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Effects of Curing Temperature on Autogenous Shrinkage, Relative Humidity, Pore Structure of Cement Pastes

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Abstract

A low water/cement ratio leads to autogenous shrinkage of cement paste at an early age. This autogenous shrinkage is related to the change of relative humidity in the pore structure that is formed during the hydration process. The relationship between autogenous shrinkage and relative humidity change are relatively well defined today, but the effects of temperature on autogenous shrinkage, relative humidity, and pore structures have been studied less systematically. This study focused on correlating alterations of these properties of cement paste hydrated at constant temperatures of 20, 40, and 60 °C. The test results clearly indicate that increasing curing temperature resulted in increased porosity, particularly for pores between 5 to 50 nm as measured by MIP, and increased autogenous shrinkages, as a consequence of a reduction of relative humidity at early ages.

Keywords : temperature, autogenous shrinkage, relative humidity, pore size distribution

1. Introduction

The relative humidity change in sealed cement paste results in physical and chemical transformations linked to hydration reactions. When cement is mixed with water, the pressure of the air entrapped in the paste is equal to the atmospheric pressure, i.e. 1 bar. However, with progress of the hydration process hydration products are formed of which the total volume is smaller than the initial volume of cement and water. The volume reduction is observed as pore volume and due to the increase of the pore volume the gas pressure in the pores decreases. With further hydration the hydration process will consume more pore water and, as a consequence, the relative humidity in the vapor-filled pores gradually decreases. This phenomenon is called self-desiccation and is the mechanism for autogenous shrinkage in cement paste[1)]. Therefore, the autogenous shrinkage is related to the change of relative humidity in the pore structure formed during the hydration process. The relationship between autogenous shrinkage and relative humidity change are relatively well defined today[2~5)], but the effects of temperature on autogenous shrinkage, relative humidity, and pore structures have been studied less systematically.

This study focused on correlation alternations of these properties of cement pastes hydrated at constant curing temperatures of 20, 40, and 60 °C. This paper presents the results of an experimental study on the effects of curing temperature on the autogenous shrinkage and the relationship between autogenous shrinkage and relative humidity in pore structure that is formed during the hydration process. It is intended to get a better understanding of the factors that influence autogenous shrinkage of concrete subjected to curing conditions that might occur in practice and to contribute to a concept for prediction of autogenous shrinkage.

2. Materials and methods

An ordinary Portland cement, containing 52 % C_3S, 24 % C_2S, 9% C_3A, 9% C_4AF, was used. The Blaine specific surface was 3310 cm^2/g. Cement paste was proportioned to have a water to cement ratio of 0.33.

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The size of the specimens for the autogenous shrinkage and relative humidity measurement was 40 x 40x 160 mm[6]. All the specimens kept in a temperature and RH controlled chamber during the testing. For the autogenous shrinkage measurement two types of sensors were used, as shown in Fig. 1. An ammeter (EX-502, Keyence) sensor was used for the measurements at 60 °C. A laser transducer sensor (LB-62, Keyence) was used for the measurements at 20 and 40 °C. For relative humidity measurements, the measuring position was in the center of the sealed 40 x 40 x 160 mm specimen. The measurements were done using the relative humidity sensor (AY-22, Keyence) with a working range within 0-100 °C, 15-97 %RH. The RH-sensor was calibrated by saturated salt solutions and has a resolution of 1 and 3 %RH. The experimental setup is shown in Fig. 2.

For measuring the porosity, cylindrical specimens with a radius of 50 mm and height 100 mm were prepared. The paste specimens were cut into approximately 5 mm cubes using a diamond saw. Specimen fragments were immediately immersed in acetone for 1 day to prevent further hydration. Thereafter, all the fragments were D-dried for about 2 weeks prior to testing. The porosity was determined using mercury intrusion porosimetry (Micromeritics Auto Pore 9420). The pressure applied was from zero to 240 MPa. The ages of the specimens for the porosity measurement were 6, 8, 12, 24, 72, and 120 hours after initial setting time. Cylindrical specimens were seal-cured and also kept in a temperature and RH controlled chamber before the testing.

3. Results

3.1 Autogenous shrinkage

Autogenous shrinkage of the pastes cured at different temperatures is shown in Fig. 3. Measurements started after initial set time. The initial set time of the pastes determined by the Vicat needle device are 110 min. at 60 °C, 136 min. at 40 °C, and 168 min. at 20 °C. The initial set time decrease with increasing the curing temperature. As shown in Fig. 3, the paste cured at high temperature exhibited a greater autogenous shrinkage at early ages. The autogenous shrinkage of the paste cured at 60 °C is about 500 x 10^{-6} at 12 hours and then it levels off. After 48 hours, however, the autogenous shrinkage of the paste cured at 60 °C is smaller than that at 20 °C. The paste cured at 20 and 40 °C exhibited a small expansion directly after initial setting time. This expansion, however, was soon canceled out by the autogenous shrinkage.

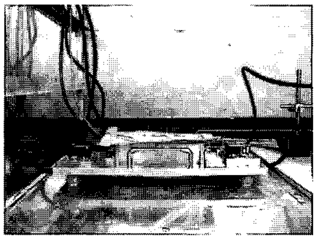

Fig. 1 Autogenous shrinkage measurement

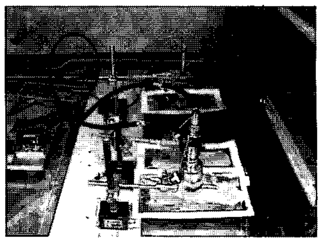

Fig. 2 Relative humidity measurement

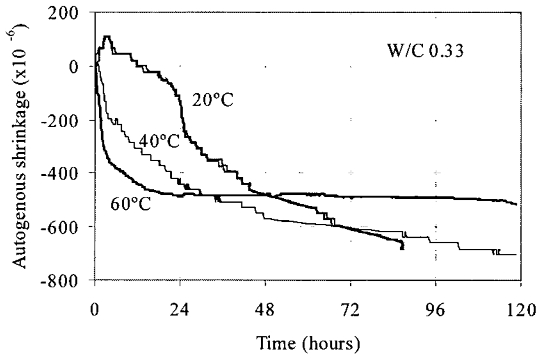

Fig. 3 Autogenous shrinkage vs. time curve

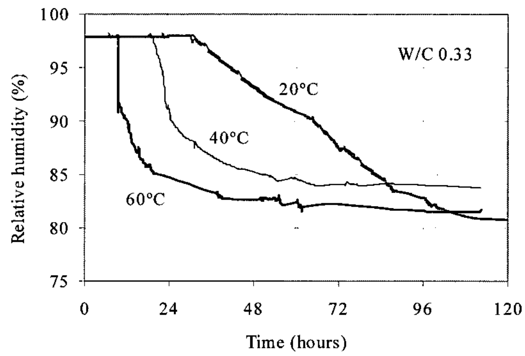

Fig. 4 Relative humidity vs. time curve

3.2 Relative humidity

Fig. 4 shows the change of the relative humidity in the pastes. The relative humidity of paste cured at higher temperature drops faster than that of cured at 20 °C. However, at 60 °C the relative humidity levels off at 24 hours and its absolute values in 96 hours are smaller than that cured at 20 °C.

3.3 Microstructure

Fig. 5 shows the development of total pore volume of the paste cured at different temperature. The total pore volume decreases linearly with the progress of hydration in the observed period. At higher temperatures, the volume of pores

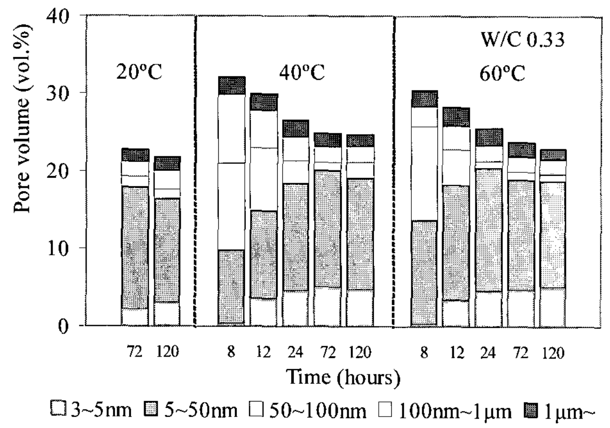

Fig. 5 Total porosity vs. time

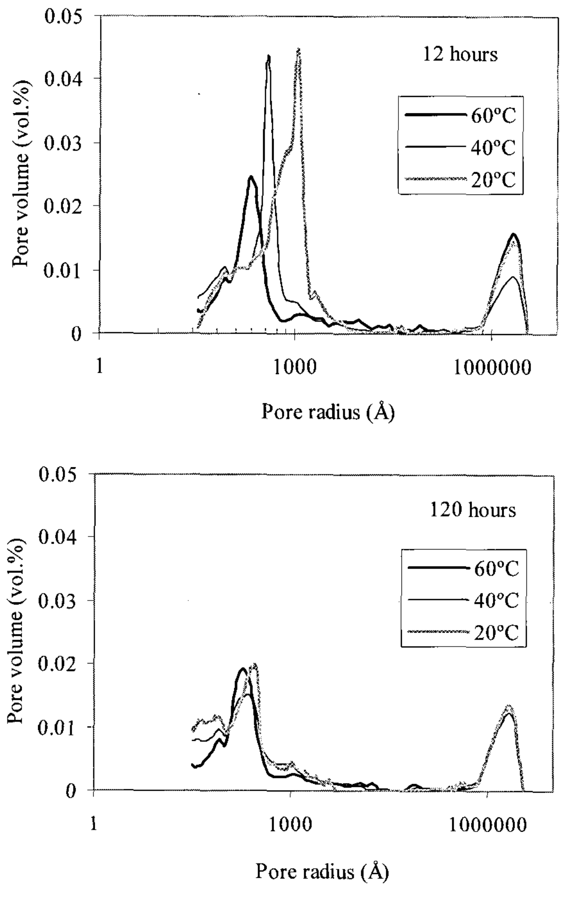

Fig. 6 Pore size distribution

between 5 to 50 nm increases at early ages.

Fig. 6 shows the pore size distribution curves of the pastes at 12 hour and 120 hours. It can be seen that the pore size distribution was significantly changed with the increase of the curing temperature at early ages. With the increase of temperature the number of pores with a larger pore radius decreases and smaller radius increase. This suggests that as the hydration process proceeds, pore sizes are reduced and the peak of the distribution curve is shifted toward the direction of smaller pores. However, at 120 hours, the pore structure was not changed with the temperatures.

4. Discussion

4.1 Autogenous shrinkage vs. relative humidity

Based on the curves shown in Figs. 3, 4, it is possible to explain the autogenous shrinkage as a function of the relative humidity. Fig. 7 shows the relationship between the relative humidity change and autogenous shrinkage. At 20 °C curing, the autogenous shrinkage occurring between 12 and 24 hours were not related to relative humidity change. However, after 24 hours the autogenous shrinkage varies linearly according to relative humidity, about 50 μ/%RH. At higher temperature the linear relationship between the relative humidity and autogenous shrinkage was also found, but about 20.5 μ/%RH at 40 °C and about 4.8 μ/%RH at 60 °C. The autogenous shrinkage of cement pastes cured at higher temperature at early age increase greatly without the change in relative humidity because a substantial proportion had already increased due to chemical shrinkage[7].

In Fig. 4, the relative humidity of cement paste cured at higher temperature drops faster than that at lower temperature. However, another literatures[8, 9] reported the internal temperature difference which causes an increase of about 0.3 %RH/°C for the concrete with W/C of 0.3. In Fig. 4, the relative humidity in paste ranges roughly between 80% and 100%. It was shown that these results could be simulated by application of the Kelvin's law[10]. In Koender[11], it was proposed to calculate the autogenous shrinkage of hardening cement paste from the reduction of the pore pressure which is associated with the decreasing relative humidity in the gradually emptying pores. The relative humidity in the gradually emptying pore space is an unknown parameter which must be calculated from the actual moisture state of the hardening cement paste. The water content of a capillary system depends on the moisture content of the surrounding air and the capillary structure of the pore system[12].

4.2 Relative humidity vs. small porosity

As hydration process, the capillary pores will be emptied, the relative humidity will decreased. For prediction of the relative humidity in the hardening cement paste, the pore structure of the space where RH changes must be investigated. The porosity emptied at relative humidity above 60 % arises from spaces between the original cement grains that have not become filled with cement hydrates and may be regards as capillary porosity[13]. In the literatures[10, 14], it has estimated that the meniscus effects can be precisely evaluated from the Laplace law and the Kelvin law for a meniscus radius greater than 5 nm. In this paper, it was assumed that the small porosity consists of pores in the range of 5 to 50 nm. Normally the small porosity increases with hydration and thus is greater at early ages when curing at higher temperatures as shown in Fig. 5. The smaller pores could induce higher capillary pressure which will be the driving force for the increase of the autogenous shrinkage. Fig. 8 shows the relationship between the relative humidity change and the small porosity of cement pastes. It can be seen that the relative humidity decreases with the increasing of small porosity, particularly at 20°C curing. However, at higher temperature the reduction of relative humidity was not sensitive to the small porosity change like that on autogenous shrinkage.

5. Conclusions

From the investigation on the effect of curing temperature on the autogenous shrinkage, relative humidity, and microstructure in cement pastes, the following conclusions can be drawn.

1) The autogenous shrinkage is significantly affected by temperature. It is found that the autogenous shrinkage and the rate of autogenous shrinkage development are higher at early age when the temperature is higher. However, at later stage autogenous shrinkage at 60 °C was found lower than that at 20 °C.
2) The reduction of relative humidity is larger at early ages at higher temperatures. The relative humidity of paste falls in the range of 80~100 %.
3) The total porosity decreases with the progress of hydration in the observed period. However, at higher temperatures the volume of pores between 5 to 50 nm increases at early ages. The time for the increase of the pore volume is related to the age when the autogenous shrinkage levels off.

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