areas and problems hard to solve for some reason generally, but in narrow sense, it means problems which are not allowed to open, but need to be determined the internal structure or whose movement should be predicted. The so-called "black-box method" refers to methods through which all the facts are available in general. But in narrow sense, it means methods which can solve problems which are not allowed to open, but need to be determined the internal structure or whose movement should be predicted. The key point of "Black box" methods is: there are no isolated things, everything is interconnected with others. So, even if we do not know the internal structure of "black box", we can achieve a better simulation target through the relevant testing methods as long as some feedback information in the box is available.

In this study, because of the complexity and uncertainty of cement hydration system, good results are unable to be obtained through traditional simulation methods; "Black box theory" develops a new road for us to continue research. The cement hydration products unit

was regarded as a black box, atoms and density were entered according to chemical formula, so as to they could mix in the black box freely, and we can judge the correctness of the structure according to the output relevant information. In this study, good results are obtained based on the black box theory combining with molecular dynamics simulation.

III. Results and Discussion

A. Analysis on Structure of Hydration Products.

After energy minimization, the structure of the system becomes more balanced, the energy curve keeps straight. From Fig.1, it can be seen that the degree of disorder in balanced system is larger, the distribution of atoms within the unit cell has no obvious periodicity, silico-oxygen tetrahedron randomly distributes in the structure as scattered units, water molecules fill in the layer, the system has layered-structure characteristic. This consistent with the conclusions that the cement hydration products are amorphous structure, the main hydration product CSH more are layered structure described in literatures.

B. X-ray Diffraction Analysis.

To determine the accuracy of the simulated structure, the structure was analyzed by XRD, and was compared with the measured profiles [16]. Horizontal axis represents 2θ , the vertical axis is relative intensity.

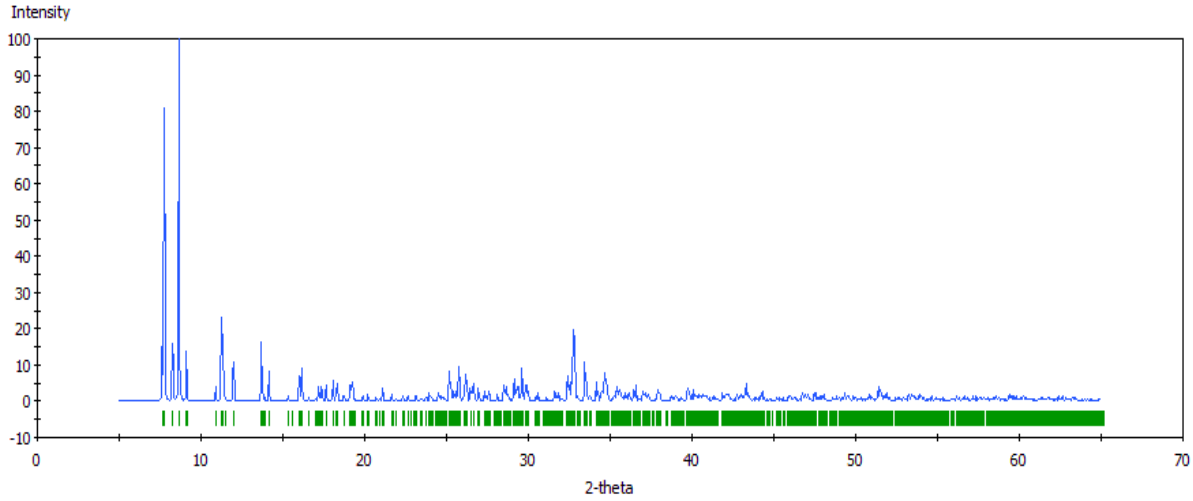

Fig2. XRD for simulated structure

From Fig.2, it can be seen the whole curve is flat except several peaks, it can be determined that structure obtained through simulation consist of crystalline materials and amorphous materials, and the proportion of amorphous is larger, maybe it's solid solution formed by combination of crystalline material and amorphous material. Based on comparing with standard pattern, it can be determined that most of the products obtained by simulation are amorphous CSH gel. According to some peak value, it's difficult to determine the corresponding material temporarily. This may be due to the errors in the simulation result, or formation of a new unknown phase because of random distribution of atoms. Taking into account the inevitable errors in the simulation, this study basically achieved satisfactory results, the usage of the models and force field is in good agreement with the actuality.

C. Radial Distribution Function g (r).

Radial distribution function (RDF), it means the ratio of local atomic density of atom β which is r away from target atom α and average density of β in system. By analyzing the partial radial distribution function g(r), bond length or inter atomic distance, coordination number and degree of structural order and other important information are available.

In Fig.3 (A-D), on the whole, four curves are tending to be flat after maximum peak appears in four figures, and eventually close to 1. Curve shows the short-range order, and long-range disorder, in addition, (c), peak splitting phenomenon occurs in partial radial distribution functions of Si-O in the vicinity of 4Å, which is typical amorphous characteristics, it's in good agreement with the results that most cement hydration products are amorphous CSH gel.

D. Distance between Atomics and Coordination Number.

Based on the partial radial distribution function, we can easily calculate the interatomic distances (ID) and coordination number (CD). Distance between atomics is the radius r corresponding to the peak value of the first neighbor peak in partial radial distribution function; coordination number is the integral value of the partial radial distribution function g (r) from zero to r corresponding to minimum value of g(r) between the first peak and the second peak. Calculated the interatomic distances and coordination number are shown in Table 1.

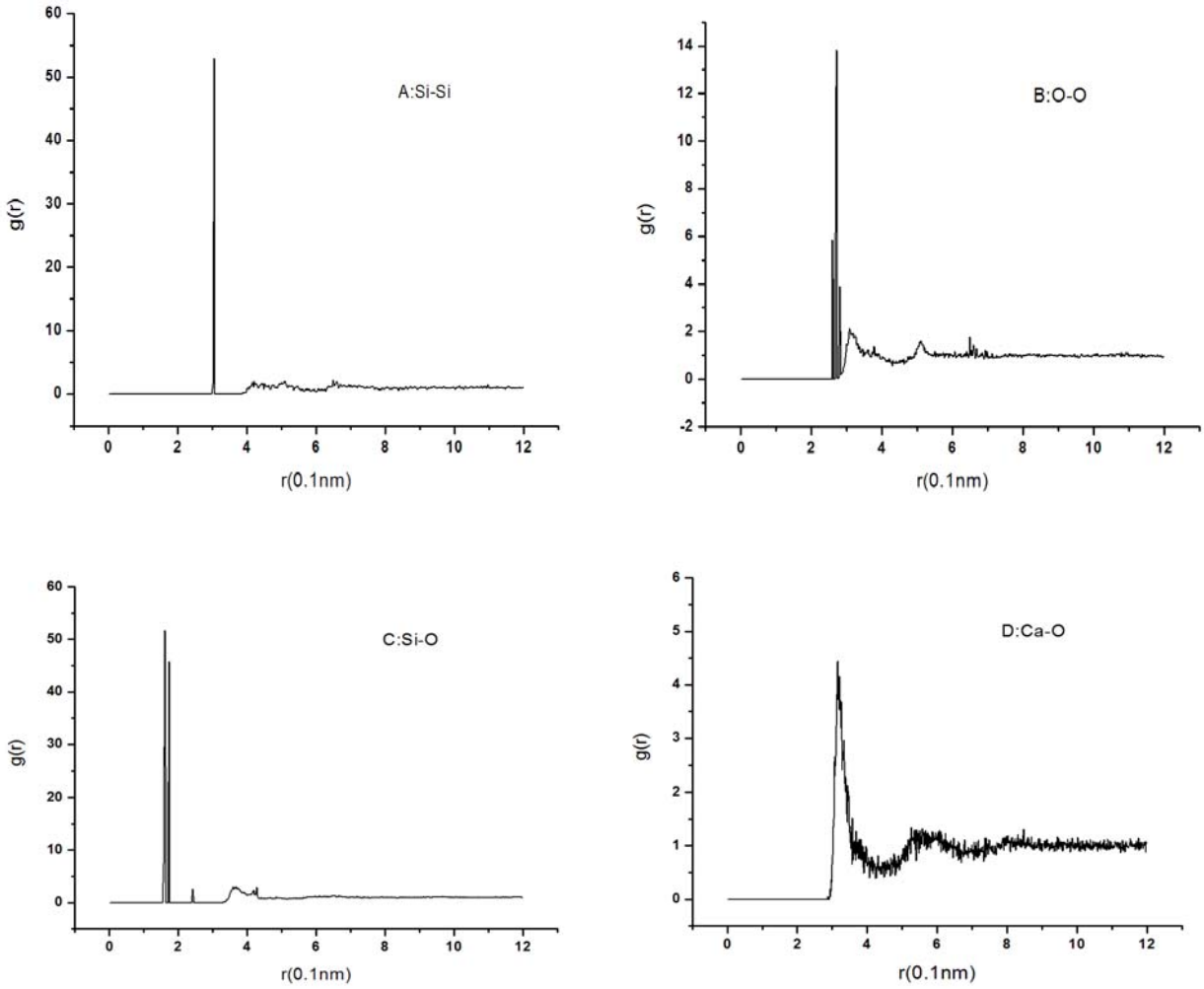

Fig3. Radial Distribution Function g (r) for Si-Si, O-O, Si-O, Ca-O

TABLE 1. SIMULATED VALUES AND EXPERIMENTAL VALUES OF DISTANCES BETWEEN ATOMICS AND COORDINATION NUMBER.

ID & CD	Simulated values	Experimental values [16]
N_{Si-Si}	1.704	-
N_{O-O}	4.436	-
N_{Si-O}	4	4
N_{Ca-O}	6.24	7
r_{O-O}	2.68	2.64
r_{Si-O}	1.65	1.62
r_{Ca-O}	3.12	2.63

According to Table 1, there only exists 2 coordination between Si and Si, it means silico-oxygen tetrahedron chains are connected only in Q2, not in Q3 and Q4, which is consistent with the NMR results provided by Wieker [17]. Coordination number of Si is 4 indicating that the basic unit is still silico-oxygen tetrahedron in this structure, which is consistent with the previous model. The data above are in good agreement with the experimental data except Ca-O. Taking into account the size in model system, boundary effects and system errors, the simulation results can reflect the actual microstructure.

IV. CONCLUSIONS

Cement hydration process is complex, its products are mostly amorphous materials, amorphous structure are obtained by method of annealing in traditional molecular simulation, in this paper, atoms were randomly distributed within the cell, the final structure obtained by

simulation, and was compared with the measured values, the following conclusions are obtained:

(1) The atoms are randomly filled in the unit cell by setting density and the ratio of atoms through black-box operation, the final structure was obtained based on energy minimization. By analyzing the XRD and the RDF curves, it can be confirmed that the cement hydration products are mostly amorphous CSH gel, in addition to the presence of other crystalline phase which remains to be further studied.

(2) Molecular modeling as new experimental method, verified its reliability and creativity in this study. Although there exist inevitable errors, it still within the acceptable range and it may become the new trend of the future study.

(3) This study provides a new way for future study on the mechanism of cement hydration, it overcomes the lack of objective conditions, enhances the understanding of cement hydration at the molecular scale.

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