Suppression of Delayed Expansion in an Ettringite-Generating High-Strength Additive

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ABSTRACT

This study verified the effect of the steam-curing method on delayed expansion when using an ettringite-generating type of high-strength additive, with the aim of determining a safe method of use. With increasing steam-curing temperature, anhydrite within the additive remains unreacted. We found that the anhydrite reacted in a wet environment to enhance the formation of ettringite and thereby bring about delayed expansion. The thermal decomposition of ettringite results in an increase of SO_3 in Calcium Silicate Hydrate (CSH); this further increases the risk of delayed expansion. A steam-curing temperature above 80 degree also leads to an increased risk of delayed expansion. To control the delayed expansion, it is important to guard against an excessive rise in the curing temperature, to fix SO_4 ions as ettringite, and to prevent the transfer of SO_4 ions within solidified concrete.

1. Introduction

In recent times, the performance required from concrete has become increasingly diverse, depending on its purpose and usage, and many studies have investigated high-performance concrete. A combination of ettringite-generating high-strength additive and steam curing enables the production of high-strength concrete [1]. It is also expected that environmental issues will be more widely considered in the future and that the effective utilization of industrial by-products will become increasingly important. In this regard, the authors studied the application of blast-furnace slag cement and ettringite-generating high-strength additive and reported that it was effective in reducing environmental burden [2].

The durability of concrete has also been widely discussed. For concrete products cured at high temperatures, deterioration is considered to result from delayed ettringite-formation [3]; some researchers have even raised the possibility of this scenario in domestic settings [4]. It is possible that a similar phenomenon might take place when an ettringite-generating type of high-strength additive is used under steam curing. Therefore, where ettringite-generating types of high-strength additive are used in the present

study, the effects of the steam-curing method on delayed expansion are investigated, and we propose a method that ensures safe use.

2. Experimental
2.1 Materials
a) Cement: The cement used in this study was normal Portland cement (Density: 3.16 g/cm^3, Blaine specific surface area: 3300 cm^2/g).
b) Fine aggregate: The fine aggregate used in this study was siliceous sand (a standard sand in accordance with JIS R5201).
c) Admixtures: We used an admixture of a high-range water-reducing admixture based on naphthalensulfonate.
d) High-strength additive: The ettringite-generating type of high-strength additive (termed HSA hereinafter) used in this study is a commercially available additive for high-strength concrete products that consists mainly of anhydrite and siliceous material with pozzolanic reactivity (anhydrite : siliceous material = 80 : 20 (wt. %))[5]. Table 1 shows the properties of the HSA. By mixing the HSA with cement and processing with steam curing, a high-strength concrete can be achieved.

Table 1 Properties of high-strength additive

LOI (mass%)	Chemical composition (mass%)						Density (g/cm^3)	Blaine (cm^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	R_2O		
2.8	17.1	2.6	0.5	33.2	42.8	0.5	2.71	6000

2.2 Mix proportion and test method for mortar and paste
2.2.1 Mix proportion and mixing of mortar and paste
The symbols are defined as follows: W = Water, C = Cement, S = Sand, B = Binding materials (cement and HSA). Mortars and pastes of W/B = 0.3 and 0.5 were mixed using a mortar mixer. The temperature of the mixture was set at 20 degree. The mortar had C/S = 1/1.5 and the HSA was added externally by C x 10% (HSA was added to a constant weight of cement and it is not a cement replacement). The pastes were added to the HSA by C x 6, 8, and 10%. To assess the effects of the siliceous material within the HSA on the reaction of anhydrite, we prepared a paste to which we added only anhydrite at W/B = 0.3; this ensured the same dosage of anhydrite as that for the case where the HSA was externally added by C x 10%.
2.2.2 Method of molding and curing
We used molds of 4 x 4 x 16 cm and 2 x 2 x 8cm to make the mortars and pastes, respectively. The mortars and pastes were then steam-cured at

various pre-curing times, rates of temperature increase, and curing temperatures. The time interval prior to steam curing (hereafter referred to as pre-curing time) was 0 or 3 hours, and the rate of temperature increase was 15 minutes or 3 hours until the specified curing temperature was achieved. The curing temperature was set to 60, 80, or 100 degree. A number of experimental pastes were tested at curing temperatures of 75 and 90 degree. After the specified steam curing, the mortars and pastes were processed with water-curing at 35 degree.

2.2.3 Test items and test methods

a) Length-change rate of the mortar: Gage plugs were embedded at both ends of the mortar in advance, and the length-change rate was measured using a dial gage. The samples were measured at 20 degree after they were cooled.

b) Quantification of compounds and hydration products in the paste: We used XRD/Rietveld analysis to quantify the compounds (constituent minerals in the cement and the HSA) and hydration products within paste immediately following steam curing and in paste that was subsequent ly water-cured for 9 months.

We used the following procedure to investigate the generation processes of ettringite and monosulfate (hereafter expressed as AFt and AFm, respectively) under steam curing at high temperatures. The paste at W/B = 0.3 with the HSA added by C x 10% was steam-cured following the temperature pattern shown in Figure 1. The pastes were extracted when the temperature reached 60, 75, and 90 degree, and after a further 3 hours of curing at 90 degree; hydration was stopped immediately with the addition of acetone. The compounds and hydration products were then quantified using XRD/Rietveld analysis.

c) Observations of hydration products: We used SEM -EDS to observe fracture surfaces within pastes immediately following steam curing and within pastes after subsequent water-curing for 9 months at 35 degree.

d) Pore-size distribution: For the same pastes as those described in c), we measured the pore-size distribution using a mercury porosimeter.
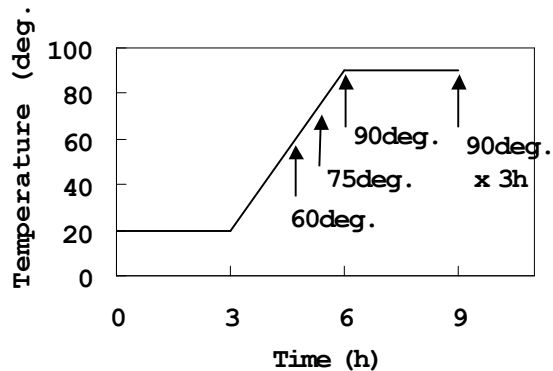
Fig.1 Pattern of steam curing

3. Experimental results and discussion

3.1 Factors affecting the length-change rate of mortars

Figures 2, 3, and 4 show the length-change rate of mortar (expansion) as a function of different influencing factors.

Figure 2 shows the effect of the steam-curing temperature. The conditions were set to W/B = 0.3, a pre-curing time of 3 hours, and the temperature was increased to the specified temperature over 3 hours. For a steam-curing temperature of 100 degree, a significant delayed expansion was recorded after the age of 6 months. This effect was less pronounced for 60 degree and 80 degree, revealing that the length-change rate varies significantly with curing temperature.

Figure 3 shows effect of W/B on the length-change rate. The steam-curing temperature was 100 degree, the pre-curing time was 3 hours, and the temperature was increased to the target temperature over 3 hours. Though the timing at which the length-change rate began to increase varied, those at the age of 9 months were approximately the same level.

Figure 4 shows the influence of pre-curing time and the rate of temperature increase on the length-change rate. In this case,
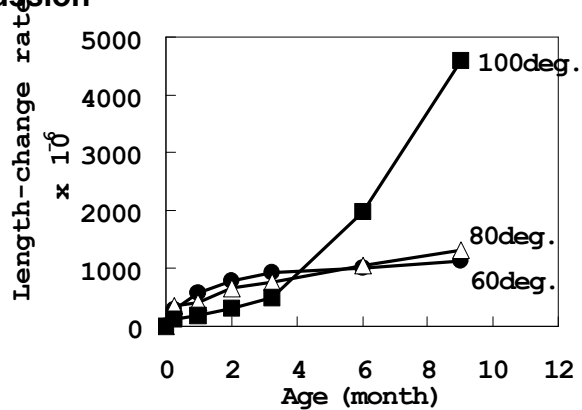

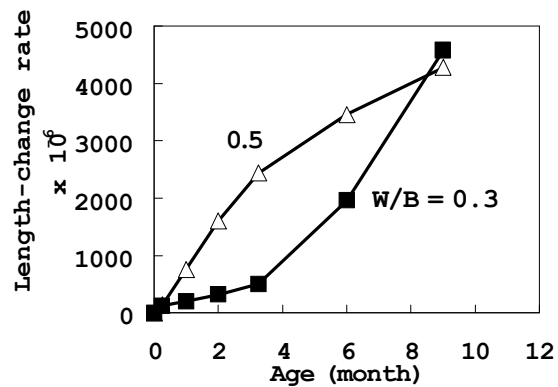Fig.2 Effect of steam-curing temperature on the length-change rate of mortar (HSA : 10%)

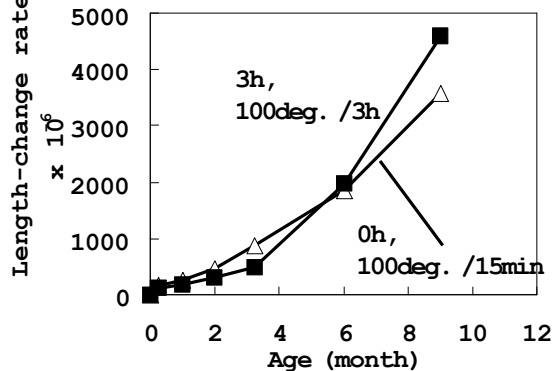
Fig. 3 Effect of W/B on the length-change rate (HSA : 10%)

Fig. 4 Effects of pre-curing time and rate of temperature increase on the length-change (HSA : 10%)

the steam -curing temperature was 100 degree and W/B = 0.3. The two

curves are almost identical; the effects of pre-curing time and rate of temperature increase are only minor. In addition, no cracks were observed within any of the test samples described above. The steam-curing temperature was found to have the greatest influence on the length-change rate.

3.2 Unreacted anhydrite immediately after steam-curing and delayed formation of ettringite

Figure 5 shows the amount of anhydrite in the pastes immediately after steam curing and after a further 9 months of water relative to the steam-curing temperature. For the cases immediately after steam curing, the amount of anhydrite increases with curing temperature. The solubility of the anhydrite decreases as the temperature increases; consequently, the anhydrite remains unreacted. For the cases following 9 months of water curing, anhydrite was absent after being completely reacted out during the water curing.

Figure 6 shows the amount of AFt generated in the pastes stored in water. The amounts were calculated by subtracting the AFt a mount generated immediately after steam curing from that after 9 months of water curing at 35 degree. As the steam-curing temperature increases, the amount of generated AFt also increases. The anhydrite that remained after the steam curing reacted during the water curing, and the amount of generated AFt increased accordingly.
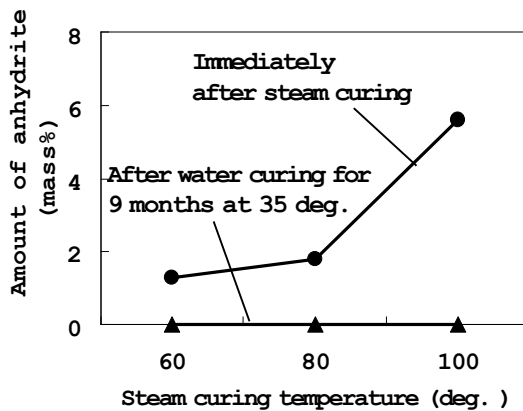
Fig. 5 Relation between steam-curing   Figure 6 Ettringite quantity
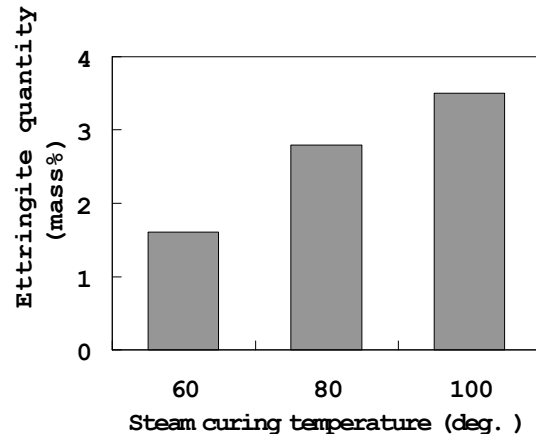temperature and amount of anhydrite   formed during water curing

3.3 Effect of siliceous material on the reaction of anhydrite

When large amounts of anhydrite alone are added to concrete, the strength of the concrete is improved but cracks occur after 1 year of exposure to air. The use of siliceous material together with anhydrite suppresses the

formation of cracks and enables a higher strength to be achieved [5].

Figure 7 shows the effects of the siliceous material on the reaction of anhydrite and the relation between the occurrence of siliceous material and the amount of anhydrite in the pastes immediately after steam curing. The pre-curing time was set to 3 hours, temperature was raised to 60 degree over 3 hours, and the samples were steam -cured at 60 degree for 3 hours. Where the HSA containing siliceous material
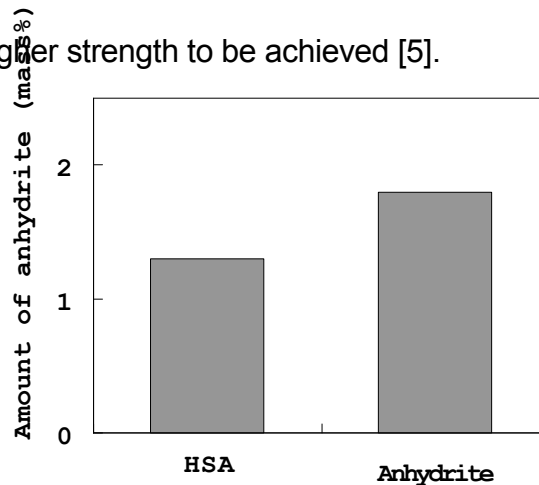

Fig 7 Effect of siliceous material on the residual quantity of anhydrite immediately after steam curing

was added, the amount of anhydrite immediately following steam curing is small compared to the case where only anhydrite was added. We consider that the reaction of anhydrite is accelerated due to the siliceous material. For the case where the HSA is used, compared with the addition of only anhydrite, the reaction of anhydrite is accelerated, only a small amount of anhydrite exists immediately after steam curing, and the occurrence of delayed expansion is considerably reduced. When the steam-curing temperature is increased, however, the effects of temperature become more significant, greater amounts of anhydrite remain immediately after steam curing, and significant delayed expansion occurs.

3.4 Danger zone of delayed expansion due to unreacted anhydrite

We hypothesize that the amount of residual anhydrite immediately after steam curing is determined by the dosage of HSA and the steam-curing temperature. This remaining anhydrite reacts late, and affects the amount of delayed expansion. As there are no mortar samples corresponding to part of the paste samples, the length-change rate of the mortar was estimated according to the following procedure.

We obtained the relationships between the dosage of HSA, the steam-curing temperature, and the length-change rate, which in turn yielded the danger zone of delayed expansion.

a) For the mortar and paste mixed with the HSA at C x 10% dosage, the relation between the amount of residual anhydrite in the paste (immediately after steam curing) and the length-change rate of the mortar (both steam-cured and after 9 months of water-curing at 35 degree) is obtained.

b) By measuring the amount of residual anhydrite (immediately after steam

curing) in the pastes made with various dosages of HSA and at various steam-curing temperatures, the length-change rate of the corresponding mortar samples can be estimated based on the relation obtained in a) above.

Figure 8 shows the relation between the amount of residual anhydrite in the paste immediately after steam curing and the length-change rate of the mortar (for the case of W/B = 0.3). The three measured data points shown in the figure define a linear trend. As the second and third points are located far apart and the basis for the linear approximation remains questionable, this trend will be studied in more detail in the future.

Figure 9 shows the relations between the addition rate of HSA, the steam-curing temperature, and the length-change rate of the mortar. In the length-change rate, closed circle indicates measured data, while others data points are estimated from Figure 8. As the addition rate of HSA and the steam-curing temperature increase, the length-change rate also increases. If the steam-curing temperature exceeds 80 degree, it is possible that significant delayed expansion will occur.
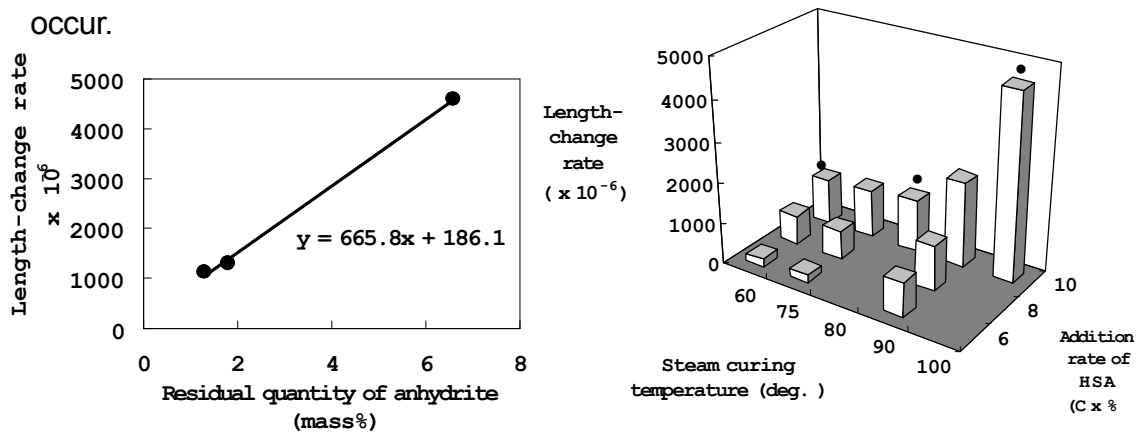

Figure 8 Relation between residual quantity of anhydrite and length change rate of mortar immediately after steam curing (W/B=0.3)

Fig. 9 Relation of the addition rate of HSA and steam curing temperature with the length-change rate of mortar (W/B=0.3)

3.5 Generation of ettringite and monosulfate in paste for steam curing at high temperatures

Figure 10 shows XRD patterns for the steam -curing process. When the steam-curing temperature is raised from 60 to 75 degree, the peak intensity of AFt increases. If the temperature is increased again to 90 degree, the peak intensity of AFt decreases and a peak in AFm occurs. After holding for 3 hours at 90 degree, the peak intensity of AFt decreases further and the

intensity of AFm increases.

Figure 11 shows the amount of AFt, AFm, C₃A, and anhydrite in the steam-curing process. During the period of temperature increase from 60 to 75 degree, the amount of C_3A and anhydrite decreases, and the amount of generated AFt increases on account of these reactions. In the course of increasing temperature above 75 degree, the facts that the C_3A amount does not change significantly means that the AFt amount decreases significantly and the AFm amount increases. Thermal decomposition of the AFt is therefore considered to have taken place. When the additive-free cement is steam-cured at high temperatures, the sulfate ions released by the thermal decomposition of AFt are adsorbed to CSH. Sulfate ions are gradual ly released from CSH over the long term, and these react with AFm or unhydrated C_3A to form AFt, delaying expansion [3]. Even for the case in which HSA is added, it is possible that similar phenomena take place due to thermal decomposition of AFt, provided that steam curing occurs at high temperatures.
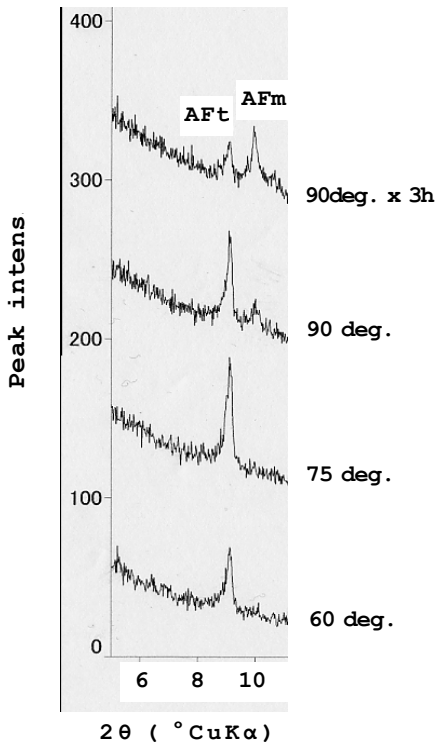

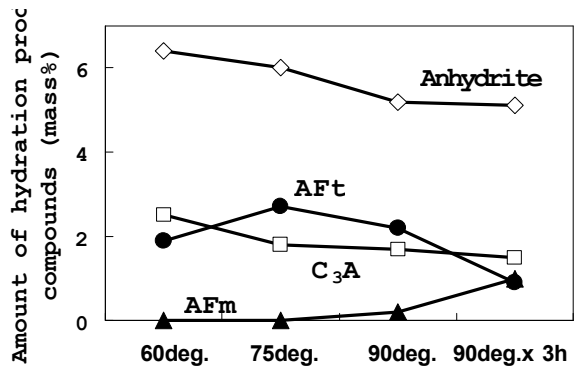Fig. 10 XRD patterns of paste for the steam-curing process

Figure 13 Quantitative results of hydration products and compounds based on Rietveld analysis

3.6 Increase of sulfate ions in CSH in paste due to the thermal decomposition of ettringite

We are able to calculate the amount of SO_3 in CSH that will be increased due to the thermal decomposition of AFt. Figure 12 shows the material balance of the processes when hydration products are generated from cement and the HSA as starting materials. From the experimental result of

the paste that was steam-cured for 3 hours at the specified temperatures, the amount of SO_3 in CSH is calculated from the chemical composition of the material used and the material balance. In this calculation, the residual amount, after subtracting any crystallized compounds quantifiable by XRD, is regarded as CSH.
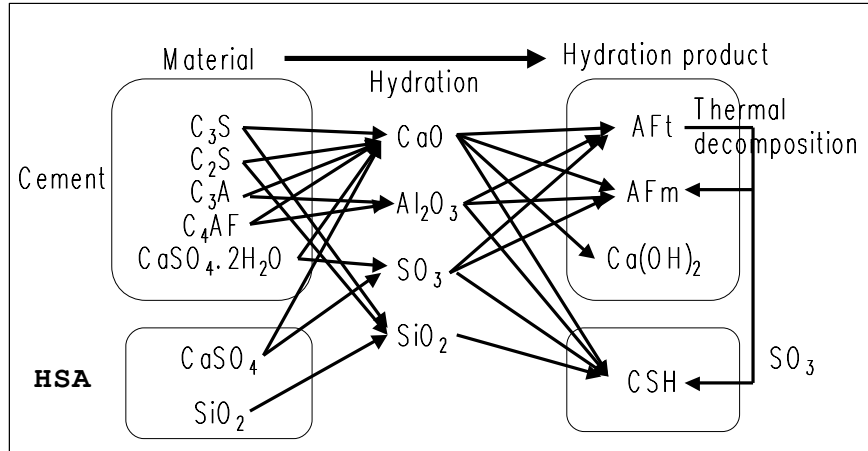

Fig. 12 Material balance for the periods before and after hydration

Figure 13 shows the increase in SO_3 within generated CSH due to the thermal decomposition of AFt. Even in the case of 60 degree, at which temperature the thermal decomposition of AFt does not occur, about 4% SO_3 occurs. When steam-cured at 90 degree, this amount increases by 10% to approximately 4.6%. Although this is a relatively small amount, there exists a greater risk of delayed expansion. Delayed expansion associated with the thermal decomposition of AFt is considered to occur in the long term [3]; accordingly, we are continuing our observations.
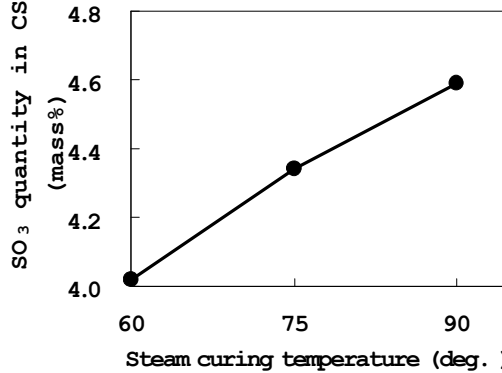

Fig. 13 Increase in SO_3 quantity in CSH in paste resulting from the thermal decomposition of AFt

3.7 Relation between steam-curing temperature and delayed expansion

Based on the above results, the relation between steam-curing temperature and delayed expansion is considered to be as follows. When the steam-curing temperature is in the range between 60 to 75 degree, large amounts of AFt are generated and the AFt is considered to occur long-term. Delayed expansion caused by unreacted anhydrite or the thermal

decomposition of AFt is considered to occur for higher curing temperatures. When focusing on material transfer in the hardened product, delayed expansion is always associated with the transfer of sulfate ions. Therefore, to control the delayed expansion it is important not to raise the steam-curing temperature too high, to fix sulfate ions as AFt, and to prevent the transfer of sulfate ions in the hardened material. As the effects of the dosage of HSA and the threshold value of the steam-curing temperature are only estimates, it is necessary to conduct additional studies in the future.

3.8 Observations of hydration products and pore-size distribution

Figure 14 shows SEM photographs of the pastes of W/B = 0.3 mixed with the HSA by C x 10%. When steam-cured at 60 degree, AFt and CSH (type I) co-exist immediately after stream curing. For a sample that was water-cured for 1 year at 35 degree, various types of AFt generated at different ages appear to occur. It is considered that the AFt generated by steam curing and AFt generated late from unreacted anhydrite co-exist. Type II and type III CSH were observed, but type I was not. In the case of steam curing at 100 degree, type III CSH was observed immediately after steam curing. Moreover, after
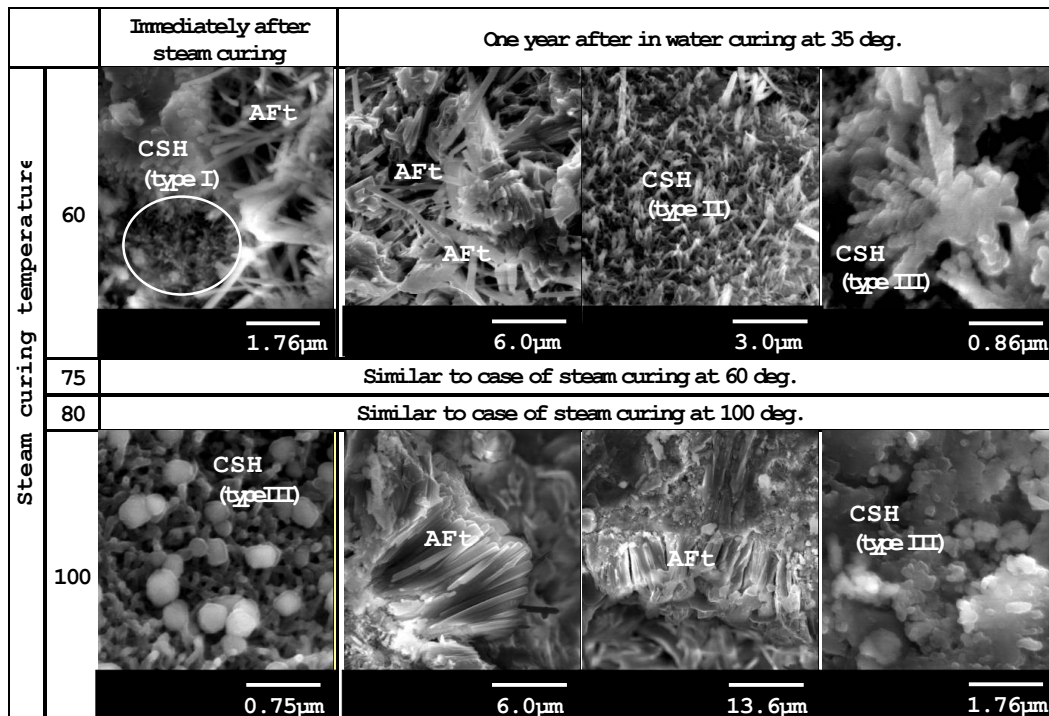

Fig. 14 SEM photograph of cement paste mixed with HSA

water-curing for 1 year at 35 degree, dense bundle-shaped AFt was observed to have been generated in small areas. The cases steam-cured at 75 and 80 degree have similar status to those steam-cured at 60 and 100

degree, respectively.

Figure 15 shows the pore-size distribution of the pastes immediately after steam curing and again after 1 year of water curing at 35 degree. For the case of W/B = 0.3, the initial pore size at the peak decreases as the steam-curing temperature increases immediately after steam curing. After 1 year of water curing at 35 degree, the amount of pore volume becomes smaller than that immediately after steam curing, irrespective of the steam-curing temperature. Similar patterns of pore-size distribution are evident for the cases of steam-curing temperatures of 60 and 80 degree. In the case of 100 degree, the pore amount at 0.01.m becomes significantly larger than the case of 60 and 80 degree. We consider that pores remain unfilled because hydration took place during water-curing, or that new pores were generated due to delayed expansion. For the case of W/B = 0.5 and steam curing at 60 degree and 80 degree, similar patterns (with two peaks) are observed immediately after steam curing. In the case of 100 degree steam curing, a pattern with just one peak is obtained, which appears
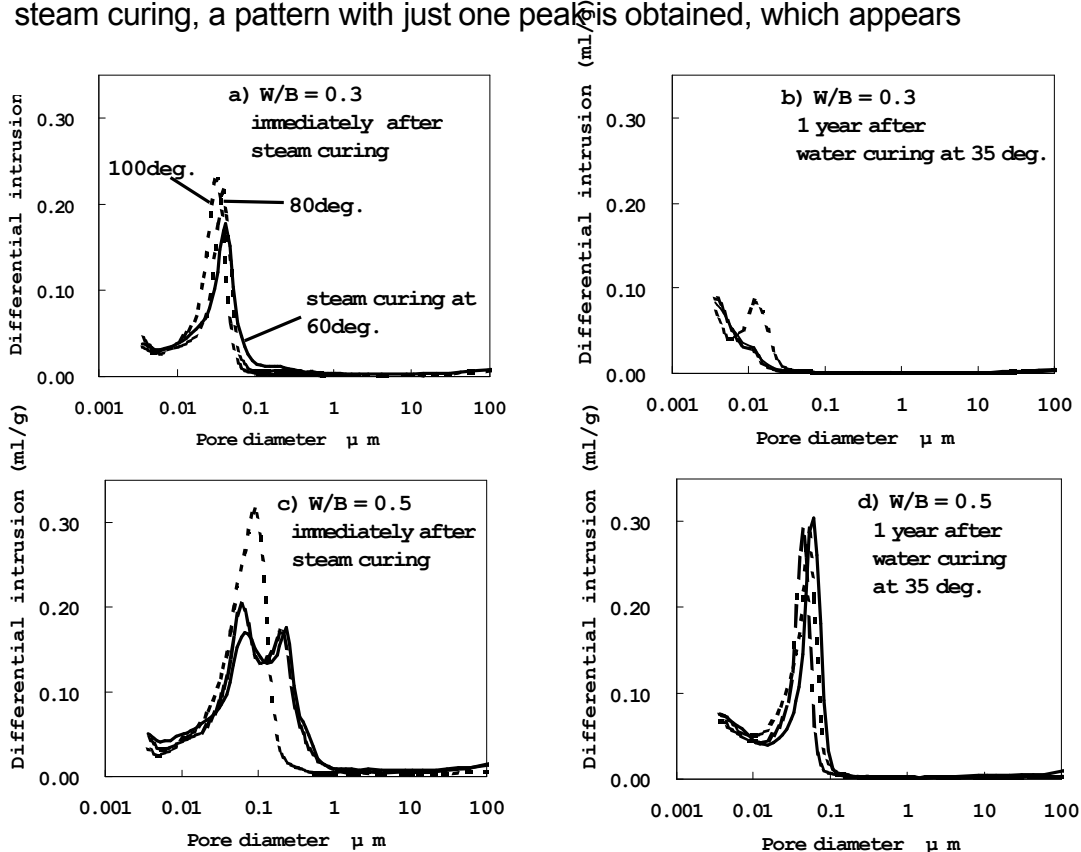

Fig. 15 Distribution of pore diameters of cement paste mixed with HSA

different to those for 60 degree and 80 degree steam curing. After 1 year of water curing, similar patterns are obtained, although the peaks are shifted to the smaller pore sizes in all the cases. As the water amount is greater for

W/B = 0.5 than W/B = 0.3, the pore volume immediately after steam curing is larger. We consider that subsequent hydration fills the remaining pores, leading to similar patterns.

4. Conclusions

. The risk of delayed expansion is high when the steam-curing temperature exceeds 80 degree.

. The reaction of anhydrite is considered to be accelerated by the siliceous material within the HSA. Compared to the case in which only anhydrite was added, the amount of anhydrite immediately after steam curing is smaller; thus, delayed expansion is reduced.

. The steam-curing temperature has a significant effect on the degree of delayed expansion. As the steam-curing temperature increases, larger amounts of unreacted anhydrite tend to remain in the sample. We consider that the anhydrite reacts under a wet environment, the amount of generated ettringite increases, and delayed expansion takes place.

. For higher steam -curing temperatures, the amount of SO_3 in CSH increases due to the thermal decomposition of ettringite; consequently, there exists a greater risk of delayed expansion.

. To control the degree of delayed expansion, it is essential that a low curing temperature is maintained, that sulfate ions are fixed as ettringite, and that the transfer of sulfate ions is prevented within the hardened material.

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