論文

EFFECTS OF PENETRATIVE CONDITIONS OF WATER FOR CURING ON PROPERTIES OF HARDENED CEMENT PASTE

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ABSTRACT: The effects of penetrative conditions of water for curing on properties of the hardened cement paste have been investigated. In the large size specimen with the low water-cement ratio (w/c) the normal water curing is not sufficient to complete the hydration throughout the whole specimen. Therefore, the different types of curing were used to investigate the properties at any layers of specimen. The curing with water containing the AE-admixture of low surface tension energy (AE-water curing) and the curing with water under high pressure (10 MPa-water curing) were obviously observed to increase the degree of hydration and decrease the degree of self-desiccation in the specimen with low water-cement ratio.
KEYWORDS: water penetrating, hydration, self-desiccation, 10 MPa-water curing, AE-water curing.

1. INTRODUCTION

The properties of the hardened paste are based on the reaction between cement and mixed water. The penetrating of water, added from outside, is important in order to increase the degree of the hydration. However, in the large size specimen with a low w/c ratio, the curing water cannot penetrate to completely fill pores formed during the hydration reaction thus causing different degree of the hydration and degree of the self-desiccation in the surface layer and in the bulk of the specimen. For this reason, the significance of curing conditions is considered and discussed.

In this paper, the effects of penetrative conditions of curing water on the properties of the hardened cement paste are experimentally investigated in the aspects of the hydration reaction, the self-desiccation and the strength. The four different types of curing water were used to cure the specimen: the normal curing water, the curing water containing AE-admixture of low surface tension energy, the curing water under high pressure and wrapping. The specimens with different water-cement ratio were prepared to study the capability of penetration of curing water into the specimen at any layers from the surface exposed to curing. Additionally, the mortar specimens were also prepared to study the effects of penetration of curing water on the strength by coring samples at any layers of the specimen.

2. EXPERIMENTS

2.1 MATERIALS

The material used in these experiments was ordinary Portland cement shown in Table 1. For the compressive strength test of mortar specimen, the crushed sand is used as the fine aggregate.

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An air-entraining and high range water-reducing agent was used for the specimens with w/c of 0.25. Alkyl-ether based air-entraining agent in accordance with JIS A 6204 (the surface tension of AE-admixture of 1 % mixture with water is about 38 dyne/cm) was added to water (AE-water curing) to reduce the surface tension energy.

Table 1. Mineral and phase composition of cement

Cement	Fineness (cm^2/g)	Specific Gravity	Mineral Composition (%)					Loss on ignition
			C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	
NPC	3290	3.16	62.4	13.5	8.3	8.5	2.4	2.01

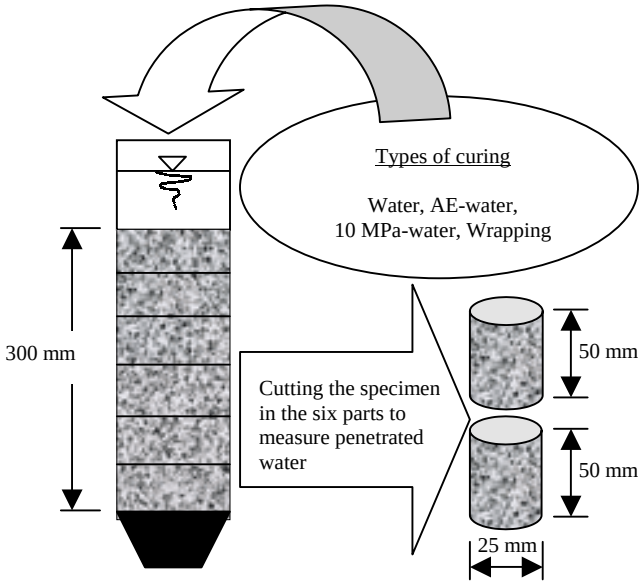

Fig.1 Measuring method of the penetration of the water in hardened cement paste

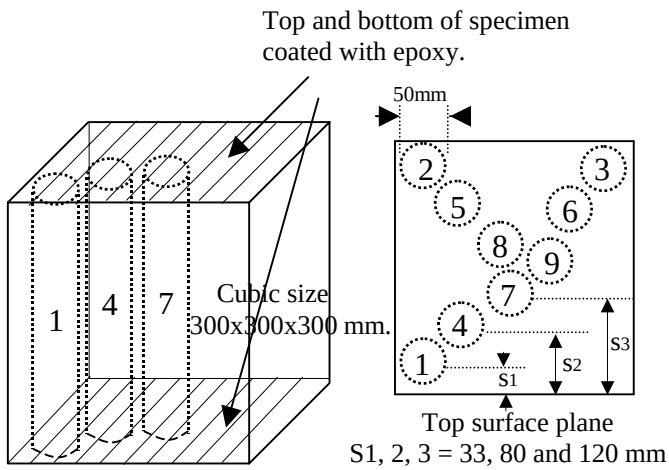

Fig.2 Coring specimen with diameter of 50 mm for penetration strength test

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Test method of the penetration of water in hardened cement paste

Cement pastes with w/c of 0.25, 0.40 and 0.6 were placed in the acrylic vessel with diameter of 25 mm up to the paste height of 300 mm. The specimens were cured in the four different types of curing water after the age of 1 day until the measuring ages. The measuring of the penetrated water was conducted after 3, 7 and 28 days by cutting the specimen in the six parts as shown in Fig. 1. The masses of hardened cement pastes at room temperature were denoted as M_{21}^{o}(g). After that, the specimens were stored for 24 hours in an oven at temperature of 105°C and their masses were measured (M_{105}^{o}). Finally, the specimens were stored for 24 hours in an oven at temperature of 950°C and then their masses were measured (M_{950}^{o}).

2.2.2 Test method of effects of the penetration of water in mortar on strength

Mortars with w/c ratio of 0.25, 0.4 and 0.6 were placed in the moulds (size 300 x 300 x 300 mm) and then stored in the curing room for 24 hours. After that taking them out from the moulds, the top and the bottom of the specimens were coated with epoxy, accepted wrapping substance, to protect the penetration of the water through these surfaces. The coated specimens were exposed

to the curing water of types: 1) Normal water curing, 2) AE-water curing, 3) 10 MPa-water curing and 4) Wrapping at temperature $20 \pm 3^{o}C$ and then after 28 days cored the specimens with diameter of 50 mm by using coring machine as shown in Fig. 2. The cored samples were cut in 3 parts and pressed by stress-strain test machine until broken.

2.3 CALCULATIONS

The total volume of paste per unit mass of cement (V_p) is given by Eq. 1[2]

$$V_p = 1/G_c + (w/c)/D_w \quad cm^3/\text{g} \tag{1}$$

where G_c is specific gravity of cement = 3.16 g/cm^3, w/c is water cement ratio and D_w is density of water = 1 g/cm^3.

The volume of hydration product per unit mass of cement reacted (V_{hp}) is obtained by considering the special case of a fully hydrated paste having the critical water-cement ratio as given by Eq. 2[2]

$$V_{hp} = (1/G_c + (w/c^*)/D_w) \times \alpha \quad cm^3/g \tag{2}$$

where w/c* is critical value of w/c = 0.38 below which complete hydration cannot occur and α is the degree of hydration.

The volume of unreacted cement per unit mass of cement (V_{uc}) is given by Eq. 3[2]

$$V_{uc} = 0.3164(1-\alpha) \quad cm^3/g \tag{3}$$

The volume of the gel water (V_g) is given by Eq. 4[2,3]

$$V_g = 0.21\alpha \quad cm^3/g \tag{4}$$

Non-evaporable water (NE.W) is given by Eq. 5[2,3]

$$NE.W = \frac{M_{105^\circ} - M_{950^\circ}}{M_{950^\circ}} \quad cm^3/g \tag{5}$$

where M_{105° and M_{950° are the masses of the specimen after heating for 24 hours at 105°C and 950°C, respectively.

Degree of hydration (D.H.) is given by Eq. 6[2,3]

$$D.H.(\alpha) = \frac{(M_{105^\circ} - M_{950^\circ})}{M_{950^\circ}} \times 1/23 \tag{6}$$

where 23 % is the content of the non-evaporable water at complete hydration.

Evaporable water (E.W.) is given by Eq. 7[2,3]

$$E.W. = \frac{M_{21^\circ} - M_{105^\circ}}{M_{950^\circ}} \quad cm^3/g \tag{7}$$

where M_{21° is the mass of the specimen at 21°C.

Degree of self-desiccation (D.S.) for the cement investigated in this experiment is defined by Eq. 8[6]

$$D.S. = \left(1 - \frac{E.W./V_p}{1-(V_{hp} - V_g + V_{uc})/V_p}\right) \times 100\,\% \tag{8}$$

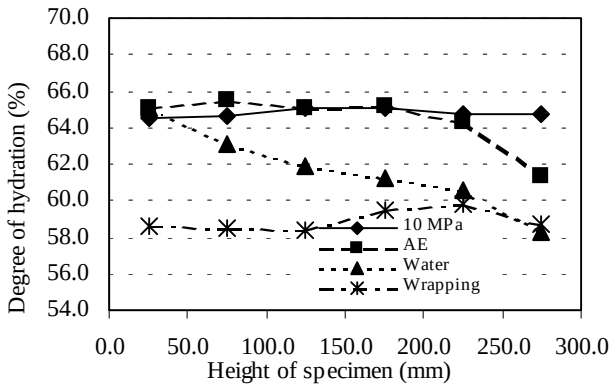

Fig.3 Relation between the degree of the hydration and the height of the specimen with w/c 0.25 after 28 days

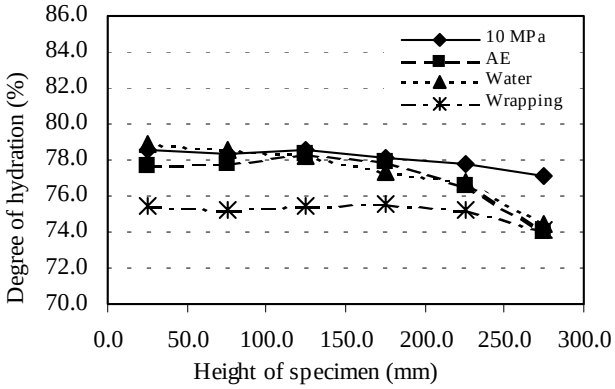

Fig.4 Relation between the degree of the hydration and the height of the specimen with w/c 0.40 after 28 days

3. RESULTS AND DISCUSSION

3.1 DEGREE OF THE HYDRATION OF HARDENED CEMENT PASTE

In the cement chemistry, the term 'hydration' denotes the totality of the changes that occur when anhydrous cement, or one of its constituent phases, is mixed with water. The chemical reactions taking place are generally more complex than simple conversions of anhydrous compounds into the corresponding hydrates. A mixture of cement and water in such proportions that setting and hardening occur is called a paste. Setting is stiffening without significant development of compressive strength, and typically occurs within a few hours. Hardening is significant development of compressive strength, and is normally a slower process. If no water movement to or from the cement paste is permitted the reactions of hydration result in the lack of water and the relative humidity within the paste decreases. This is known as the self-desiccation. Since gel can form only in water-filled space, the self-desiccation leads to a lower degree of the hydration compared with a moist-cured paste.

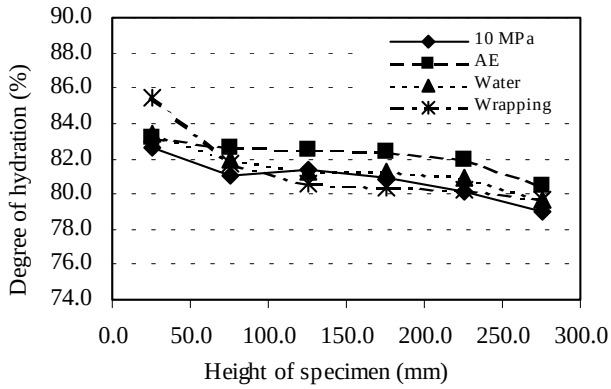

Fig.5 Relation between the degree of the hydration and the height of the specimen with w/c 0.60 after 28 days

The content of non-evaporable water, relative to that in a fully hydrated paste of the same cement, was used as a measure of the degree of the hydration following Powers-Brownyard model. The degree of the hydration, calculated from Eq.6 on different heights of the specimen with water-cement ratios 0.25, 0.40 and 0.60 after 28 days are shown in Fig. 3, 4 and 5. The different degree of hydration, especially in the specimen with the low water-cement ratio were found for the four types of curing used in this investigation. It could be seen that for the specimen with w/c of 0.25 cured by AE-water or 10 MPa-water the hydration progressed more than in the one subjected to the normal water curing as shown in Fig.3. However, for the 10MPa-water cured specimen the degree of hydration of about 65 % is constant regardless the height, may be due to possibility of the curing water to penetrate throughout the specimen. For the specimen under AE-water curing, the degree of the hydration is about 65 % for less than 175 mm from surface, while it slightly decrease between 175 and 275 mm from surface. The degree of the hydration in the

specimen with water-cement ratio 0.40 and 0.60 is not so affected by changing the types of water curing as shown in Fig.4 and 5.

3.2 SELF-DESICCATION OF HARDENED CEMENT PASTE

Most of the hydration products are initially colloidal and as hydration continues the surface area of the solid phase largely increases and a large amount of free water can be absorbed through this surface. However, in the sealed systems where the absorption and desorption of water are not allowed, only previously added water will take part in the reaction of hydration and the relative humidity within the paste will decrease. This is known as self-desiccation. Since gel can form only in water-filled space, self-desiccation leads to a lower degree of hydration comparing to a moist-cured paste. The amount of free water in hardened cement bulk gradually decreases as the hydration reaction of cement minerals proceeds and fine pores are formed in hardened cement. The degree of self-desiccation is calculated using Eq.8:

$$D.S. = [1 - V(c.w. + g.w.)/V(c.p. + g.p.)] \times 100\ \%$$

where c.w. = capillary water, g.w. = gel water, c.p. = capillary pore, and g.p. = gel pore. The degree of self-desiccation depends on the capability of curing water to fill pore created by hydration.

The degree of self-desiccation, calculated from Eqs.1-8, for the different types of curing at each height of the specimen is shown in Fig.6, 7 and 8. The type of curing has a significant effect on the degree of the self-desiccation, especially in the low water cement ratio as can be seen in Fig.6. Under the curing with water under high pressure (10 MPa-water), water was able to penetrate more deeply into the specimen to fill pore created due to the hydration than under the other types of curing. The experimental results showed that the 10MPa-water curing comparing with sealed curing (wrapping) was able to reduce the degree of self-desiccation around 8 %, 4 % and 2 % for specimen with w/c ratio 0.25, 0.40 and 0.60, respectively.

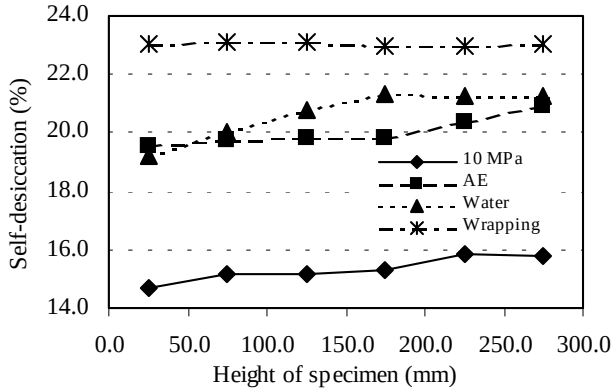

Fig.6 Relation between the degree of self-desiccation and the height of the specimen with w/c 0.25 after 28 days

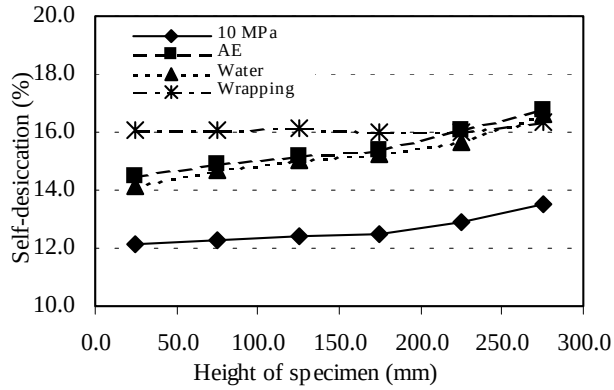

Fig.7 Relation between the degree of self-desiccation and the height of the specimen with w/c 0.40 after 28 days

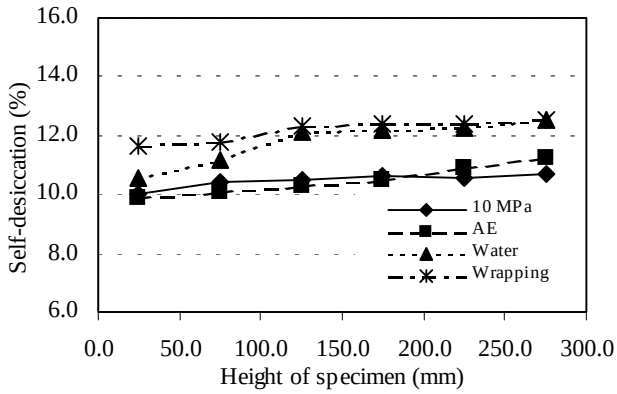

Fig.8 Relation between the degree of self-desiccation and the height of the specimen with w/c 0.60 after 28 days

3.3 EFFECT OF PENETRATING WATER ON THE STRENGTH

It is known that large range of self-desiccation occurs in the cement paste with low water-cement ratio because water from outside cannot penetrate in the central part of the specimen. As shown in Fig.9, for the specimen subjected to high pressure water curing (10MPa-curing), the highest strength comparing to the other types of curing was found. This effect could be ascribed to the higher degree of hydration and the lower degree of self-desiccation, subsequently presented in section 3.1 and 3.2. In the specimen treated by the AE-water curing, alkyl-ether based air-entraining agent added to water to reduce the surface tension energy, water was able to penetrate more deeply into the specimen than into the normal water curing or wrapping treated specimens. Thereby, the higher degree of hydration leads to the higher strength as well.

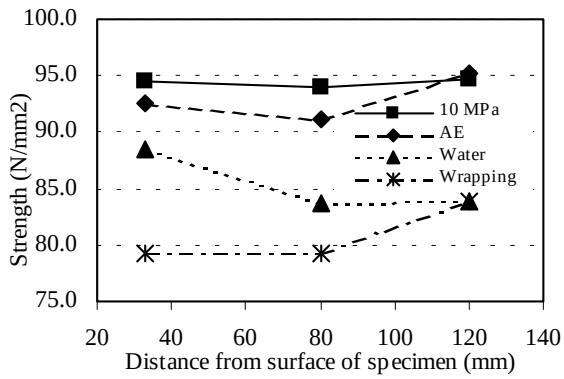

Fig.9 Relation between the strength and the penetrated water distance of the specimen with w/c 0.25 after 28 days

4. CONCLUSIONS

The water capability of penetrating into the specimen during the hydration has a large influence on the degree of the hydration, the self-desiccation and the strength of the specimen, especially for the low water cement ratio. Under normal water curing, the water cannot penetrate to the parts of the specimen far from the surface exposed to curing. Thus, the degree of the hydration in the bulk of a specimen is smaller than in the surface area. However, the same degree of hydration in the bulk and in the surface area is achieved for specimen treated by high-pressure water curing. AE-water curing shows the same effect only until the distance of 175 mm from the surface. In addition, the high-pressure water curing reduces the degree of self-desiccation and increases the strength of the specimen.

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