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Effects of SAP on the properties and pore structure of high performance cement-based materials

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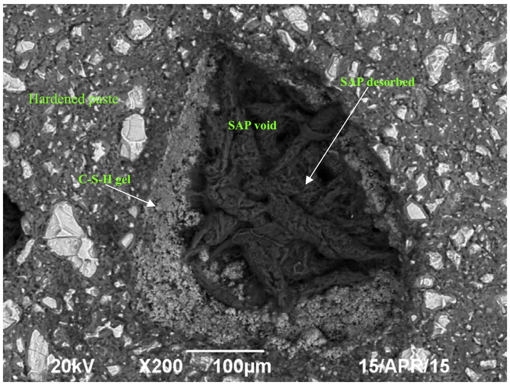
HIGHLIGHTS

- SAP significantly weakens the effects of water-to-binder ratio on the performance.
- Larger SAP particles have better effectiveness in improving pore structure and the permeability.
- The hydration diffusion layer in SAP pore and the refinement of pore improve the performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Water-to-binder ratio (w/b) directly affects the pore structure and performance of concrete, and drying conditions enhance the influence of water-to-binder ratio. Superabsorbent polymer (SAP) is effective to adjust the water in the concrete. In this paper, the effect of SAP and extra water on drying shrinkage, pore structure and the permeability of high performance cement-based material with w/b from 0.18 to 0.24 were studied to reveal the adjusting role of SAP for the influence of water-binder ratio at a 60% of relative humidity (RH). The permeability was determined through the vacuum saturation method, the diffusion of steady-state Cl^- ion and carbonation testing. The structure of harden mortar and SAP voids were evaluated by mercury intrusion porosimetry (MIP) and backscatter electronic microscopy (BSEM). At the same effective w/b, SAP reduces the strength, and raises the drying shrinkage and permeability. However, the effect of SAP on the above properties is exactly opposite when the same total w/b is used. The greater the SAP particle size is, the more obvious those favorable effects are. SAP can weaken the effect of total w/b. The addition of SAP also results in the formation of the hydration diffusion layer in SAP void and the refinement of pore structures.

1. Introduction

Water-to-binder ratio (w/b) is a very important parameter for mix proportioning of concrete. It influences not only the strength of concrete, but also the permeability and durability. In the drying

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condition, a high w/b will increase drying shrinkage and deteriorate the performance of concrete [1].

Superabsorbent polymer (SAP), an internal curing material of high performance concrete, can obviously delay the decrease in internal humidity [2], restrain autogenous shrinkage [2,3], and promote the hydration of cementitious materials at the ages of 7 and 28 days [2]. To obtain the same flowability, extra water is added to counteract the water absorbed by SAP. The addition of extra water, however, will increase total w/b resulting in reduction of strength and increases in porosity [4–7], especially for the pores of 2 nm–50 nm pores [5,6]. But afterwards, extra water will promote further hydration of cementitious materials and keep the capillary porosity at the same value for mixtures with the same effective water-to-cement ratio [8,9]. In addition, the type of supplementary cementitious materials will affect the effectiveness of SAP to the porosity and silicate fume takes on a different effect with fly ash [10].

When the internal humidity in concrete drops, SAP begins to release water [2,3] and a large pore, namely SAP void, will gradually be formed near SAP particle. The size of SAP void is related to the swelling volume and can reach several hundred microns [11]. The shape of SAP void depends on the synthetic process of SAP and is generally irregular [2,5,12,13] or spherical [11]. SAP desorbed looks like a layer of organic film which is coated on the wall of SAP void [5,14]. Calcium hydroxide [2] or Ettringite [12] is found to exist in SAP void.

The addition of SAP also affects the resistance to penetration of water, O_2 [10,15], and CO_2 [10,16,17] which are related to total w/b. The effect of SAP on freezing-thawing resistance varied from insignificant to pronouncedly positive [16,18–21]. The improvement of freezing-thawing resistance is usually contributed to the formation of SAP voids [4,14,22], and also depends on the testing laboratory and method [21]. The chloride ion permeability also varies from the weakness to the enhancement [5,15,18]. For example, chloride ion penetration coefficient is decreased for sample with SAP at a water-to-cement ratio of 0.50, but is increased when water-to-cement ratio is reduced to 0.40 [18]. Hasholt and Jensen [18] attributed the difference to the effect of SAP on gel space ratio.

The permeability of cement-based material is closely related to the structure of pores, but the results on the structure of pore mainly confine to that obtained by MIP. In the MIP test, sample needs to be cut into small particles and the structure of pores may be destroyed. SAP or air pore may also be opened. The relationship of the permeability with the structure of pore, therefore, is not easy to be established.

In the seal curing, when total w/b is the same, SAP has almost no effect on the final hydration degree and porosity [8,9]. In the North China, an important industrial and agricultural area, the relative humidity (RH) is usually 50–70%. In that condition, the evaporation of water will reduce w/b in the concrete, especially in the surface layer, and the control of water becomes very important.

Whether can SAP effectively reduce the evaporation of water and the deterioration of concrete performance and pore structure? How does the particle size of SAP affect on the adjusting role of SAP? The authors [23] surmise that the migration of water between capillary pore and SAP void and the evaporation may increase the connectivity of pores. In this paper, the effects of extra water and the size of SAP on pore structure were studied by the internal and surface porosity test, and the permeability was evaluated through the vacuum water absorption and carbonation and chloride ion penetration tests in the 60% RH. The interface between SAP void and hardened matrix was also analyzed by BSEM.

2. Materials and methods

2.1. Materials

PI 42.5 Portland cement, class II fly ash and silica fume were used. Their chemical compositions are shown in Table 1. River sand with size in the range of 0.15–2.36 mm was used. Its fineness modulus was 2.7. Polycarboxylate-based superplasticizer with solid amount of 40% was used.

SAP H100 and H30 were used. They have the same kind of angular covalently cross-linked acrylamide/acrylic acid copolymer, but the distributions of their particle size were different. The size range of H100 was from 20 to 250 μm and the median diameter was 125 μm. The size range of H30 was from 250 to 1400 μm and the median diameter was 840 μm. The choice of H30 was to enlarge the effect of particle size, although it may cause the formation of large SAP void. The saturated water amounts of H100 and H30 were 210 g/g and 300 g/g, respectively, in tap water, but only 5.4 g/g and 6.2 g/g, respectively, after 5 h in the cement suspension liquid with w/c of 10.

2.2. Mix proportion

Design of mix proportion is shown in Table 2. w/b of samples without SAP were from 0.18 to 0.24. The amounts of SAP were 0.3%, 0.6% and 0.9% (wt) of cementitious materials, respectively. Extra w/b was increased by 0.02 with the amount of SAP. The amount of superplasticizer was adjusted to meet the same initial slump flow (230 ± 10 mm).

2.3. Mixing and curing

Mixing program of materials was carried out according to Fig. 1. Water, superplasticizer and silica fume were firstly mixed in order to improve the dispersibility of silicate fume particles.

All samples molded were kept in the condition of 20 °C and 98% RH for 24 h. They were then demoulded and continued to be cured in the above condition for 2 days. Finally, they were moved to a room with 20 °C and 60 ± 5% RH and cured for 25 days.

2.4. Testing methods

2.4.1. Compressive strength

The strength testing was carried out according to GB 17671. The size of sample was 40 mm × 40 mm × 160 mm. Each batch had three samples.

2.4.2. Drying shrinkage and mass loss

Drying shrinkage was carried out according to JC/T 603. Sample with size of 25 mm × 25 mm × 280 mm was used. In experiment, the self-desiccation shrinkages of samples were found to mainly take place during the first 3 days, so the deformation after 3 days was thought to be caused by drying shrinkage in this paper. The length and mass of sample on the third day was recorded as initial length and mass. A comparator with an accuracy of 0.01 mm was used to measure the length. An electronic balance with an accuracy of 0.01 g was used to weigh the mass.

Shrinkage ratio and mass loss at n days was calculated according to Eqs. (1) and (2).

$$s = (l_n - l_3)/250 \times 100 \tag{1}$$

$$a = (m_n - m_3)/m_3 \times 100 \tag{2}$$

where s is shrinkage ratio, %; l_3 is the length on the third day, mm; l_n is the length on the nth day, mm; a is the mass loss, %; m_3 is the mass on the third day, g; m_n is the mass on the n^{th} day, g.