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Effect of water and nano-silica solution on the early stages cement hydration

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HIGHLIGHTS

- The effect of nanosilica on the early stage of cement hydration process.
- The effect of water and nanosilica on the modulus of elasticity and surface adhesion force of cement in early stage of hydration.
- Using AFM to characterize the nanostructures of cement paste in water and nanosilica solution.
- Investigation of the transition zone between C-S-H colonies in water and nanosilica solution.

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ABSTRACT

The nanoscopic young's modulus of cement paste during early ages of hydration in water and nano-silica was investigated by the application of atomic force microscopy (AFM). Peak-Force Quantitative Nano-Mechanical (PFQNM) imaging mode in atomic force microscopy was used to determine elastic modulus of cement paste before and after immersion in water and nano-silica solution. The results clearly show how mechanical and physical properties of cement grains changes progressively to higher values during the hydration process in water and nano-silica.

Moreover, an empirical theory on mechanism of hydration development is proposed in the current study based on experimental observations. Average Young's modulus of condensed cement powder was changed from about 15 GPa, for unhydrated state, to 11.3 GPa after two hours of hydration in water environment. The average roughness trend was also altered from 8.31 nm to 18.2 nm during hydration process. Results show that the cement hydration rate in nano-silica solution is much higher than water environment. Moreover transition zone between C-S-H colonies have much higher mechanical properties than the hardest colonies in every ages. In the presence of nano-silica, transition zone has a width of less than 10 nm and a surface area of 5% of the overall surface area.

1. Introduction

Since the common use of Portland cement and its ability to use as a binder material, the cement hydration process has been an interesting research subject all over the time [1,2]. Despite all valuable studies, investigating nanomechanical properties of cement and the effect of nano-silica at early ages of hydration and before setting time has still remained unknown. However, it could be due to the semi-liquid status of cement paste before its setting time where conventional instrument for measuring nanomechanical properties (e.g. nanoindenter) cannot work properly. As a result, most of the efforts are concentrated on visco-elastic properties of this material before hardened state [3–7].

Using nanotechnology in future will make it possible to design materials for their specific purpose of application. The nano-SiO_2 particles fill the voids of the C–S–H gel structure and act as nucleus to tightly bond with C–S–H gel particles, making binding paste matrix denser, resulting in an increase in long-term strength and durability of concrete. Nano-scale SiO_2 behaves not only as filler to improve mortar cement microstructure, but also as a promoter of pozzolanic reaction [8].

With the addition of nano-silica, the viscosity of concrete significantly increases, which causes that more air is entrapped in the fresh mixtures and the porosity of the hardened concrete correspondingly increases. In contrary, due to the nucleation effect of

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nano-silica, the hydration of cement can be promoted and more C–S–H gel can be generated. Hence, it can be concluded that there is an optimal nano-silica amount for the production of UHPC with the lowest porosity, at which the positive effect of the nucleation and the negative influence of the entrapped air can be well balanced [9]. At the microscopic level, the interfacial transition zone (ITZ) of the concrete became denser and the formation of C-S-H gel was promoted after adding NS [10].

Within the two last decades, using nanoindentation and atomic force microscopy test methods to characterize cement properties have been widely become popular [11,12]. Recently, it was observed that nanoindenters cannot be an apt device to measure nanomechanical properties of the main products of cement hydration (i.e. C-S-H) owing to very large scale of their tips in comparison with dimensions of C-S-H formations [13]. In this regard, compared to an atomic force microscope (AFM), a standard nanoindenter end tip radius range (40 nm for cube corner up to 200 nm for Berkovich) is much bigger than that of atomic force microscope which has typical end tips mostly bellow 10 nm used for investigating nano-scale characteristics of heterogeneous materials such as cement-based composites [14]. Therefore, concerning evaluating C-S-H nanomechanical properties, AFM would be a suitable replacement for nanoindenters and accordingly can be utilized for statistical nanoindentation testing [15].

According to the above mentioned, the aim of this study is the investigation of the early age properties of cement hydration in water and nano-silica solution through a new AFM device. Thus, a fast-scan AFM was used for imaging the cement surface and measuring the changes in nanomechanical properties as well. As far as it is known that cement particles hydrate so fast in the presence of water, using common force-volume measurement by normal AFM is unsuitable for understanding the exact changes in cement particle properties during very early ages. Consequently, the fast-scan AFM was applied to scan all over the sample area in every three minutes rather than twenty minutes scanning interval in normal AFM at high similar resolution (512×512 pixels). Accordingly, the capability of using new mode of atomic force microscope which is called Peak-Force Quantitative Nano-Mechanical (PFQNM) in the case of cement hydration process was experimented. This is fulfilled to understand how mechanical and physical properties of cement would be changed during hydration process within early ages in the presence of water and nano-silica.

2. Experimental programs

2.1. Materials

Cementitious material containing type II Portland cement was used in this work. Chemical and physical characteristics of the cement are illustrated in Table 1. Distilled water was used for casting all of the specimens.

Table 1
Physical and chemical characteristics of cement.

Physical properties	
Specific gravity (g/cm^3)	3.15
Blaine (m^2/kg)	295
Chemical analysis (%)	
SiO_2	22.20
CaO	65.65
Al_2O_3	4.71
Fe_2O_3	2.85
MgO	1.95
Na_2O_3	0.16
K_2O	0.48
Loss on ignition (LOI)	1.41
Bogue potential compound composition (%)	
Tri calcium silicate (C_3S)	62.2
Di calcium silicate (C_2S)	16.9
Tri calcium aluminate (C_3A)	7.6
Calcium ferric aluminate (C_4AF)	8.7

2.2. Samples preparation

As gathering cement particles together to evaluate their hydration progress can be a cumbersome effort due to their lack of fixity on the glass lamella, there is a crucial need to compress these particles for exact nanomechanical measuring. This method has two distinct advantages. Firstly; the fixity of cement particles help AFM probe gather data precisely without causing error of changing in particles positions and secondly; one can probe the nanoscale changes in two-dimensional platform which is of vital importance for AFM test method. Therefore, a condensed sample of cement particles were prepared. To produce the condensed cement particles sample, three major steps were taken:

1. Compressing the cement powder through hydraulic pressure machine by applying 400 kN force to make a solid prismatic specimen ($5 \times 5 \times 15$ mm^3) in a vacuumed cylinder with heating up to 200 °C temperature in about one hour (see Fig. 1, left). It should be noted that this procedure cannot alter cement particles composition due to its very low temperature compared to very high temperature range of producing cement clinkers (1450–1550 °C).
2. Milling the sample surface to extract a thin lamella of $40 \times 40 \times 2$ μm^3 with high-current beam of Focus Ion Beam (FIB) as is shown in Fig. 1, middle.
3. Using a Micromanupolator to attach the obtained thin lamella to a copper grid beam, which is typically used to prepare samples for Transmission Electron Microscopy (TEM), by platinum welding and then polishing the ultimate surface with low-current beam of FIB device to achieve a very flat surface for AFM scanning process (see Fig. 1, right).

Concerning the method used (FIB) to prepare the surface of prismatic condensed cement specimen rather than using typical grinding and polishing method to achieve as smooth surface as possible for AFM investigation, there are two main reasons to select such a procedure:

1. In the case of condensed cement powder prepared in this study, using a typical method of grinding and polishing would obviously lead to a rougher surface because of moving particles out from the surface where particles are just attached to each other physically.
2. The sample prepared based on this method gives us the opportunity to investigate a specific region with both SEM and AFM to measure small changes in chemical and mechanical properties simultaneously.

According to the use of nano-silica in cement paste and concrete, hydration of cement particle in nano-silica solution has been investigated. Fig. 2 shows the preparation of the cement layer which have been compressed using FIB machine. In order to fill the cavities and cracks of the cement sample, epoxy has been injected. In Fig. 2d, black surfaces between cement particles are epoxy. The experiment stages are precisely similar to those of the previous one with the exception that instead of placing the sample immersed in the water, the sample has been immersed in nano-silica solution (MEYCO MP320) with the colloid density of 40%.