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Impacts of various factors on the rehydration of cement-based materials with a low water–binder ratio using mathematical models

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HIGHLIGHTS

- Ultrahigh performance concrete has a low water–binder ratio.
- Rehydration of unhydrated cementitious components can affect concrete performance.
- The effects of various conditions on the rehydration degree of samples were tested.
- The ambient temperature has a significant impact on rehydration.
- A modified rehydration model was developed and validated.

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ABSTRACT

When cement-based materials with a low water–binder ratio are exposed to water, the internal unhydrated cementitious components undergo rehydration. Rehydration tests of paste samples with a low water–binder ratio were conducted to determine the hydration degree under water immersion conditions. A modified rehydration model was developed based on a thermodynamic model for cement hydration and used to predict the hydration degrees of samples at different times. The modified rehydration model closely agreed with the test data. The ambient temperature significantly impacted material rehydration. The temperature effect on the rehydration reaction rate constant follows the Arrhenius law.

1. Introduction

With the continuous development of cement-based materials, ultrahigh strength and performance concrete has attracted widespread attention for practical applications. A low water–binder ratio (w/b) is necessary to obtain ultrahigh strength and performance. Generally, a lower water–binder ratios results in higher strength, lower hydration degree, lower generation of hydration gel, and more unhydrated cementitious material. According to the theory proposed by Powers [1], cement cannot be completely hydrated when the water–cement ratio is less than or equal to 0.38. For sealed conditions, the minimum water–cement ratio is 0.44 for the complete hydration of cement [2]. The water–cement ratio of ultrahigh performance concrete is commonly less than 0.38; the unhydrated cementitious material is a major factor that affects the long-term performance of concrete. In this paper, "rehydration" mainly refers to the hydration reaction between external water entering cement-based materials with a low water–binder ratio and the existing unhydrated cementitious materials. Yang and Guan [3] and Guan et al. [4] indicated that the rehydration of concrete with a low water–cement ratio could lead to concrete damage, an obvious decline in the compressive strength, and poor durability. A lower water–cement ratio increases the damage generated by the rehydration of unhydrated cementitious materials. Their specimens with water–cement ratios of 0.22, 0.25, 0.28, 0.31, and 0.47 all showed a decline in strength after 7 d of hydration, which was accelerated by high-temperature water. In particular, the specimen with a water–cement ratio of 0.22 exhibited a decrease in strength of 21.0%. However, it has also been suggested that once moisture enters concrete cracks, the hydration products from the rehydration reaction of unhydrated cementitious materials tends to repair these cracks to a certain extent. Yao et al. [5] suggested that the self-healing process of damaged concrete essentially involves the hydration of unhydrated cementitious materials at damaged locations and

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the generation of new hydration products to bridge the cracks. Zhu et al. [6] studied the change in the loading performance of damaged engineered cementitious composite (ECC) materials after freeze–thaw cycles. Their results demonstrated that the rehydration reaction during the freeze–thaw cycles can help heal the cracks generated during preloading to a certain extent. Huang et al. [7,8] showed that the rehydration of unhydrated cement can repair microcracks and thus help repair the damage to concrete. Sahmaran et al. [9] investigated the chloride permeability of concrete damaged during preloading under the three curing conditions of water, air, and freeze–thaw cycle. Their results suggested that unhydrated cementitious materials have significant effects on the self-healing of concrete cracks. Granger et al. [10] prefabricated cracks by utilizing the three-point loading method and subsequently studied the changes in the bending strength and integral stiffness of the damaged concrete after water immersion. Although the product of a calcium–silicate–hydrate (CSH) gel generated from unhydrated cementitious materials during the rehydration reaction from immersion in water may differ from the CSH gel generated in the early hydration process, the values of the stiffness are close.

The hydration process of cement is highly complex. Mathematical models describing the hydration process have long been a popular topic of research. Various approaches to hydration models have been developed. For example, numerical models [11] calculate the product composition of cement hydration from the chemical equations of the reaction between each component of cement and water. Mathematical expression models establish the relationship between the hydration rate and the hydration degree based on the bound water, the variation in the hydration heat, etc. Examples include the model of three basic processes proposed by Krstulovic and Dabic [12] and the shrinking-core model proposed by Tomosawa [13]. Although the rehydration process has a significant impact on the long-term performance of concrete, there have been few studies related to rehydration models. Huang et al. modeled the rehydration of unhydrated cement on the basis of the hydration of single clinker components and nuclear magnetic resonance (NMR) tests [14]. The results showed that the hydration degree of the cement paste increased from 67% to approximately 82%, which was much higher than that for the case without extra water. Moreover, the capillary porosity of the paste adjacent to the crack surfaces decreased to less than 4%.

In this study, rehydration tests of paste samples with low water–binder ratios were performed to examine the effects of silica fume, the curing conditions, and the ambient temperature on the rehydration degree. The rehydration degree refers to the increase in the hydration degree of specimens that were placed in water. In addition, it can be calculated by the difference between the hydration degree after rehydration and the hydration degree before rehydration. The variation in the compressive strength of undamaged ultrahigh performance concrete after natural immersion was measured, and the potential impacts of rehydration on the macroscopic performance were analyzed. These results were used to develop a rehydration model. The above contributions should provide a reference for research on the long-term performance of cement-based materials with low water–binder ratios in water.

2. Experiments

2.1. Mixing ratio

In this test, 42.5# ordinary Portland cement (OPC) was adopted; the C_3A, C_4AF, C_2S, and C_3S contents were 7.4%, 8.9%, 18.1%, and 60.5%, respectively. The microsilica fume contained more than 90% SiO_2 with an average diameter of 0.31 μm. The superplasticizer had a water-reducing rate of 29% and a solid content of 31%. The three diameter ranges of quartz sand particles were 0.16–0.315 mm, 0.315–0.625 mm, and 0.625–1.25 mm with a mixing ratio of 1:4:2. The tensile strength, diameter, and length of the short thin steel fibers were 2800 MPa, 0.22 mm, and 13 mm, respectively. Six different mixing ratios were used in this test, as presented in Table 1. The concrete sample with the mixing ratio LWB0 had dimensions of 100 mm × 100 mm × 100 mm and was used to determine the compressive strength. Paste samples with other mixing ratios had dimensions of R10 mm × 20 mm and were used to measure the bound water.

2.2. Test methods

The molds of the formed samples were removed after 24 h of curing at room temperature. Then, the samples were placed in a steam-curing box at 75 °C for another 72 h of curing; both the heating and cooling rates were maintained at 15 °C/h. The samples were finally placed and stored in a standard curing room (T = 20 °C and RH > 95%) for curing for up to 28 d. When the curing was finished, the samples were immersed in water for the rehydration tests. The samples were removed for measurements after a certain period of time and then immersed in acetone to suspend the hydration reaction.

The bound water was measured by the loss-on-ignition method at a calcination temperature of 950 °C. The amounts of bound water were measured in samples immersed for 0, 7, 14, 28, 56, 90, and 180 d. The results were used to develop a rehydration model and analyze the effects of the silica fume, water–binder ratio, and ambient temperature on rehydration. In order to further analyze the impact of rehydration on the performance of ultrahigh performance concrete, a natural immersion test of the LWB0 concrete sample was conducted in an immersion environment at 20 °C. After a certain immersion time, the compressive strength was measured.

3. Kinetic model of the hydration of cement-based material

The kinetic model of the hydration reaction proposed by Krstulovic and Dabic [12] describes the relationship between the hydration degree of cement and the reaction time. In general, the early stage of the hydration reaction is considered to be controlled by nucleation and crystal growth. The intermediate stage is controlled by a phase-boundary reaction, and the final stage is mainly regulated by diffusion. Eq. (1) expresses the model controlled by diffusion:

$$d\alpha/dt = 3/2k_3(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}] \tag{1}$$

where α, t, and k_3 are the hydration degree, rehydration time, and hydration reaction rate constant, respectively. k_3 ignores the impact of the particle diameter but is affected by factors including, the hydration conditions, etc.Compared with cement hydration, rehydration mainly differs in two aspects. First, rehydration occurs in hardened cement, and unhydrated cement particles may be surrounded by the gel generated during the initial hydration. Second, the water for the rehydration reaction penetrates from the outside. Therefore, the rehydration reaction is primarily dominated by diffusion, and the rehydration process can be described by a model in which k_3 is the rehydration reaction rate constant. However, the rehydration model does not include parameters that measure the diffusion rate. Hence, the effective diffusion coefficient of water in the CSH gel D_e was introduced to further modify the model for the diffusion process. D_e is essentially affected by the hydration degree and satisfies the equation $D_e = D_{e0}\ln(1/\alpha)$ [13,15].