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Self Similarity of the Spherical C-S-H Particle in Cement Paste

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Abstract: Cement paste with low water/cement ratio of 0.3 was observed using AFM. It is found that C-S-H has self similarity trait from scanning scale 20 μm×20 μm down to 300 nm×300 nm, and the feature of C-S-H at large scale is very similar to those smaller scales. It can be concluded that C-S-H is composed with some fundamental spherical globule, the fundamental globules agglomerate into bigger ones, moreover the bigger ones agglomerate into even bigger one. A C-S-H globule fractal model was put forward to describe the self similarity of the C-S-H globule, which can be used to reveal how the C-S-H globule contacts with each other.

Key words: self-similar; C-S-H; cement paste; fundamental unite; granular; pattern

1 Introduction

In mathematics, a self-similar object is exactly or approximately similar to a part of itself, *e g*, the whole has the same shape as one or more of the parts. Many objects in the real world, such as coastlines, are statistically self-similar: parts of them show the same statistical properties at many scales[1]. Self-similarity is a typical property of fractals, fern and some kinds of tree exhibit affine typical self-similarity. Scale invariance is an exact form of self-similarity where at any magnification there is a smaller piece of the object that is similar to the whole. Calcium-silicate-hydrate (C-S-H) is the binding phase in cement paste, from the beginning of the last century, different kinds of method is used to study the microstructure of the cement paste, in 1967, S Diamond used scanning electronic microscopy (SEM) to observe the microstructure of the cement paste and found four types of C-S-H, later H Jennings used transition electron microscope (TEM) to observe the C-S-H and found five types of C-S-H, those work was done on the cement paste with high water/cement ratio of 0.5-0.6. Currently, the super plasticizer is widely use and the cement paste has much lower water/cement ratio than those pastes studied by S Diamond and H Jennings[2], in the cement paste with normal consistency, the cement paste looks more like a bulk or equate particles. Up to now it is widely recognized that the C-S-H has a colloid (gel) nanostructure and it is the one of the most complex gel system[2-5]. Taylor[3] proposed that at nano-scale the structure of C-S-H gel is short range orderly and composed of tobermorite or jennite nanoparticles, which was referred to “the nanostructure model”. Jennings put forwarded a model which could describe the nanostructure of the C-S-H exactly, and it showed that C-S-H consists of the foundational structural unit—globule with diameter of 5.2 nm[5](SANS test results showed 4.4 nm[4,6]), two type of C-S-H, *i e*, high density (HD) and low density (LD) C-S-H are formed due to difference of packing density of the nanogranule, Ulm[7]confirmed the nanogranular nature of C-S-H by nanoindentation method which supported Jennings’s model. The atomic force microscope (AFM) has a higher resolution which can be used to observe the microstructure or morphology of the cement based materials at atomic scale directly and accurately[8], eventually a new research field on the nano-scale microstructure of the cement based material can be explored with AFM[9]. Since 1993, many researchers began to study the microstructure of the cement-based materials by AFM, the nanogranular nature of the cement-based materials was more intuitively and further confirmed. Whereas the size of C-S-H nanoparticle measured by different researchers has very large range, *e g,* S P Shah[9] founded that the particle size of C-S-H ranges from tens nanometers to several hundreds nanometers by studying the microstructure of the fracture section of the cement paste with AFM; Nonat[10] sug-

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gested that C-S-H is composed of a basic brick-type nanoparticles (lamellae) of dimension 60 nm×30 nm×5 nm which is uniformly assembled to construct a gel like matter; Benon[11] experimental research supposed that the C-S-H consists of spherical and egg-type particles with a size can be smaller than 2.5 nm. Other researcher, *e g,* Richardson[12] investigated hydration products of cement based on TEM, nuclear magnetic resonance (NMR) and electron-probe microanalyzer (EPMA) methods, the results showed that the fibrillar morphology of outer product (OP) of the C-S-H is composed of clusters of elongated particles which are about 3 nm in their smallest dimension and of variable length, ranging from a few nanometers to many tens of nanometers. Many researchers believe the cement paste has very strong tendency to be fractural traits and self-similar in various scales[6], this trait has no been studied fully with the obvious proof yet. In this paper, the AFM was used to study the microstructure from micro to nano scale, the self similarity traits of the C-S-H particles was founded and a fractal modal of C-S-H globule was put forward.

2 Experimental

2.1 Raw materials

The cement of PO42.5R(rapid hardened ordinary portland cement) was produced by the Huaxin Cement Company Ltd., whose chemical compositions are listed in Table 1. The polycarboxylate high performance water reducer used was supplied by the Shanghai Master Construction Chemical High-tech Company Ltd., and the dosage of which in the cement paste ranged from 1.2% by mass of the cement.

Table 1 Chemical compositions and physical property of cement/%

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	IL
21.06	6.04	3.63	63.98	2.67	2.25	1.07
Blaine specific surface area is 376 cm^2/g						

2.2 Preparation and treatment of specimens

The cement paste with appropriate fluidity was prepared with 1.2% of polycarboxylate water reducer and a water/cement ratio of 0.3, and the fracture section of a paste was used to observe the morphology of the C-S-H at scale larger than 3 μm.

The C-S-H specimen was prepared by a special surface-replica method: the cement paste was poured on the glass substrate with high smoothness degree, and then the cement paste was vibrated on a vibration table with a frequency of 55 Hz in order to make it flow flatly. After a certain curing time, a thin specimen of gel C-S-H with a smooth enough surface for the AFM observation was obtained on the glass substrate, then the specimens were spilled from the glass substrate and dried with a vacuum.

2.3 Measurement

A DI Nanoscope type IV scanning probe microscope (SPM) produced by the United States Veeco Precision Instruments Ltd was employed to measure the particle size, surface morphology and roughness of specimens. All the specimens were tested at temperature of 20±5 ℃ with relative humidity (RH) of 60%±10%.

3 Results and Discussion

3.1 The morphology at fracture surface of cement paste

The fracture surface of the cement paste was observed with AFM taping model, and Fig.1 is the morphology of the C-S-H with imaging size of 20 μm×20 μm. There is a whole spherical C-S-H particle (around 27 μm similar to the result of S Diamond) made with some smaller particles (around 9 μm), and those particle still made of even smaller ones. Fig.2 shows the feature of some spiracle particles around 3 μm and some smaller particles around 1 μm, and those particles are made or some even smaller ones with around 100-300 nano meter. So the spherical particles have a tendency to form larger spherical particle, and the morphology of the paste is very similar when scaling up the observation scale.

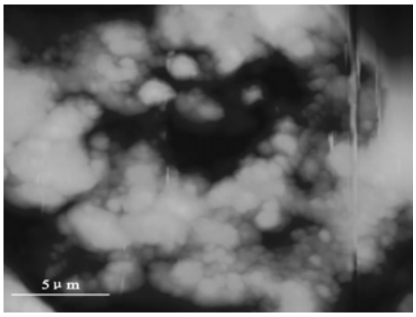

Fig.1 Image size: 20 μm×20 μm

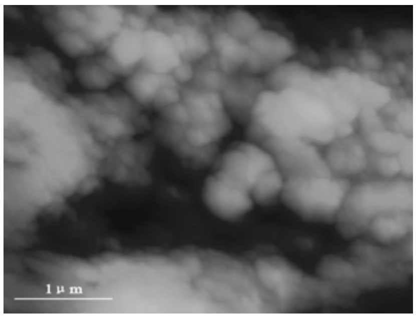

Fig.2 Image size: 5.0 μm×5.0 μm

3.2 The morphology at smooth surface of cement paste

The smooth specimen prepared by special surface-replica method was observed with AFM also. Fig.3 is the image with a scanning size of 3.0 μm×3.0 μm, the particle size is around 0.4 μm, and the smaller particle has size around 50 nm. When the magnification time increases, the cement paste still makes of spherical particles. In Fig.4, some 250-400 nm can be found, and they are also made of particle around 50-75 nm.

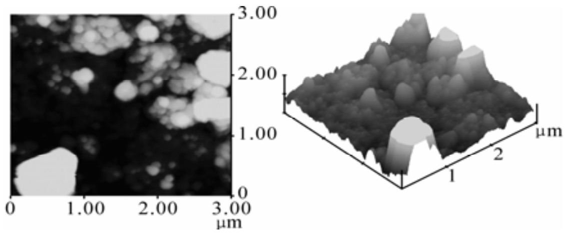

Fig.3 Images size: 3.0 μm×3.0 μm

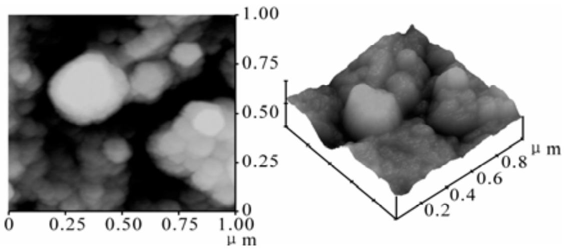

Fig.4 Images size: 1.0 μm×1.0 μm

From Fig.5, the particle can be seen more clean. The bigger particles have some very small particle around 20-30 nm, but the edge of the particles is very ambiguous, so it is very difficult to figure out the exact size of the basic unite particles. Shen Weiguo[13] observed the C-S-H sample corroded by the NH_4NO_3 solution has the size of the fundamental unite of C-S-H around 5 nm, and the basic globules agglomerate (or self assemble) into some bigger particles.

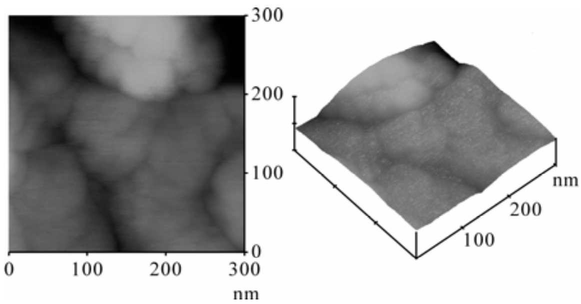

Fig.5 Image size: 0.3 μm×0.3 μm

3.3 The self similar model of the C-S-H

Fig.6(a) illustrates the agglomerate morphology of C-S-H particle, the fundamental unite of the C-S-H is globule as supposed by Jennings[6], those unites agglomerate into bigger globule, the particles do not only pack or aggregate together, they contact with each other driven by particle-to-particle contact force, those bigger ones agglomerate into some even bigger ones. As illustrated in Fig.6(b), the fundamental particle and the smaller ones fill in some pores among the bigger ones and act as some contacts. The globule agglomerate into globule of different scale, and the globule with different scale agglomerate together and composed a bulk of paste with some pore, which is the main binding phase of cementitious material. This can used to reveal how the nano globules agglomerate into the micro meter equates of C-S-H.

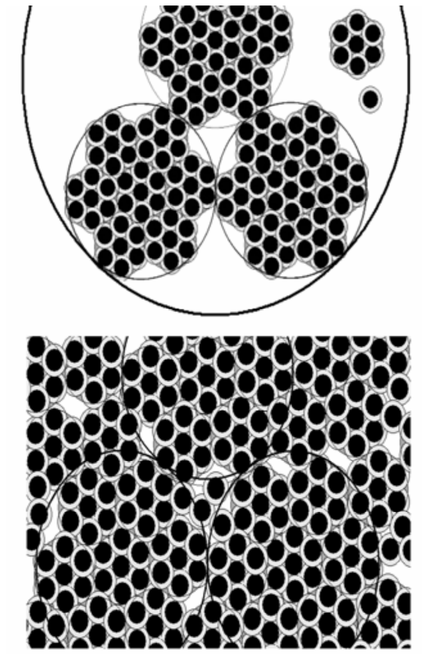

Fig.6 Schematic diagram of the agglomerate of the C-S-H particle
(a) The agglomerate of C-S-H nano particles;
(b) The self similar pattern of the C-S-H particles

4 Conclusion

C-S-H is made of globule from tons of micro meters to around tens of nano meter in cement paste with low water/cement ratio.The agglomerate of C-S-H particle in different scale is approximately similar and represents a kind of fractal pattern.The self similar globules with various scales agglomerate together and form the porosity C-S-H bulk.

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