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Effect of a Calcium Silicate Hydrate-Type Accelerator on the Hydration and the Early Strength Development of Concrete Cured at 5 or at 20 Degrees Centigrade

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ABSTRACT

This paper describes the effect of a new hardening accelerator on the early hydration of cement and the strength development of concrete, at 5 or at 20 degrees C. The new hardening accelerator consists of a suspension of fine dispersed particles of precipitated calcium silicate hydrates (C-S-H). The mechanism of action of C-S-H type accelerators is described. It is confirmed that both the setting and early strength development of concrete mixed and cured at 5 or at 20 degrees are accelerated by the addition of the accelerator. The effect of the accelerator on the hydration and porosity of cement paste having the same water-to-cement ratio and mixing/curing temperature as the concrete specimens is also evaluated. The addition of the accelerator accelerates the early hydration of cement at both temperatures, and also decreases the porosity of the concrete.

Keywords: Accelerator, C-S-H, Concrete, Strength, Hydration

INTRODUCTION

Concrete is an essential material for building social infrastructure. There is no alternative to concrete as a construction material in terms of its cheapness, availability, mass production and consumption. Therefore, many consider that the importance of concrete as an essential material contributing to sustainable social development will continue to grow. Concrete is also a material for which a large amount of energy is consumed and a large amount of $CO_{2,}$ is emitted, not only in the production of concrete's raw materials but also in the placement of concrete during construction. Thus, the reduction of this energy consumption and CO_2 emission concerned with concrete is a great issue in concrete sustainability.

Accelerators are added to concrete to shorten its setting time, or to increase the rate of early strength development, or to achieve both. Through these effects, accelerators have been contributing to rapid concrete production and construction. Additionally, the use of accelerators can reduce energy consumption during concrete production, which means a reduction in CO_2 emissions. For example, winter conditions of low temperature delay both setting and early strength development. To overcome these problems, concrete is cured with heat. In order to minimize the greater requirement of energy consumption for this heating, some accelerators can be used. It is considered that the use of accelerators as a means to reduce energy used for concrete will be more important for concrete sustainability in the future.

BASF has developed a new accelerator consisting of a suspension of fine dispersed particles of precipitated calcium silicate hydrates (C-S-H) (Nicoleau, 2010, 2011). In this paper, the effect of C-S-H type accelerator on the early hydration and the early strength development at low and at normal temperatures were evaluated.

ACTION MECHANISM OF CALCIUM SILICATE HYDRATE-TYPE ACCELERATORS

The mechanisms of action of calcium silicate hydrate-type accelerators during cement hydration are quite different from that of conventional accelerators (Thomas, 2009, Nicoleau, 2010): firstly, the nucleation energy barrier to be surmounted is lowered (or even suppressed) due to the presence of these particle seeds in the pore solution of cement paste; secondly, the further growth of C-S-H occurs mainly onto these fine particles which collectively develop an immense surface area; and thirdly, the thickness of the hydrate layer, usually present on cement particles which limits the hydration rate due to the necessary diffusion, is reduced as a result of 2). These three action mechanisms greatly accelerate the hydration of the anhydrous silicates phases and thus promote early strength development.

EXPERIMENTAL OUTLINE

Materials

The cement used in the experiments was commercially available ordinary Portland cement, compliant with JIS R 5210:2010. The density and the specific surface area of the cement, determined according to the norm JIS R 5201:1997, are 3.15 g/cm^3 and 3370 cm^2/g, respectively. The chemical composition of the cement used in the experiments was determined according to the norm JIS R 5202:2010 and is shown in Table 1. The accelerator used was a C-S-H suspension-type accelerator (hereinafter the accelerator is described as “X100”). A polycarboxylate superplasticizer, sand taken from a old riverbed (surface dry density and water absorption rates of 2.60g/cm^3 and 2.0%, respectively) and crushed gravel (surface dry density and water absorption rates of 2.66g/cm^3 and 1.0%, respectively) were used to prepare concrete specimens.

Table 1. Chemical composition of the cement

Chemical compositions (mass%)										
LOI	Insol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl
2.80	0.29	20.08	5.36	2.89	64.29	1.13	2.43	0.25	0.40	0.01

Concrete tests

(1) Mix design of concrete

Concrete specimens were prepared at two different temperatures. The experimental conditions of mixing were 5 degrees C or 20 degrees C. The water-to-cement ratio and the water content of the concrete were 40.0% and 160 kg/m^3, respectively. The dosages of X100 were 0%, 2% and 4% by cement weight. The target slump value and air content were 12 cm and 4.5%, respectively. Table 2 shows the mix design, slump, air content and slump of the mixing concrete. A 55-liter horizontal biaxial forced-mixing mixer was used to prepare the concrete.

(2) Setting time

After concrete mixing, mortar and coarse aggregate were immediately separated by a wet screening method. The separated mortar was used in setting time measurements. Setting time was measured according to the norm JIS A 1147:2007.

(3) Compressive strength

After concrete mixing, φ10 × 20 cm specimens of concrete were immediately made in preparation for strength testing. The specimens were stored at the mixing temperature and a relative humidity of 60%. The specimens were demolded one day after placing and were cured in water at the same temperatures as mixing up to the predetermined age. Compressive strength was measured according to the norm JIS A 1108: 2006.

Table 2. Mix design of concrete

W/C (%)	s/a (%)	Unit contents* (kg/m^3)	Mixing temp. (^{O}C)	Dosage of SP (Cx%)	Dosage of X100 (Cx%)	Slump (cm)	Air cont. (%)	Con. temp. (^{O}C)
40.0	44.5	W=160 C=400 S=773 G=987	20	0.80	0.0	12.5	4.2	22
				0.70	2.0	12.0	4.3	21
				0.60	4.0	12.0	4.5	21
			5	0.50	0.0	12.0	4.3	8
				0.45	2.0	12.5	4.5	8
				0.40	4.0	12.5	4.4	8

* W: Water, C: Cement, S: fine aggregate, G: Coarse Aggregate

Cement paste tests

(1) Heat release rate

Heat release rates of cement paste with or without X100 were measured by isothermal calorimetry. The water-to-cement ratio of the cement paste was 50%. The dosages of X100 were 0, 2.0 and 4.0%. Experimental temperatures were controlled at 5 degrees C or at 20 degrees C. Heat release rates were measured for each temperature.

(2) Specimen preparation

Cement paste specimens were prepared. These had a water-to-cement ratio of 40%, X100 (dosages were 0% and 4%) by weight of cement, and were mixed and cured at 5 degrees C or at 20 degrees C. After mixing, the cement paste specimens were put in a closed vessel and seal-cured at the same temperature as mixing, up to the predetermined age. When the age of the specimens reached the predetermined age, they were roughly crushed and soaked in acetone to terminate the hydration of the specimens. After termination of hydration, the specimens were dried at 105 degrees C for 24 hours

(3) Reaction ratio of alite

The reaction ratio of alite was calculated from the quantity of unreacted alite determined by X-ray diffraction, using the internal standard method. Specimens prepared in (2) were used. A total of 20.0% of each specimen was replaced by corundum powder as the internal standard material. Cu-Kα was used as the radiation source. The diffraction planes of the diffraction peaks used for quantitation were as follows: alite [040][620], corundum [024]. The areas of the diffraction peaks are calculated by numeric integration after background removal. The reaction ratio of alite was calculated by equation 1:

$$\alpha(\mathrm{t}) = \frac{\frac{A_{alite}(t)}{A_{corundum}(t)} \times \frac{100}{100-LOI(t)}}{\frac{A_{alite}(0)}{A_{corundum}(0)} \times \frac{100}{100-LOI(0)}} \times 10 \tag{1}$$

Here, *t* is the curing age of the specimen, α(*t*) is the reaction ratio of the alite of the specimen at the age of *t* days, $A_{alite}(t)$ is the peak area of the alite, $A_{\mathrm{corundum}}(t)$ is the peak area of the corundum as the internal standard material, and LOI(*t*) is the loss on ignition of the specimen determined by mass reduction at 1,000 degrees C by means of TG-DTA.

(4) Bound water ratio

The specimens prepared in (2) are pulverized. Loss of ignition of the pulverized specimen from room temperature to 1,000 degrees C was measured by TG-DTA. The bound water ratio was calculated from LOI as the ratio to the mass of the test samples after ignition.

(5) Porosity

The porosity of the specimens prepared in (2) was measured by a method based on Archimedes' principle. Pure water was used as the soak liquid. The specimen was soaked in pure water under reduced pressure to fill the pores with water. After soaking, the weight of specimen was measured in water. Finally, the weight of soaked specimen was measured after wiping the surface of the specimen. Total porosity was calculated from equation 2:

$$\mathrm{Porosity} = \frac{\text{weight of soaked specimen} - \text{weight of specimen before soaking}}{\text{weight of soaked specimen} - \text{weight of soaked specimen in water}} \tag{2}$$

RESULTS AND DISCUSSION

Setting time

Figure 1 shows the initial and final setting times of the concrete specimens. Regardless of curing temperature, the initial and final setting times were accelerated by the addition of X100, and the times decreased with the increase of the dosage of X100. The ratios of the reduction in setting time by the addition of X100 to the setting time of the control in the specimens cured at 20 degrees C were approximately 25% and 40 to 45% by dosing 2.0% and 4.0% of X100, respectively. Additionally, the reduction ratios at 5 degrees C were approximately 30 to 35% or 50% by dosing 2.0% or 4.0% of X100, respectively. The use of X100 is effective in the shortening of setting time even at a normal temperature of 20 degrees C and at a low temperature of 5 degrees C.

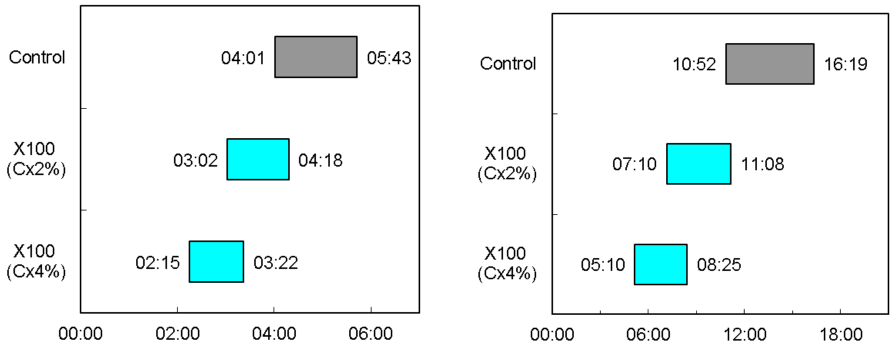

Figure 1. Initial and final setting times of concrete specimens (Left figure: cured at 20 degrees C; right: cured at 5 degrees C)..

Compressive strength

Figure 2 shows the compressive strength of concrete containing X100. It was confirmed that the strength development of the concrete was accelerated by the addition of X100. The compressive strength of the concrete increased with the increase of the dosage of X100 in each curing age, regardless of curing temperature.

The times taken for the compressive strength to become 5MPa in the specimens cured at 20 degrees C were approximately 14.5 hours, 11.0 hours and 9.0 hours at X100 dosages of 0%, 2% and 4%, respectively. If the demolding strength in the concrete construction is 5MPa, the addition of 2% and 4% of X100 can shorten the time required by approximately 3.5 and 5.5 hours at 20 degrees C, respectively. In specimens cured at 5 degrees C, the times were approximately 32 hours, 26 hours and 21.5 hours at X100 dosages of 0%, 2% and 4%, respectively. The addition of 2% or 4% of X100 can shorten the time required by approximately 6.0 and 10.5 hours at 5 degrees C, respectively.

The use of X100 is effective not only in the shortening of setting time but also in the increasing of early strength development, even at a normal temperature of 20 degrees C and at a low temperature of 5 degrees C.

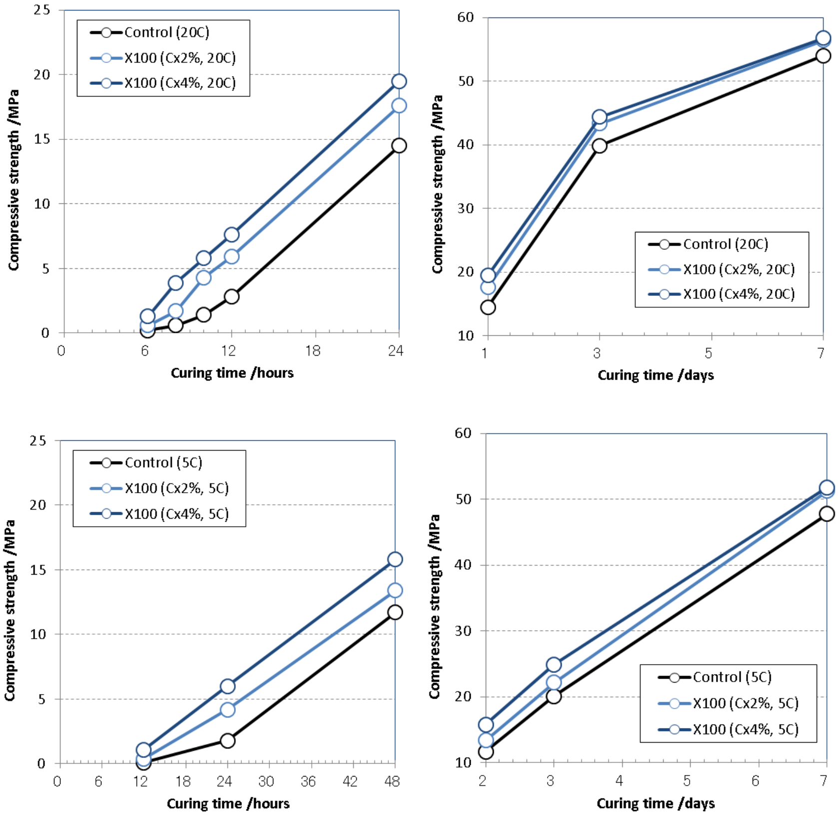

Figure 2. Compressive strength of concrete specimens
(Top figures: cured at 20 degrees C; bottom figures: cured at 5 degrees C)

Heat release rate

Figure 3 shows the heat release rate of cement paste with and without X100. The rise time of the second heat release peak due to alite hydration was accelerated by the addition of X100, regardless of the curing temperature. This result is related to the results of the shortening of the time of setting by the addition of X100, which are shown in Figure 1. The seeding effect of X100 on the shortening of setting time was also assured by the result of isothermal calorimetory. The time of the second peak was accelerated by the addition of X100, and the peak heights were also increased with the increase of the dosage of X100. The early hydration of alite is accelerated by the addition of X100 regardless of curing temperatures.

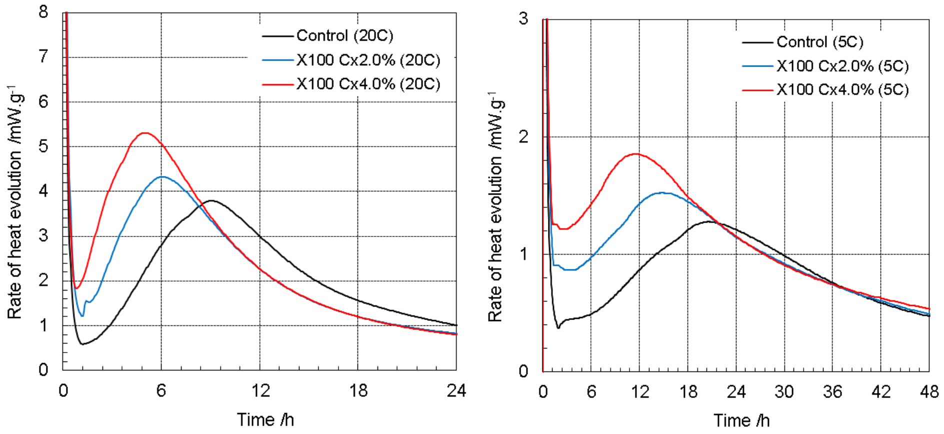

Figure 3. Heat release rate of cement paste
(Left figure: cured at 20 degrees C; right: cured at 5 degrees C)

Reaction ratio of alite

Figure 4 shows the result of quantitative analysis of the reaction ratio of alite in the cement paste specimens at the curing age of 1day, 3 days and 7 days. The reaction ratio of alite was accelerated by the addition of X100, particularly in the earlier curing age. The acceleration of the early hydration of alite by addition of X100, regardless of curing temperature, is assured by quantitative analysis.

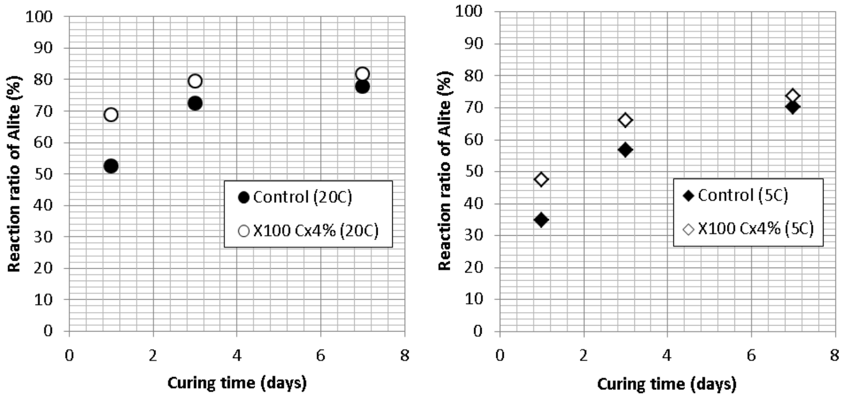

Figure 4. Reaction ratios of alite of cement paste specimens
(Left figure: cured at 20 degrees C; right figure: cured at 5 degrees C)

Bound water ratio

The bound water ratio is generally related to the total reaction of all cement phases. Figure 5 shows the relationships between the reaction ratio of alite and bound water ratio of cement paste specimens. It is confirmed that the bound water ratio has a high correlation with the reaction ratio of alite. This result suggests that the early hydration of cement can be evaluated by the reaction of alite.

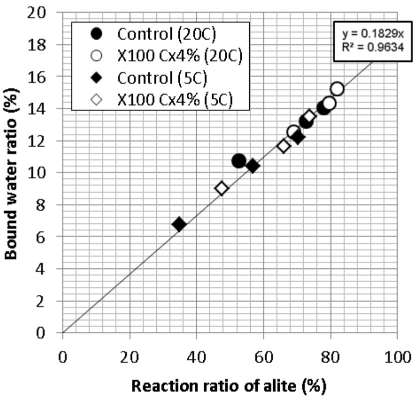

Figure 5. Relationships between reaction ratio of alite and bound water ratio

Porosity

Figure 6 shows the porosity of cement paste specimens. It was confirmed that the porosity was lowered by the addition of X100 due to the acceleration of cement hydration by the X100. Generally, it is known that the strength development is correlated to porosity. Figure 7 shows the relationships between the porosity of cement paste specimens and the compressive strength of concrete specimens. Although the specimens evaluated were different, it was thought that there are only slight differences in the reaction of cement and the pore structure development because water-to-cement ratio and mixing/curing temperature of each specimen were the same. It was confirmed from Figure 7 that the porosity had a high correlation with compressive strength.

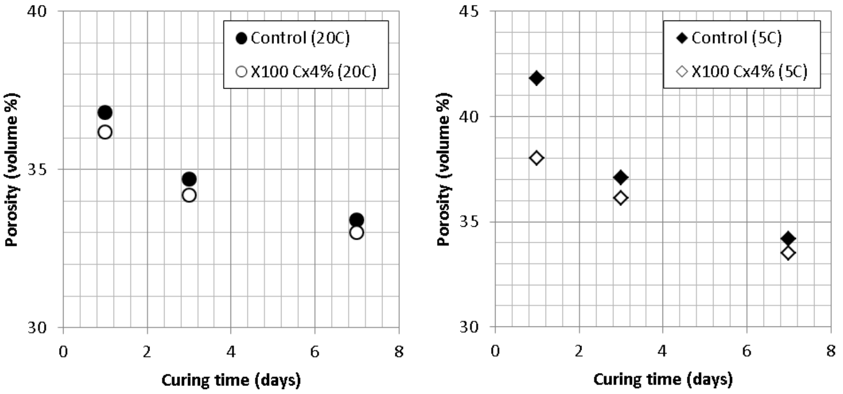

Figure 6. Porosity of cement paste specimens
(Left figure: cured at 20 degrees C; right figure: cured at 5 degrees C)

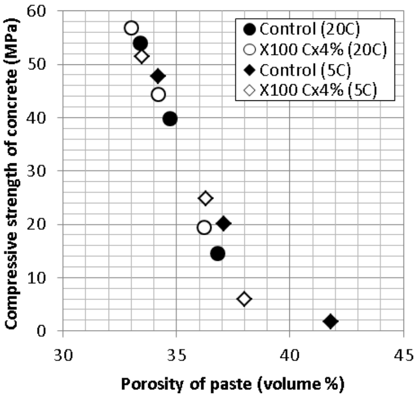

Figure 7. Compressive strength of concrete specimens and porosity of cement paste specimens
(Left figure: cured at 20 degrees C; right figure: cured at 5 degrees C)

CONCLUSIONS

In this paper, the effect of C-S-H type accelerator on the early hydration and the early strength development at 5 or at 20 degrees C, were evaluated. The conclusions are as follows:

1) The setting time and the early strength development of concrete cured at 5 degrees C or at 20 degrees C are accelerated by the addition of C-S-H type accelerator.

2) Early hydration of cement is accelerated by the addition of C-S-H type accelerator at both low and normal temperatures. The acceleration of alite hydration by the addition of C-S-H type accelerator was confirmed quantitatively.

3) Porosity is decreased by the addition of a C-S-H type accelerator at each temperature. It was confirmed that the porosity had a high correlation with compressive strength.

4) It was confirmed that the C-S-H type accelerator acts not only at 20 degrees C but also 5 degrees C.

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