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Effect of free water on the flowability of cement paste with chemical or mineral admixtures

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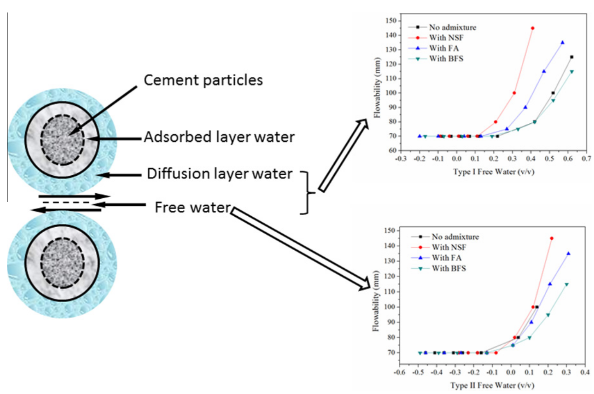
HIGHLIGHTS

- Free water was measured in the cement paste.
- Effect of free water on the flowability of paste was studied.
- Composite effect of mineral admixtures and cement was described.

GRAPHICAL ABSTRACT



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ABSTRACT

The particle packing state in cement paste and the characterization methods of free water were studied. The changes of free water in cement paste by adding mineral admixture and chemical admixture were measured, and the relationship between flowability and internal structure of cement paste was analyzed. The results showed that: water in cement paste can be classified by plastic limit test and liquid limit test. Excess water over the plastic limit which was the surplus water after filling the accumulate void of cement particles can only achieve the purpose of separating cement particles. When water exceeded the liquid limit, the free water caused the flow of paste under gravity. The improvement of flowability by adding superplasticizer was not only due to dispersion of flocculation structure, but mainly because of lower adsorption force field of cement particles to water. Superplasticizer reduced the thickness of water diffusion layer, and increased the flowability of the paste. The mineral admixture influenced the packing state and water adsorption capacity of particle materials.

1. Introduction

Water is the cheapest component of concrete, but it plays a pivotal role on concrete performance: water/cement ratio is one of the most important factors to control the mechanical properties of concrete, and unit water dosage plays a crucial role on regulating the performance of fresh concrete. Researches [1–4] suggest that water is part of the most important factors for concrete performance. Water content is the contradiction of controlling both properties of fresh concrete and hardened concrete. Superplasticizer subtly regulates this contradiction points to promote the development of high-strength concrete and high flowability

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concrete. Therefore, the distribution and the effect of water are essential to regulate the concrete performance.

Water is the most fundamental factors that affect the concrete flowability. The effects of superplasticizer, mineral admixtures, sand ratio or some other parameters on concrete flowability are usually explained through quantitative analysis of the amount of free water. The flocculation of cement particles is the main factor to impede the flow of the paste, and superplasticizer can improve the flowability by dispersing the flocculation structure [5,6]. A classic explanation can be represented as superplasticizer molecules are adsorbed on the surface of cement particles. The flocculation structures are dispersed by electrostatic repulsion [7] or steric hindrance [8], and the water inside the flocculation is released. This process increases the "free water", thereby increases the paste flowability. As functional components of concrete, mineral admixtures can improve the flowability, and the mechanism is that the mineral admixture can improve the overall distribution of the gelled material particle system so as to improving the compacted packing density [9]; The surface characteristics of some mineral admixture, such as fly ash, is spherical which reduced resistance in the process of the relative motion of the system [10]. Despite the importance of water, there continues to be a paucity of evidence on the water distribution and the content of "free water". A systematic understanding of how effective water contributes to flowability is lacking. Study on the role of "free water" and quantitative characterization is a key way to improve the flow mechanism, thus to achieve regulation of cement based material performance. How to determine the amount of free water and the correlation between free water and paste flowability still had no definite conclusion.

Powers [11] proposes that concrete can be considered as a mixture of aggregate and cement paste. Cement paste fills the void among aggregates, while the aggregates are coated by excess paste. The coating paste layer lubricates the aggregate relative motion. In the cement paste system, similar relationship can be described as that: water is firstly filling the packing voids of cementitious material; and the water coating film which is an important factor to move the paste will be formed on the surface of particles since the surplus "free water" is generated. Based on the basic ideas, Kwan et al. [12] and Kwan and Wong [13,14] performs a series of experiments to illustrate how to determine the packing density of cement in the water. Wong and Kwan [15] and Fung and Kwan [16] study the effect of water film on the performance of paste. Few studies have investigated free water in any systematic way. So it is necessary to explore the basic characteristics of free water, combine the regulation mechanism of admixtures on flowability and establish a perfect flow theory for cement base material.

The specific objective of this study is to reveal the generation of "free water" and the mechanism of action. This study uses a correlation analysis approach to investigate the change process both macro performance of the cement paste and the internal structure of paste. Combined with the related concepts of plastic limit and plasticity index in soil mechanics, an attempt is made to establish a "free water" characterization method. Further, explain chemical admixtures and mineral admixtures on cement paste flowability change mechanism and lay a foundation for fine regulation of cement base material performance.

2. Experiments

2.1. Raw materials

Cement: PII52.5 Portland cement (PC) was complying with GB175-2007; its density was 3.14 kg/m^3.

Mineral admixtures: Fly ash (FA) and blast furnace slag (BFS); their densities were 2.18 kg/m^3 and 2.6 kg/m^3, respectively.

Chemical admixture: Naphthalene-based superplasticizer (NSF); paste water reducing rate was 23% at the dosage of 0.75% of cement weight.

2.2. Sample preparations

The aim of this study was to determine how the characteristics of cement paste changed along with water–binder ratio (by volume). The test was separated into four systems: cement paste without superplasticizer and cement paste with 0.75% naphthalene superplasticizer, cement paste with fly ash replacing 15% Portland cement by mass and cement paste with blast furnace slag replacing 15% Portland cement by mass. The water–binder ratio was varied from 0.194 to 0.452.

2.3. Test methods

2.3.1. Determination of paste volume

First step was to measure the density of the paste, and the paste volume equaled mass divided by density. A frustum-shaped cup was used to measure the density of cement paste. It was made from hard plastic, and its volume was 185 ml. Due to relatively large changes over the range of the water–binder ratio, the performance of pastes had significant fluctuations. To ensure the consistency of the filling state, fixed experimental rules were setting: the paste was filled into the cup over the edge of 3–5 mm. A knife was inserted into the pasted nine times along the inner circle at a distance of 10 mm to the edge, and then three times for each in two orthogonal directions. The surface was smoothed using a steel rule. After mixing, the above procedure should be completed quickly, and followed by measuring the weight. The entire process should be completed within ten minutes.

The calculation formulas of the density of paste ρ_0 and the total volume were shown below:

$$\rho_0 = m_0/V_0 \tag{1}$$

$$V_{Total} = (m_c + m_w)/\rho_0 \tag{2}$$

In formulas: m_0 was the mass of the paste in the cup, V_0 was the volume of the cup; m_c and m_w were the mass of mixed cement and water respectively.

2.3.2. Calculation of the solid concentration of paste

The solid concentration of paste was defined as the ratio between the solid volume and the void volume of the paste. The void space contained water and air void. Therefore, the solid concentration of paste can be used to express the most tightly packed ability of solid particles in the paste. It can be calculated by the following formula:

$$e = \frac{V_c}{V_{Total} - V_c} \tag{3}$$

In the formula: e was the solid concentration; V_{Total} was the total volume including the void; V_c was the volume of cementitious binder, which can be calculated from the mix proportions.

2.3.3. Determination of the flowability of cement paste

After the mixing process, the flowability was measured complying with GB/T8077-2000. The flowability was measured in terms of flow spread using the mini slump cone test. It concluded: (a) Pour the cement paste slowly into the slump cone until the slump cone is completely filled up; (b) Lift the slump cone gently and allow the cement paste to spread; (c) At the time of 30 s since lifting the cone, measure the diameters of the cement paste patty in two orthogonal directions, calculate the average diameter as the flow spread of the cement paste.

The rheology parameter can be determined by NXS-11B rotary viscometer. The test samples were poured into a cylinder container, and then the spindle of the viscometer was introduced in the container for measurement. The viscometer measured the torque required to rotate the standard spindles in paste. Two shear stress–shear rate curves were obtained, one at increasing shear rate and the other at decreasing shear rate. The curve at decreasing shear rate, which is generally more consistent and repeatable, was used for evaluating the rheological properties of the cement paste sample. A linear regression analysis was carried out to determine the plastic viscosity (Pa s) and the yield stress (Pa) as slope and intercept of the regression line drawn through the data points in shear stress potted against shear rate plot.

3. Results and discussion

3.1. Particles packing state and paste plasticity

According to the knowledge of soil mechanics, with the gradual increase of moisture, the soil particles would be show different states, which were bulk powder, hardened solid, plastic state and the flow state, respectively. Plastic limit of the soil was defined as the critical moisture content of the transition from semi-solid