

# Effects of Penetrative Conditions of Water for Curing on The Degree of Hydration and Content of Non-evaporable Water of Hardened Cement Paste

by

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(Received on Mar. 31, 2003, accepted on May. 28, 2003)

## Abstract

Effects of penetrative conditions of water for curing on properties of hardened cement paste have been investigated. In a large specimen with low w/c, normal water curing is not sufficient to complete hydration throughout the entire specimen. Thus, curing conditions have a large influence on the degree of hydration and content of non-evaporable water of the parts of the specimen located at different distances from the curing position. Therefore, different types of curing were used to investigate the properties at any layers of the specimen. The curing with water containing an AE admixture of low surface tension energy (AE water curing) and the curing with water under high pressure (10 MPa water curing) were observed to increase the degree of hydration, the content of non-evaporable water and the strength of the specimen. Furthermore, the decrease in the degree of self-desiccation in the specimen with low water-cement ratio was also observed.

**Keywords:** water penetration, hydration, non-evaporable water, 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 aspects of the hydration reaction, the non-evaporable water, the self-desiccation and the strength. The four different types of curing water were used: the normal curing water, the curing water containing AE-admixture of low surface tension energy, the curing water under high pressure and wrapping. The different specimens with w/c ratios 0.25, 0.4 and 0.6 were prepared to study the capability of penetration of curing water into the specimen at the distances of 25, 75, 125, 175, 225 and 275 mm from the surface exposed to curing. Additionally, the mortar specimen in the cube form with dimension 300 x 300 x 300 mm was also prepared to study the effects of penetration of curing water on the strength by coring samples at any layers of the specimen. The AE-water curing and 10MPa-water curing were used to increase the degree of the hydration, the non-evaporable water and the strength

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of the low w/c specimen. Furthermore, the reduced degree of self-desiccation was investigated too.

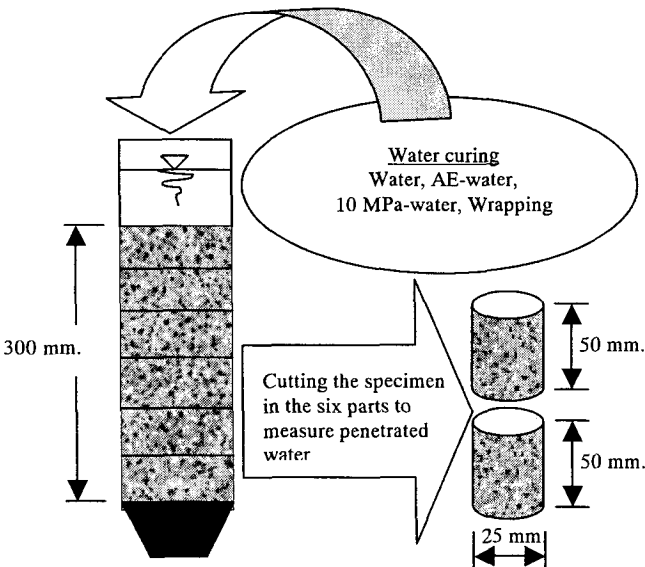
**2. Experiment**

**2.1 Materials**

Ordinary Portland cement is used in these experiments as shown in Table 1. The crushed sand for the compressive strength test of cement is used as the fine aggregate. An air entraining and high range water-reducing agent is used for the specimens with w/c of 0.2 and 0.3. Micro-air 101 in accordance with JIS A 6204 (1% mixes with water, surface tension is about 38 dyne/cm<sup>2</sup>) is used to mix with water to reduce surface energy comparing with water curing.

**Table 1. Mineral and phase composition**

Cement	Fineness (cm <sup>2</sup> /g)	Specific Gravity	Mineral Composition (%)					Loss on ignition
			C3S	C2S	C3A	C4AF	CaSO4	
NPC	3290	3.16	62.4	13.5	8.3	8.5	2.4	2.01



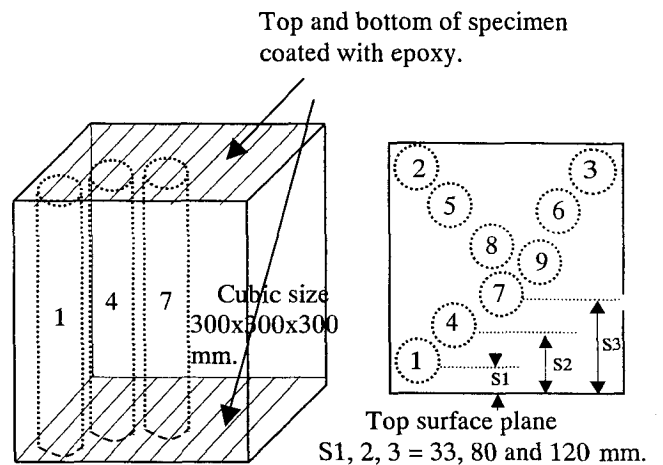
**Fig.1** Measuring method of the penetration of the water in hardened cement paste

**2.2 Experiment procedure**

**2.2.1 Test method for penetrating 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 d=25 mm up to

the paste height of 300 mm. The specimens were cured after one day using four different types of curing water: 1. Supply water, 2. AE-water curing, 3. High pressure water curing and 4. Wrapping. The measuring of the penetrated water were conducted after 3, 7 and 28 days by cutting the specimen in the six parts to measure the mass of them. The mass of hardened cement pastes at room temperature were denoted as M<sub>21</sub><sup>o</sup>(g). After that, the specimens were stored for 24 hours in an oven at temperature of 105<sup>o</sup>C and their masses were measured (M<sub>105</sub><sup>o</sup>). Finally, the specimens were stored for 24 hours in an oven at temperature of 950<sup>o</sup>C and then their masses were measured (M<sub>950</sub><sup>o</sup>).



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

**2.2.2 Test method for penetrating water in mortar with different distance of water to penetrate**

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 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 ± 3<sup>o</sup>C and then after 28 days cored 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 Calculation

The total volume of paste per unit mass of cement ( $V_p$ ) is shown in Eq. (1)<sup>2)</sup>.

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

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

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 shown in Eq. (2)<sup>2)</sup>.

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

where  $w/c^*$  is critical value of  $w/c = 0.38$  below which complete hydration cannot occur, and  $\alpha$  is the degree of hydration.

The volume of unreacted cement per unit mass of cement ( $V_{uc}$ ) is shown in Eq. (3)<sup>2)</sup>.

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

Specific volume of non-evaporable water ( $v_n$ ) is obtained by taking the volume of hydration product less those of the cement from which it was formed and the gel water, and dividing by the mass of non-evaporable water as shown in Eq. (4)<sup>2)</sup>.

$$v_n = [(w/c^*)/D_w - v_g M_g] / M_n \quad (4)$$

where  $v_g$  is specific volume of the gel water = 1 cm<sup>3</sup>/g,  $M_g$  is mass of gel water per unit mass of cement = 0.21, and  $M_n$  is mass of non-evaporable water per unit mass of cement = 0.23.

The porosity of hydration product is given by dividing the volume of gel pores per kg of reacted cement ( $V_g$ ) by that of hydration product ( $V_{hp}$ ) as shown in Eq. (5)<sup>2)</sup>.

The maximum degree of hydration  $\alpha_{\max}$  or  $D.H._{\max}$  for a paste with  $w/c \leq w/c^*$  can be calculated in two cases<sup>2)</sup>.

1. An unrestricted supply of water is available during curing.

$$D.H._{\max} = (w/c)/0.38 \quad \text{Unseal sample} \quad (5)$$

2. If no such water is available, the degree of hydration is limited by the amount of water presented initially.

$$D.H._{\max} = (w/c)/0.44 \quad \text{seal sample} \quad (6)$$

The porosity of hydration product is given by dividing the volume of gel pores per kg of reacted cement ( $V_g$ ) by that of hydration product ( $V_{hp}$ ) as shown in Eq. (7)<sup>2)</sup>.

$$V_g / V_{hp} = v_g \times M_g / [V_c + (w/c^*)/D_w] \quad (7)$$

The volume of gel water ( $V_g$ ) is shown in Eq. (8)<sup>2,3)</sup>.

$$V_g = 0.21\alpha \quad \text{cm}^3/\text{g} \quad (8)$$

Non-evaporable water (NE.W) is shown in Eq. (9)<sup>2,3)</sup>.

$$NE.W = \frac{M_{105^\circ} - M_{950^\circ}}{M_{950^\circ}} \times 100 \quad \% \quad (9)$$

where  $M_{105^\circ}$  and  $M_{950^\circ}$  are the mass of the specimen after heating for 24 hours at 105°C and 950°C, respectively.

Degree of hydration (D.H.) is shown in Eq. (10)<sup>2,3)</sup>.

$$D.H.(\alpha) = \frac{(M_{105^\circ} - M_{950^\circ})}{M_{950^\circ}} \times 100 / 23 \quad \% \quad (10)$$

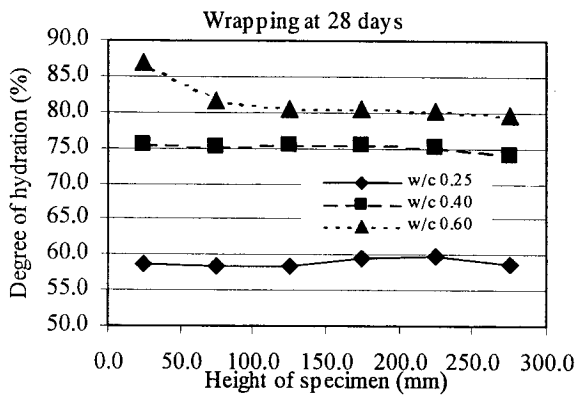
where 23% is content of non-evaporable water at complete hydration<sup>2,3)</sup>.

Evaporable water (E.W.) is given by Eq. (11)<sup>2,3)</sup>.

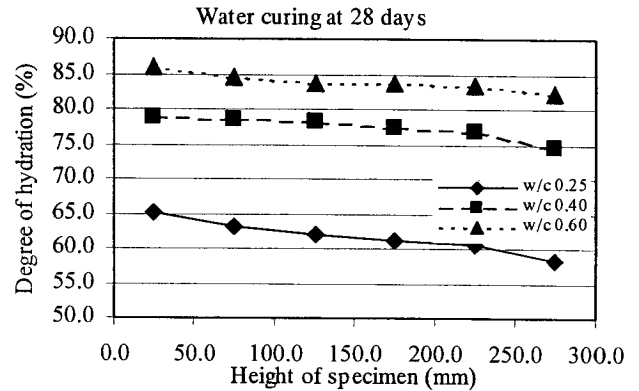
$$E.W. = \frac{M_{21^\circ} - M_{105^\circ}}{M_{950^\circ}} \quad \text{cm}^3/\text{g} \quad (11)$$

Degree of self-desiccation (D.S.) is shown in Eq. (12)<sup>2,3)</sup>.

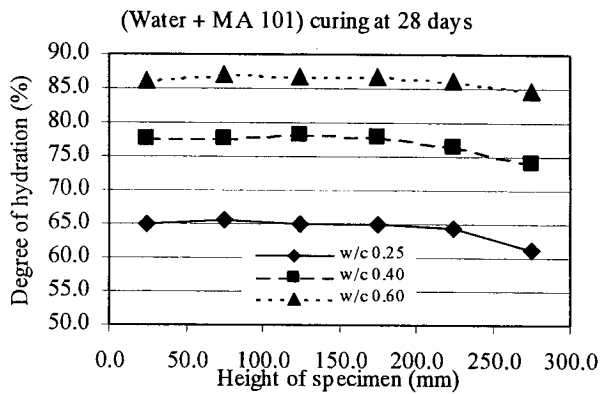
$$D.S. = \left(1 - \frac{E.W./V_p}{100 - (V_{hp} - V_g + V_{uc})/V_p}\right) \times 100 \quad \% \quad (12)$$



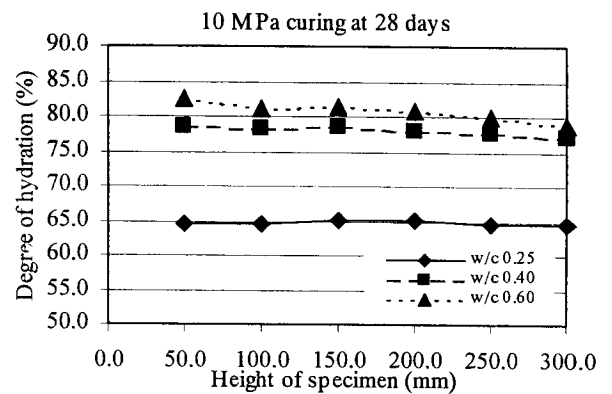
**Fig.3** Relation between the degree of the hydration and the height of the specimen for wrapping after 28 days



**Fig.4** Relation between the degree of the hydration and the height of the specimen for water curing after 28 days



**Fig.5** Relation between the degree of the hydration and the height of the specimen for AE-water curing after 28 days



**Fig.6** Relation between the degree of the hydration and the height of the specimen for water pressure curing after 28 days

### 3. Result 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 occurs 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.

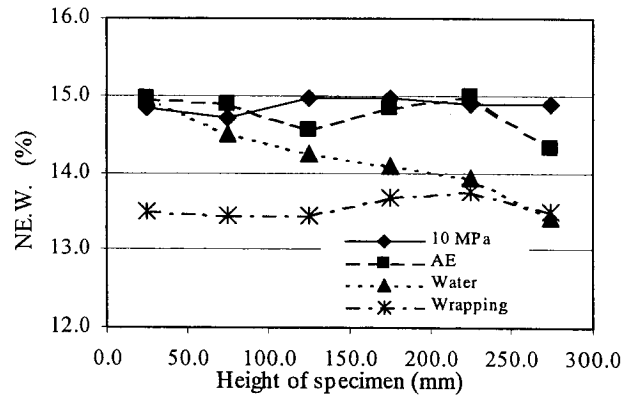
The content of non-evaporable water, relative to that in a fully hydrated paste of the same cement, was used as a measure of the degree of the hydration following Powers-Brownyard model. The degree of the hydration, calculated from Eq.10 on different heights of the specimen with water-cement ratios 0.25, 0.40 and 0.60 after 28 days are shown in Fig. 3, 4, 5 and 6. The wrapping specimen is protected the movement of the water through the surface of the specimen.

The degree of hydration after 28 days was about 58%, 75% and 80% for the specimen with water-cement ratio of 0.25, 0.40 and 0.60, respectively as shown in Fig. 3. The degree of the hydration at any layer was the same excepted at the surface layer of the specimen with w/c 0.60 which was much more influenced from the bleeding. The different degrees 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 cured by AE-water curing or 10MPa-water curing, as shown in Fig.5 and 6 the hydration progressed more than in the one subjected to the normal water curing and wrapping. 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.

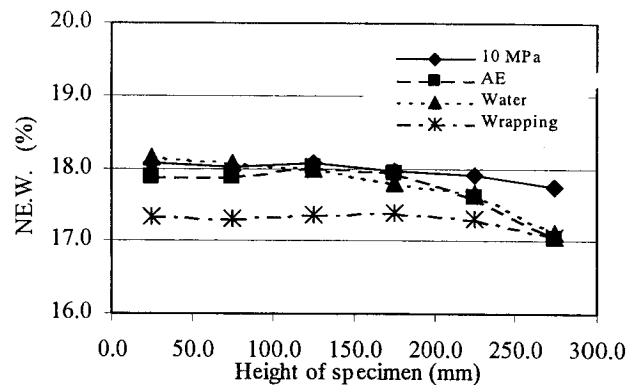
**3.2 Non-evaporable water of hardened cement paste**

The presence of water in hydrated cement has been mentioned. The cement paste is indeed hygroscopic owing to the hydrophilic character of cement coupled with the presence of submicroscopic pores. The actual water content of the paste depends on the ambient humidity. A convenient division of water in the hydrated cement, necessary for investigation purposes, though rather arbitrary, is into categories: evaporable and non-evaporable. The evaporable water can be determined by the loss upon drying at a higher temperature, usually 105°C, or by freezing out, or removing with solvent. In general terms, the non-evaporable water contains nearly all chemically combined water and also some water not held by chemical bonds. 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 vapor pressure. The amount of non-

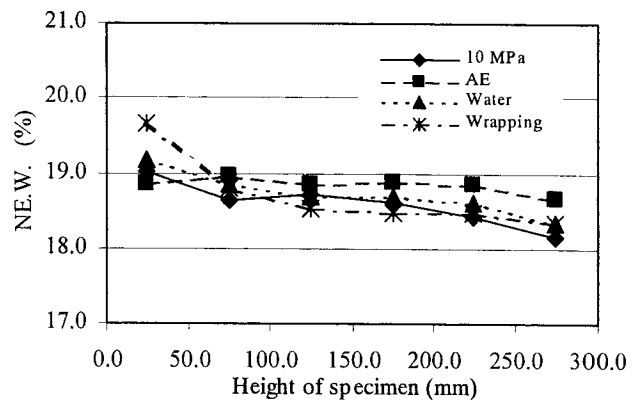
evaporable water increases as hydration proceeds, but in a saturated paste non-evaporable water can never become more than one half of the total water present. In well-hydrated cement the non-evaporable water is about 18 per



**Fig.7** Relation between Non-evaporable water (N.W.) and the height of the specimen with w/c 0.25 after 28 days



**Fig.8** Relation between Non-evaporable water (N.W.) and the height of the specimen with w/c 0.40 after 28 days



**Fig.9** Relation between Non-evaporable water (N.W.) and the height of the specimen with w/c 0.60 after 28 days

cent by weight of the anhydrous material; this proportion rises to about 23 per cent in fully hydrated cement<sup>3)</sup>.

The during cement hydration, external water is absorbed by the hydrating cement paste to replace that consumed by chemical shrinkage. The penetration of curing water into the specimen is important to continue the hydration reaction because the complete hydration reaction cannot occur if w/c is below a value in the region of 0.38. The content of non-evaporable water, calculated from Eq.9 at any distance on the specimen with w/c 0.25, 0.40 and 0.60 after 28 days are shown in Fig. 7, 8 and 9. In case of wrapping, the content of non-evaporable water is about 13.5%, 17.3% and 18.5% for the specimen with water-cement ratio of 0.25, 0.40 and 0.60, respectively. The non-evaporable water at any layers of the specimen with w/c 0.25 is clearly shown the effect by changing the types of water curing as shown in Fig. 7. It could be seen that for the specimen cured by AE-water curing or 10 MPa-water curing the non-evaporable water is larger than in the one subjected to the normal water curing. The specimen with w/c 0.40 and 0.60 is not so affected by changing the types of water curing as shown in Fig. 8 and 9.

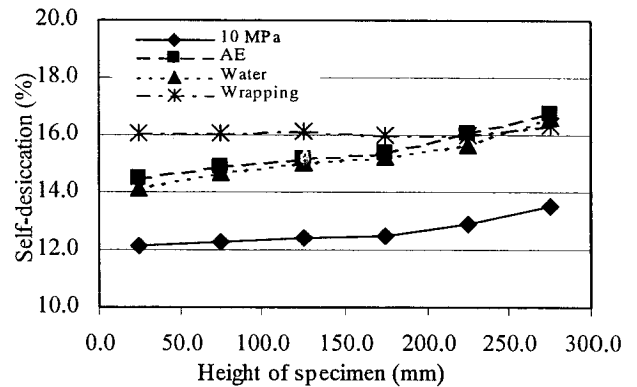
**3.3 Self-desiccation of hardened cement paste**

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

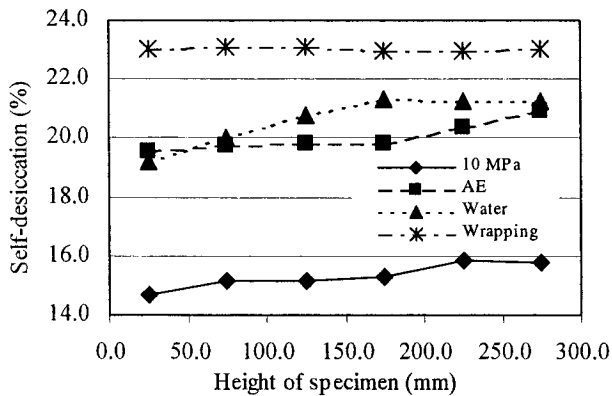
not allowed, only previously added water will take part in the reaction of hydration and the relative humidity within the paste will decrease. This is known as self-desiccation. Since gel can form only in water-filled space, self-desiccation leads to a lower degree of hydration comparing to a moist-cured 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.12:

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

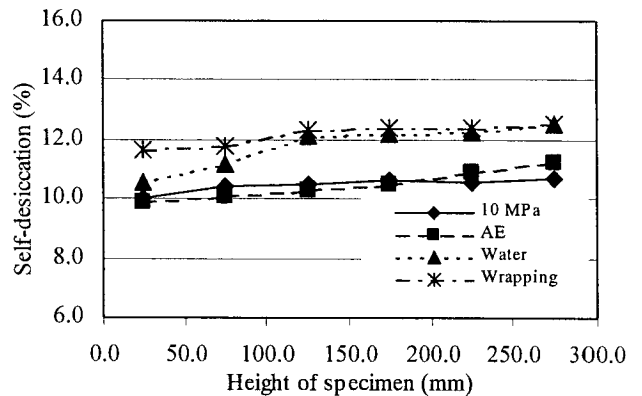
where c.w. = capillary water, g.w. = gel water, c.p. = capillary pore, and g.p. = gel pore. The degree of self-desiccation depends on the capability of curing water to fill pore created by hydration.



**Fig.11** Relation between the degree of self-desiccation and the height of the specimen with w/c 0.40 after 28 days



**Fig.10** Relation between the degree of self-desiccation and the height of the specimen with w/c 0.25 after 28 days



**Fig.12** Relation between the degree of self-desiccation and the height of the specimen with w/c 0.60 after 28 days

The degree of self-desiccation, calculated from Eqs.1-12, for the different types of curing at each height of the specimen is shown in Fig10, 11 and 12. The types of curing have a significant effect on the degree of the self-desiccation, especially in the low water cement ratio as can be seen in Fig.10. 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 about 8 %, 4 % and 2 % for specimen with w/c ratio 0.25, 0.40 and 0.60, respectively.

### 3.4 Effect of penetrating water on the strength

It is known that large range of self-desiccation occurs in the low water-cement ratio because water from outside cannot penetrate in the central part of the specimen. The self-desiccation affects strength of mortar by decreasing of hydration. It was found that the longer distance from surface, the lower the strength became in the specimen with water-cement ratio of 0.2 as shown in Fig.13. The specimens with w/c of 0.4 and 0.6 have enough water to react with cement to complete the hydration reaction. In this case the distance from the surface does not affect the strength of specimen so much. The distance from the surface clearly has the effect on the strength of the specimen

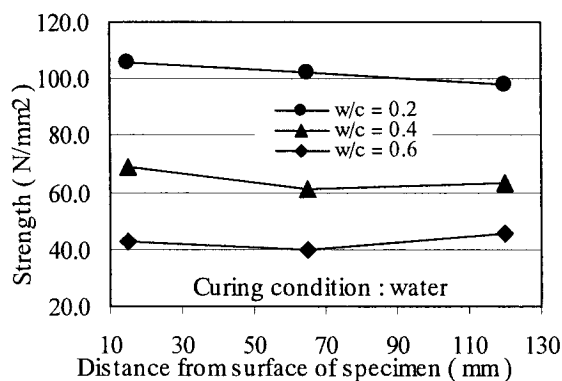


Fig.13 Relation between the strength and the penetrated water distance of the specimen with w/c 0.2, 0.4 and 0.6 after 28 days

with water-cement ratio of 0.2 but it has clearly no effect on the specimens with w/c of 0.4 and 0.6.

In case of the specimen with w/c 0.25 as shown in Fig.14, 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 non-evaporable water and the lower degree of self-desiccation, subsequently presented in section 3.1, 3.2 and 3.3. 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.

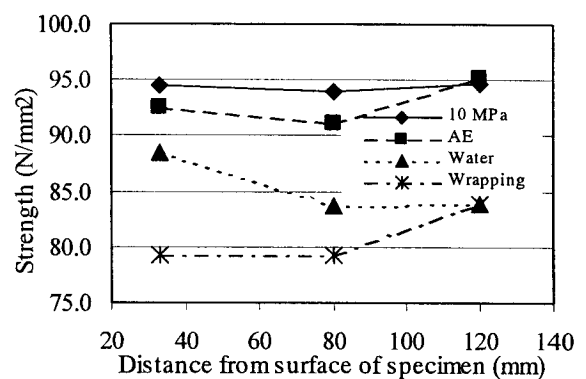


Fig.14 Relation between the strength and the penetrated water distance of the specimen with w/c 0.25 after 28 days

## 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 and non-evaporable water in the bulk of a specimen are smaller than in the surface area. However, the same degree of hydration and non-evaporable water in the bulk and in the surface area are

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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