Effects of Low Surface Tension Water Curing on Degree of Hydration

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Abstract

Effects of penetrative curing water on degree of hydration were investigated. In a large-size specimen with a low water-cement ratio (W/C), both the mixing water and penetrative water at standard water curing are not sufficient to complete the hydration of the entire specimen. Therefore, curing conditions were studied to improve the properties of the specimens at any distances from the surface during hydration process. When W/C is low, specimens cured with water containing AE-admixture, which has low surface tension, was able to improve the degree of hydration more than those subjected to the standard water curing.

Keywords: Water penetration, Hydration, Chemical shrinkage, Self-desiccation, Low surface tension water curing

1. Introduction

The reaction between cement and mixing water causes difference of the hardened paste. In the case of high strength concrete, the mix proportion does not have enough water to complete the hydration. The penetrating water from outside is important to continue the hydration reaction. However, in the low water-cement ratio (w/c) and large specimen, the curing water cannot completely penetrate to fill pores formed during the hydration reaction thus causing different degree of hydration and degree of self-desiccation in the surface layer and in the bulk of the specimen1)-3). For this reason, influence of dynamic character of high strength concrete is considered in these experiments. Additionally, possibility of applying the same method of curing and testing on the normal strength concrete and on the high strength concrete will be discussed. Proper curing is essential to achieve a discontinuous pore structure, which is the discontinuity in capillary pore network that formed during the hydration in concretes. With W/C lower than 0.45, the discontinuous pore structure will be formed easily. The discontinuous pore structure is important for a durable concrete, as it will limits both water and ion ingress into the concrete structures4). Based on the measurement of permeability, Powers has concluded that capillary pore discontinuity is a function of both W/C and degree of hydration: a higher W/C requiring longer hydration time to achieve a discontinuous capillary pore structure5). He, therefore, suggested curing concretes until this discontinuity is achieved, as further "saturated" curing would result in vain unless any additional water flows into the concrete6). Self-desiccation takes place when the pores created by the hydration are not supplied with water from the surrounding environment during the curing process1), and empty pores are created within the microstructure8).

In this paper, effects of low surface tension water curing on degree of hydration were experimentally investigated. The results of experiment were expressed by measuring the amount of water penetrated into the hardened cement paste at various distances from the surfaces. The measurement was compared with chemical shrinkage, degree of hydration, self-desiccation and non-evaporable water. Additionally, SEM was used to investigate the hydration products of specimens at any types of curing.

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RECEIVED 24 June, 2005
ACCEPTED 3 April, 2006

2. Materials

An ordinary Portland cement with characteristics as shown in Table 1 was used. For the compressive strength test of mortar, the crushed sand (density: 2.58 g/cm^3, absorption: 2.28 %) was used as a fine aggregate. An air entraining and high range water-reducing agent were used for specimens with a W/C of 0.2, 0.25 and 0.3. A Silicone Antifoaming Agent was added to reduce the air content in all type of pastes. The air content of pastes was decreased less than 0.1%. Alkyl-ether based air-entraining agent of 1% added with water, in accordance with JIS A6204 of, was used in AE-water curing to reduce surface tension of curing water. This amount is quite larger than the case of concrete mixture. The surface tension of water for AE-water curing was approx. 38 mN/m which is nearly one half of that used in standard water curing. It was measured by Du Nouy surface-tension meter at a room temperature of 22°C and 50 % RH.

3 Experimental procedures

3.1 Test method for chemical shrinkage

Mass of a glass vessel was measured with accuracy of 0.1g. This value was referred to as M_1(g). The cement paste with a W/C of 0.2, 0.3, 0.4 and 0.6 were placed in the glass vessel with a thickness of approx. 10mm in height, and then the total mass of cement paste and the vessel were measured with an accuracy of 0.1g. This value was referred to as M_2(g). The vessel was filled slowly with water in order to prevent the disturbance of the interface, and then a measuring pipette was inserted perpendicularly into the sample vessel through a rubber plug. Subsequently water was added from the upper inlet of the measuring pipette by a funnel or washing bottle to a measuring range, and then sealed the upper parts of measuring pipette with a paraffin wrap and this specimen was stored in the curing room as shown in Fig.1. The initial water level in the pipette was read with an accuracy of 0.05 ml. This value was

Table 1 Physical properties and mineral composition of cement

Cement	Fineness (cm^2/g)	Density (g/cm^3)	Mineral Composition (mass%)					Ig. Loss (mass%)
			C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	
OPC	3290	3.16	62.4	13.5	8.3	8.5	2.4	2.01

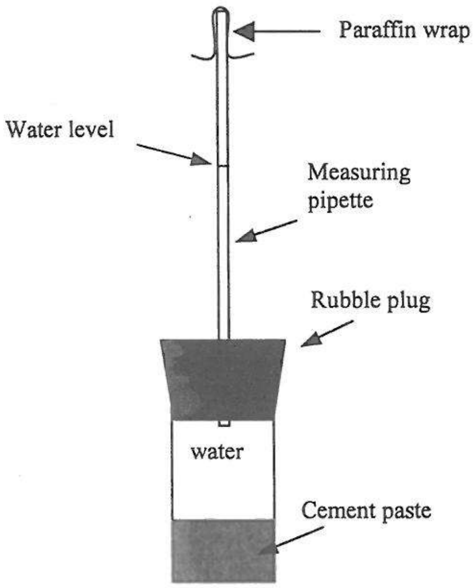

Fig.1 Measuring method of chemical shrinkage

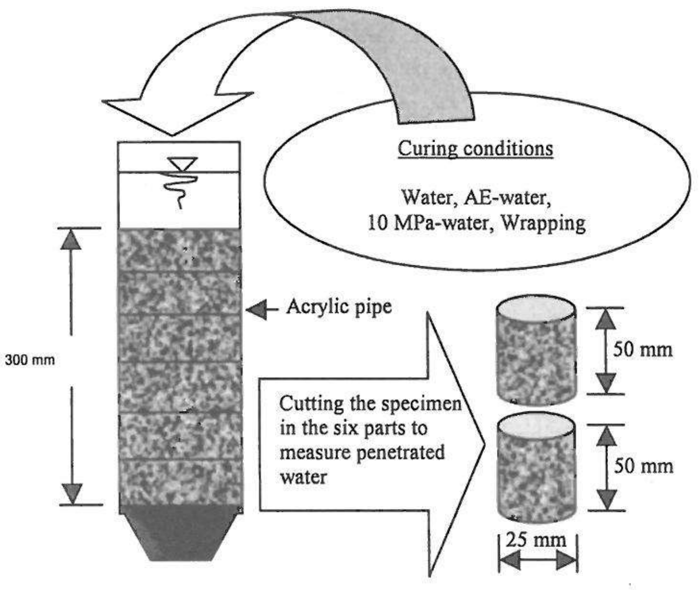

Fig.2 Measuring method of the penetrative curing water in hardened cement paste

referred to as H_0 (ml) when starting the measurement. Subsequently the values of water level in the pipette were read during hydration. These values were referred to as H_n (ml). The chemical shrinkage of hardened cement paste can be calculated using Eqs.(1) and (2).

3.2 Test method for water penetration in hardened cement paste

In this test method, the masses of each hardened cement pastes, as prepared at a room temperature 22°C, were measured by M_{21}(g). Subsequently, the specimens were stored for 24 hours in an oven at a temperature of 105°C and their masses were measured again (M_{105}). Finally, the specimens were stored for 24 hours in an electric furnace at a temperature of 950°C and then their masses were measured (M_{950}).

Cement pastes with a W/C of 0.25, 0.40 and 0.6 were placed in the acrylic pipe with a diameter of 25 mm and with a paste height of 300 mm. The specimens were cured after one day using four different types of curing: the standard water curing (Water curing), the low surface tension water curing (AE-water curing) and the sealed curing(Wrapping). The penetrated water was determined after 3, 7 and 28 days by cutting the specimen in six parts as shown in Fig.2 and their masses were measured.

In a specimen with a W/C of 0.4 and 0.6, bleeding generally occurs. However, it will be ignored at this stage because we used double mixing method for mixing cement paste to decrease the bleeding.

3.3 Curing conditions

1) The standard water curing (Water curing): The Water curing with a surface tension approx. 70 mN/m was used as the standard water curing.

2) The low surface tension water curing (AE-water curing): Alkyl-ether based air-entraining agent (MA101, MA202, MA775) of 0.1~2.0% were added with water to measure surface tension of AE-water as shown in Fig.3. The surface tension of AE-water which added MA101 is lowest so it was used in this thesis.

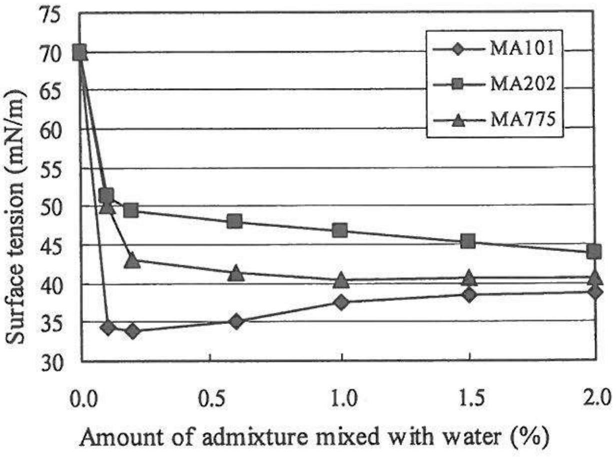

Fig.3 Surface tension of curing water at different type of AE mixed

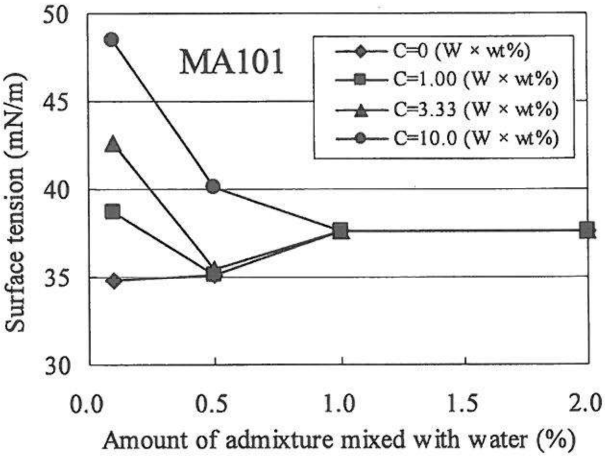

Fig.4 Surface tension of AE-water curing (MA101) at different amount of cement mixed

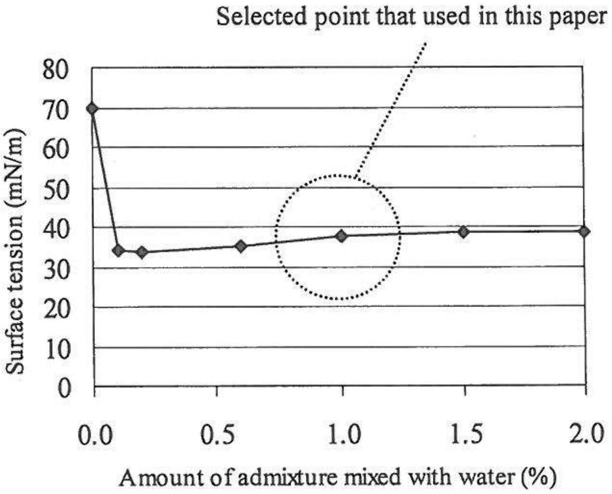

Fig.5 Surface tension energy of AE-water curing (MA101)

Furthermore, different amounts of cement (0, 1.0%, 3.33% and 10.0 % of water) were added in AE-water to examine an appropriate amount of AE admixture as shown in Fig.4. At the point of MA101 1% added with water, its surface tension did not change although it was added with different amounts of cement. For this reason, MA101 1% was added with water to be used in AE-water curing. Its surface tension was approx. 38 mN/m as shown in Fig5.

3) Sealed curing (Wrapping): plastic sheets were used to prevent the water movement through the surfaces.

4. Calculation

In this research, air content was reduced by adding Silicone Antifoaming Agent. Thus, in all cases of calculation, the air content was neglected.

The chemical shrinkage ratio of cement paste as described in 3.1 is given by Eq.(1)[1].

$$S_{hyn} = \frac{H_n - H_0}{V_p} \times 100\ (\%) \qquad (1)$$

where S_{hyn} is chemical shrinkage ratio at an age n, H_0 (ml) and H_n (ml) are water level at the start and at the age n and V_p is the volume of cement paste as given by Eq.(2)[1].

$$V_p = \frac{(M_2 - M_1) \times ((W/C)/D_w + 1/D_c)}{W/C + 1} \quad (ml) \qquad (2)$$

where M_2 is the mass of cement paste and glass vessel, M_1 is the mass of glass vessel, and D_c is density of cement = 3.16 g/cm^3.

The total volume of the paste per unit mass of cement ($V_{p/c}$) is given by Eq.(3)[2].

$$V_{p/c} = 1/D_c + (w/c)/D_w \quad cm^3/g \qquad (3)$$

where D_w is the density of water = 1 g/cm^3.

The volume of evaporable water per unit mass of cement ($V_{ew/c}$) is obtained by the amount of gel water and capillary water that can be evaporated at 105°C from the experiment (2).b, and given by Eq.(4)[2],[3].

$$V_{ew/c} = \frac{(M_{21^\circ} - M_{105^\circ})/D_w}{M_{950^\circ}} \quad cm^3/g \qquad (4)$$

where M_{21} is the mass of specimen at room temperature, $M_{105}{}^{0}$ and $M_{950}{}^{0}$ are the mass of the specimen after heating for 24 hours at 105°C and 950°C, respectively.

The non-evaporable water contains nearly all chemically combined water. This water has a vapor pressure lower than that of the ambient atmosphere and the quantity of such water is in fact a continuous function of the ambient relative humidity. The volume of non-evaporable water per unit mass of cement ($V_{new/c}$) can be determined by the loss upon drying at temperatures from 105°C to 950°C. It can be expressed by Eq.(5)[2],[3].

$$V_{new/c} = \frac{M_{105^\circ} - M_{950^\circ}}{M_{950^\circ}} \times V_n \quad cm^3/g \qquad (5)$$

Degree of hydration (DH) is obtained by the proportionality between the amount of non-evaporable water and the solid volume of the cement paste where the former volume can be used as a measure of the quantity of the degree of hydration. It can be expressed by Eq.(6).

$$DH(\alpha) = \frac{M_{105^\circ} - M_{950^\circ}}{M_{950^\circ}} \times 100/23 \quad \% \qquad (6)$$

where 23% is the content of non-evaporable water at the complete hydration[2],[3].

5. Results and discussion

5.1 Chemical shrinkage and degree of hydration

The chemical and physical changes that occur during hydration are accompanied by a reduction in absolute volume. The combined volume of the liquid and solid components after hydration is less than the initial volumes of water and anhydrous cement. The chemical shrinkage for cement paste in different water-cement ratio is shown in Fig.6. The change of chemical shrinkage for cement paste with W/C of 0.2 and 0.3 was very large at the early stage, but it decreased after approx. four or five days and became blunted after 28 days due to the

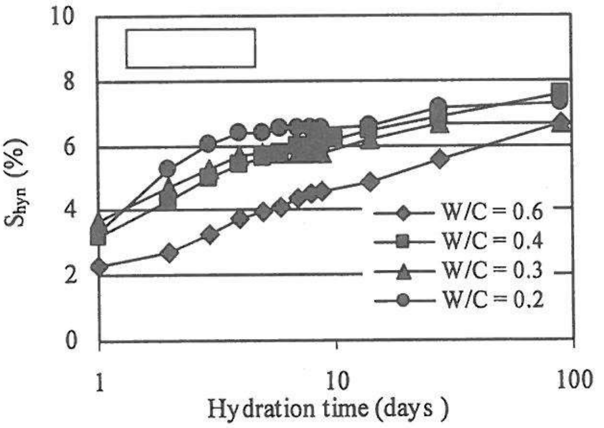

Fig.6 Relation between chemical shrinkage and hydration time

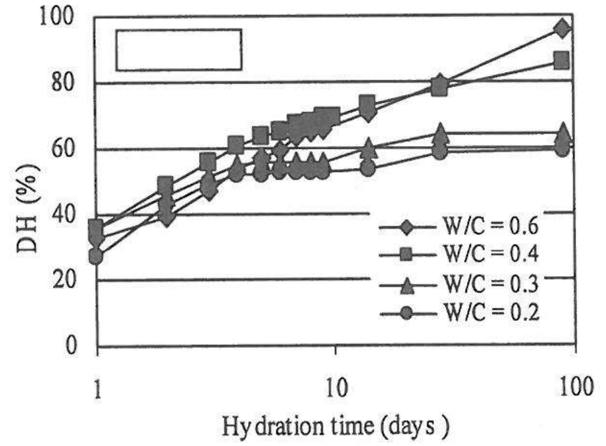

Fig.7 Relation between degree of hydration and hydration time (by chemical shrinkage)

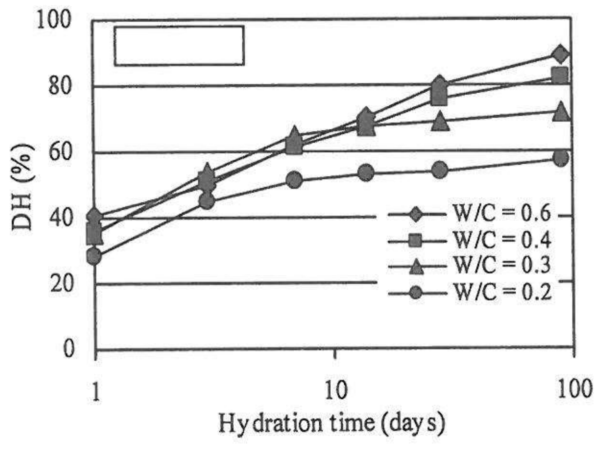

Fig.8 Relation between degree of hydration and hydration time (by non-evaporable water)

absence of enough water to react with cement. The change of chemical shrinkage of cement paste with W/C of 0.4 and 0.6 lasted slowly after 28 days until the hydration completed.

The degree of hydration (DH) for pastes with different water-cement ratios are shown in Fig.7 and Fig.8. DH is calculated by chemical shrinkage as shown in Fig.7 and DH can be also calculated from the quantity of non-evaporable water at that time as shown in Fig.8. DH for specimen with W/C of 0.2 and 0.3 increased very slowly after four or five days and finally becomes blunted after 28 days because of the lower content of water than that necessary to continue the hydration. The cement pastes with water-cement ratio of 0.4 and 0.6 seemed to have enough water to continue the hydration reaction even after 28 days.

5.2 Effect of W/C on degree of self-desiccation

The degree of self-desiccation of specimens with different W/C is shown in Fig.9. It was calculated from the hardened cement pastes with thickness of about 5 mm. The specimen with W/C of 0.2 shows larger range of self-desiccation during the hydration while that with W/C of 0.6 shows small range of self- desiccation. The change in DH became blunted after 28 days for the specimens with W/C of 0.2 and 0.3 because the near-surface-area became hardened and impenetrable for the water from outside. However, the change in DS still gradually increased because the inside of specimens there remained a little water to react with cement and the empty pores were formed. Likewise, in the specimen with W/C of 0.6, the near-surface-area became hardened during the hydration, and the water penetration to fill pores was partly obstructed. Therefore, it is thought that DS is gradually increased until 12% after 90 days as shown in Fig.9. The hydration increases the gel content and, in mature and dense paste, the capillaries may become segmented by the gels and interconnected solely by the gel pores. The absence of continuous capillaries may be

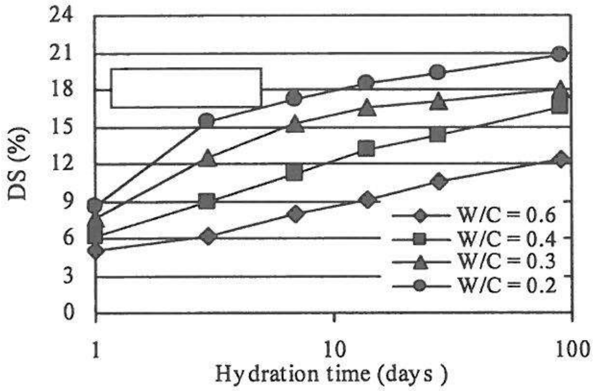

Fig.9 Relation between Self-desiccation and hydration time

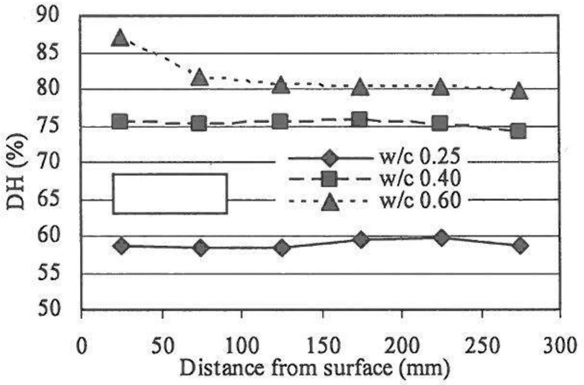

Fig.10 Relation between DH and distance from surface at 28 days (Wrapping)

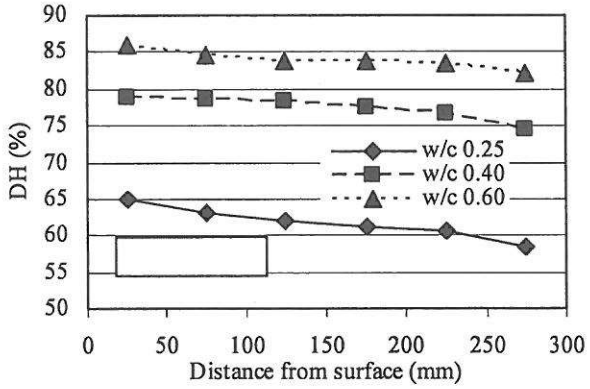

Fig.11 Relation between DH and distance from surface at 28 days (Water curing)

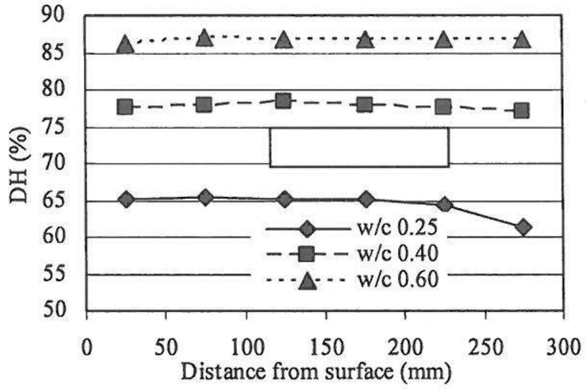

Fig.12 Relation between DH and distance from surface at 28 days (AE-water curing)

obtained by a combination of suitable W/C and moist curing of sufficiently long time. Thus, if a specimen with a low W/C is not given more water from the outside, the larger range of self-desiccation during hydration may occur.

5.3 Effect of distance with any types of curing on degree of hydration

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 according to Powers-Brownyard model. The degree of hydration calculated from Eq.(6) for any distance of the specimen with water-cement ratios of 0.25, 0.40 and 0.60 after 28 days are shown in Figs.10-12. The different degrees of hydration, especially in the specimen with a low water-cement ratio, were found for the three types of curing used in this investigation. It could be seen that for the specimen with W/C of 0.25 treated by AE-water curing, the hydration progressed more than those subjected to the standard water curing and sealed curing. However, for the specimen under AE-water curing, the degree of the hydration was about 65 % at a distance smaller than 175 mm, and then slightly decreased at larger distances of specimen as shown in Fig.12. The degree of hydration in the specimens with water-cement ratio of 0.40 and 0.60 was not so affected by the types of curing.

5.4 Effect of curing on hydration products of hardened cement paste investigated be SEM

As discussed before about the effects of water penetration into the low W/C specimens, the hydration reaction, non-evaporable water, and strength increase when water from outside penetrates into the specimens because of the penetrated water filled pores. May be it was made some products of hydration in the pores. Therefore, effect of curing (AE-water curing, Water curing) on hydration products of hardened cement paste with water-cement ratio of 0.25 after 28 days were investigated by Scanning Electron Microscope (SEM) as shown in Figs.13-14. The pores were concentrated investigation of hydration products by the SEM.

The different types of curing have effects with amounts and characteristics of pores as shown in Figs.13-14. The pores were filled with some product of hydration for the specimens curing with AE-water curing as clearly shown in Fig.14, but in case of Water curing the empty pores were occurred as shown in Fig.13.

6. Conclusions

1) For the hardened cement pastes with low W/C, such as W/C of 0.20, 0.25 and 0.30, it was found that the mixing water was unable to fill pores formed as a result of hydration reaction, and to penetrate into the central part of hardened cement pastes. A larger self-desiccation occurs in the middle part of specimens and the progress of hydration became slower.

2) At any distance from surface to middle part of the specimen with a low W/C, different degree of hydration and self-desiccation due to the lack of hydration were shown.

3) The low surface tension of AE agent, the AE curing water was able to penetrate well into the specimen, in the distance less than 175 mm from the surface area, more than that with the standard water curing, especially at a low W/C.

4) The high-strength concrete with low W/C that treated by the standard water curing clearly showed difference in degree of hydration and self-desiccation in the bulk and in the surface layer. Consequently, it is not suitable to apply the same curing condition as applied to the normal concrete because of the difference in surface tension. The degree of the penetration of water into the specimen and degree of self-desiccation were different by the curing water. Further investigations to find the appropriate curing condition as standard for the high-strength concrete, are needed. Nevertheless in this paper, it was found that low surface tension water curing was able to develop hydration reaction more than that with the standard curing, especially at a low W/C ratio.

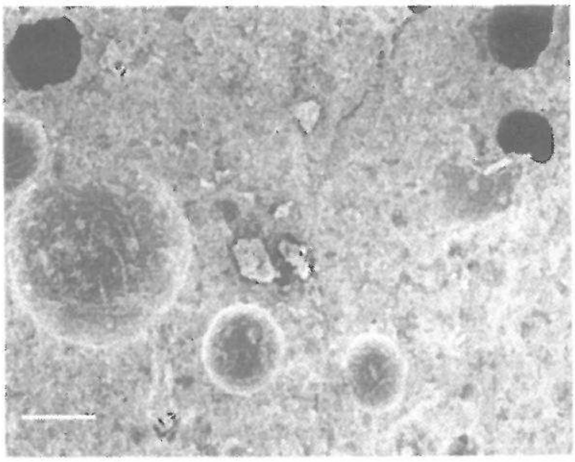

Fig.13 A picture of specimen with W/C of 0.25 curing by Water

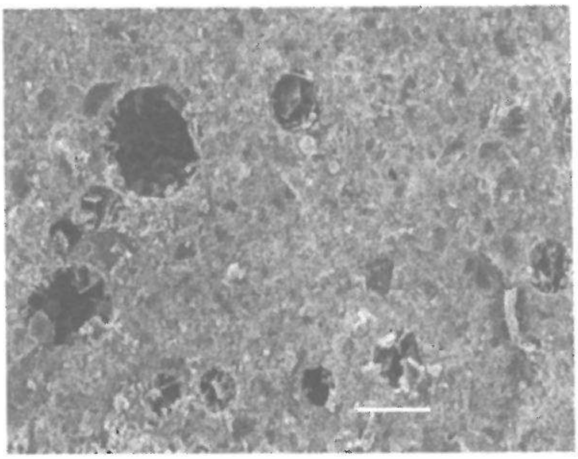

Fig.14 A picture of specimen with W/C of 0.25 curing by AE-water

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