# METHOD OF ADDING AND PORE REFORMING MECHANISM BY USING C-S-H TYPE HARDENING ACCELERATOR

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#### **ABSTRACT**

Development and investigation of a C-S-H type hardening accelerator having a hardening accelerator mechanism different from recent hardening accelerators has been advanced. This hardening accelerator can be cured without waiting for the formation of hydride product C-S-H by cement hydration reaction, unlike conventional methods. That is, the hydration reaction is progressing intermittently. There are few cases of applying such hardening accelerators at the construction site and it is thought that consideration on durability is also necessary. In this study, we investigated whether the addition method which focuses on the concentration in the unit water amount is whether to add the hardening accelerator to the cement mass. Regarding the modification of the pore contributing to strength development, attention was paid to the transition zone, capillary pore, and the area in which the pore is modified was studied. As a result, it was conceived that the concentration of the admixture in the unit water amount was greatly influenced by the C-S-H type hardening accelerator rather than contributing to the cement. Therefore, it was confirmed that concentration addition to unit water amount is desirable. In consideration of the pore diameter to be densified by air permeability test, the water cement ratio was high, the effect of densifying the pore in the transition zone area was observed in a small amount addition. Densification of the bulk portion is also recognized by the addition of a large amount, so it is considered that the added amount influences the properties of the concrete.

**Keywords:** C-S-H type hardening accelerator, adding method, unit water amount, transition zone, capillary pore, air permeability test.

#### 1. BACKGROUND

In case of improving convertibility of concrete formwork or hardening accelerator in winter construction, consider utilization of the hardening accelerator. Generally, a nitrite type hardening accelerator is often used. And this hardening acceleration mechanism promotes cement hydration reaction by promoting the ionic contamination from cement particles, thereby accelerating the development of strength. On the other hand, in recent year C-S-H type hardening accelerator has been developed and investigated<sup>1-4)</sup> such as different from a hardening mechanism of nitrite type. This C-S-H type hardening accelerated is a hardening accelerated mainly composed of calcium silicate hydrate nanoparticles. According to many study of such hardening accelerators it's reported<sup>2-4)</sup> that many possibilities such as productivity improvement in secondary products and shortening of steam curing time. Mostly reported about hightemperature curing at low water cement ratio. According to the report, it is said that by the addition of the C-S-H type hardening accelerator, the compressive strength develops early and does not hinder the development of strength over a long period of time. Unlike conventional hardening accelerators, this hardening accelerator does not accelerate the hydration reaction of cement. Therefore, hydration of cement is considered to progress continuously. On the other hand, a certain amount of high water cement ratio is required for use at construction sites. However, there are not many cases of application or examination in such a case. In addition, there is not much study on durability.

In general, admixtures are not included in the volume of concrete. It is used by dissolving in water for mixing.

W/C (%)	s/a (%)	air (%)	Unit Weight (kg/m³)					Amount of ACX		Admixture		Fresh Properties		
			W	Bin OPC	der BFS	S	G	Ratio (%)	Dosage (kg/m³)	SP	AE	CT (°C)	Slump (cm)	air (%)
40	44			213	213	743	975	0	-	0.40%	4.5A	20.8	13	4
								C×4%	17.0	0.30%	2.5A	22.5	10.5	4.5
								W×10%	17.0					
60	48	4.5	170	142	142	870	971	0	-	0.40%	3.5A	20.8	19.5	3.9
								C×4%	11.4	0.30%	4.5A	21.1	18	3.6
								W×10%	17.0		5.0A	21.3	20	3.5
70	50			121	121	923	952	0	1	0.30%	4.25A	20.5	15.5	4.7
								C×4%	9.7		5.5A	20.4	13.5	4.6
								W×10%	17.0		6.0A	20.5	12	4.6

Table 1. Mix proportion

The addition method in the hardening accelerator is generally added at a certain rate relative to the mass of the cement. This is presumably because the conventional hardening accelerator react with the cement. However, C-S-H type hardening accelerator mixes the nucleus of C-S-H generation, the amount of contamination is considered to be important. Therefore, we consider that the concentration in the unit water amount is more important than the addition amount of cement to the admixture addition method.

In addition, we consider that the reason of the strength development and the improvement of the durability by the addition of the C-S-H type hardening accelerator is to densify the pores in the concrete. However, it is unclear which area in the concrete the pores in the concrete are densified by adding the C-S-H type hardening accelerator, and it is necessary to investigate the mechanism. In particular, we consider that the pore diameter to be densified also differs between strength and mass transfer resistance.

In view of the above, this study aims to investigate the method of adding the C-S-H type hardening accelerator and to emphasize the pore area densified by pores by addition. In this study, by changing the water cement ratio and the aggregate amount, making concrete which has different sizes and amounts of pores. Examined about the modification of pore by adding C-S-H type hardening accelerator.

# 2. OUTLINE OF STRENGTH DEVELOPMENT TEST

#### 2.1 Outline of experiment

We focused on the hardening accelerator mechanism of the C-S-H type hardening accelerator. It is a mechanism that ion eluted from the cement to react with a C-S-H type hardening accelerator to accelerate hardening. We consider that the C-S-H type hardening accelerator would have a great influence on the amount of the nucleus of C-

S-H generation. That means the concentration of C-S-H which is the solid fraction in the water used has a great influence for the accelerate hardening. Therefore, we considered that it is necessary not to add to cement mass as usual admixture. However, to keep concentration in unit water amount constant. According to previous studies1), strength develop by adding 4% hardening accelerator to cement mass. W/C at that time was 40%. The concentration in water used in this mix proportion was set as a reference value. Table 1 shows the mix proportion of this experiment. The unit water amount was fixed at 170kg/m<sup>3</sup>. This is to make the addition amount of the C-S-H type hardening accelerator equal. In addition, we changed the water cement ratio to 40, 60, 70%. The C-S-H type hardening accelerator was added in three patterns of Water  $\times$  10% (W $\times$ 10%), Cement  $\times$  4% (C $\times$ 4%), and no addition (ACX×0%). A compressive strength test according to Japan Industrial Standard (JIS) was conducted in this mix proportion. The test specimen was subjected to sealing curing under a constant temperature and humidity environment (20°C, 60% RH), and the mold released from the age (1, 3, 7, 28 days) was used for the compressive strength test.

Also, in order to confirm the mass transfer resistance, an air permeability test was carried out. The size of the specimen were cylindrical specimens of  $\phi 100 \times 50$  mm, and two specimens were prepared for each age. The test specimen was subjected to sealing curing under a constant temperature and humidity environment (20°C, 60% RH), and the mold released from the age (7, 28 days). Concrete used as a sample was left in a drying oven at 40°C until constant weight to remove moisture contained in pore. The purpose of setting at 40°C is to avoid removing bound water ratio in concrete. By giving a constant pressure of 0.2N/cm² to the specimen, the air dropped was measured by the water replacement method. Air permeability coefficient was calculated from the obtained air permeation amount.

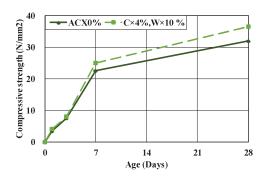


Fig. 1. Compressive strength development (W/C 40%)

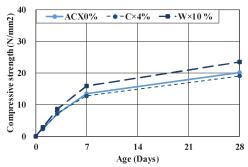


Fig. 2. Compressive strength development (W/C 60%)

# 2.2 Strength development result at constant concentration in unit water amount

Figure 1, 2 and 3 is a part of the result of the compressive strength test according to JIS. From the figure, it was confirmed that the compressive strength was improved at W/C 40%. However, at W/C 60% and W/C 70% compressive strength development could not be confirmed with C×4% to ACX 0% which the C-S-H type hardening accelerator was added and not added. Also in W/C 70% the compressive strength development due to the addition of the C-S-H type hardening accelerator was not remarkable as in W/C 60%. When the addition amount was set to W×10%, strength development was confirmed at any water cement ratio. The result showed that the rate of increase in strength of C×4% compared with that without addition was about the same or lower. However, strength increase of about 20% could be confirmed by adding W×10%. From the above results, when a C-S-H type hardening accelerator was added at a fixed ratio to the mass of cement, strength development was not confirmed at a high water cement ratio. However, when added at a constant ratio to the unit water amount, it was possible to confirm the strength developing property of the C-S-H type hardening accelerator at the same ratio in all water cement ratios. In this way, it was confirmed that the strength was increased by adding it at a constant

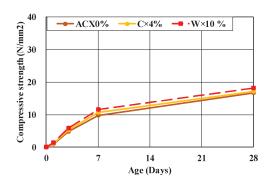


Fig. 3. Compressive strength development (W/C 70%)

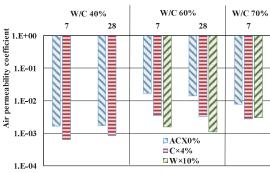


Fig. 4. Result of air permeability test

concentration in the unit water amount in the strength characteristic. Therefore, it was confirmed the mass transfer resistance of the concrete made with a constant concentration of the admixture by the C-S-H type hardening accelerator.

#### 2.3 Result of air permeability test

Figure 4 shows the result of air permeability test. From the figure, the phenomena of the air permeability coefficient due to the addition of the hardening accelerator were confirmed regardless of the addition amount of the C-S-H type hardening accelerator compared with ACX 0% at W/C 40% and 60%. In addition, the results showed that the effect of improving the air permeability was large at W/C 60%, which has a larger pore than W/C having a dense pore structure of 40%. Therefore, it was found that as the water cement ratio is high and the pore is larger, the pore becomes denser and the air permeability coefficient becomes smaller by adding the C-S-H type hardening accelerator.

# 3. INVESTIGATING OF DENSIFIED PORE DIAMETER

From the above, mass transfer resistance was reformed at low addition of hardening accelerator at high water cement ratio. It was confirmed that when high addition in all the water cement ratios, mass transfer

**Table 2**. Mix proportion

	W/C (%)	s/a (%)	air (%)		Unit Weig	tht (kg/m³)	Amount of ACX			
Symbol				W	С	S	G	Ratio C×(%)	Ratio W×(%)	Dosage (kg/m³)
50%-100	50	100		265	539	1350		C×0%	W×0%	-
								C×5%	W×10%	27
								C×10%	W×20%	54
								C×15%	W×30%	81
50%-56	50	56	4.5	190	380	951	761	C×0%	W×0%	-
								C×4%	W×9%	17
								C×9%	W×18%	34
								C×13%	W×27%	51
		48		170	340	852	951	C×0%	W×0%	-
								C×5%	W×10%	17
								C×10%	W×20%	34
								C×15%	W×30%	51
50%-40		40		150	300	752	1141	C×0%	W×0%	-
								C×6%	W×11%	17
								C×11%	W×23%	34
								C×17%	W×34%	51
30%-48	30	48	4.5	170	567	762	850	C×0%	W×0%	-
								C×5%	W×16%	28
								C×10%	W×34%	57

resistance and strength development were reformed. In this chapter, in order to clarify the mechanism of which area of pore is reforming mass transfer resistance and strength development, we investigated by considering transition zone and the pore between mortar portion.

#### 3.1 Outline of experiment

The target of the pore were transition zones at the interface of the coarse aggregate in the concrete and capillary pore in the mortar. The s/a was set to 40, 48, 56% by changing the amount of coarse aggregate. This is to change the transition zone amount. As a result, we expected to increase the transition zone volume<sup>6)</sup> due to internal bleeding formed on the lower surface of the aggregate by increasing the amount of coarse aggregate. At the same time, mortar (s/a 100%) not affected by the lower surface of the coarse aggregate was also prepared. Table 2 shows the mix proportion of concrete produced. With respect to the addition of the C-S-H type hardening accelerator, the amount added in concrete with s/a of 48% was W×0, 10, 20, 30, and the same amount as the amount of admixture mixed therein was adopted for other s/a. In other words, admixture in the concrete was made in the same amount. Concrete was prepared using an om mixer. In order to measure the substance permeability, we measured the air permeability test and the total pore volume in the specimen which affect it. The specimen was

subjected to 7 days of sealing curing in a constant temperature and humidity chamber ( $20^{\circ}$ C, 60% RH). For the porosity test, the Archimedes method was adopted, and the specimen was used which after completion of the air permeability test. In order to calculate the porosity, firstly, it was left to stand at  $40^{\circ}$ C oven drying until the mass of the specimen reached a constant mass. The absolute dry mass was calculated therefrom. Saturated water treatment and mass in water were measured by performing vacuum saturation treatment.

#### 3.2 Result of experiment

### 3.2.1 Porosity test (Archimedes method)

Figure 5 shows the results of porosity test by the Archimedes method. From the results, it was confirmed that the mortar has more pore volume than concrete. It is considered that there is no pore in the coarse aggregate. It was assumed that the transition zone and the capillary pore existed in the mortar portion excluding the coarse aggregate. Therefore, we decided to evaluate the experimental results per unit mortar in concrete. Figure 6 is a summary of the results. It was confirmed that there were more pores in concrete without C-S-H type hardening accelerator than in mortar. It is considered that the difference from this mortar is a pore mainly composed of the transition zone of the coarse aggregate surface. In addition, it can be seen that the addition of the C-S-H type

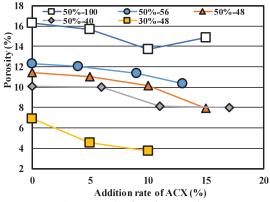
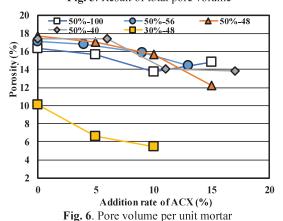


Fig. 5. Result of total pore volume



hardening accelerator reduces the porosity in any mix proportion.

## 3.2.2 Air permeability test

Figure 7 shows the results of the air permeability test. The coarse aggregate was considered not to permeate, and it coefficient became smaller in any mix proportion as the was indicated by the air permeability coefficient per unit mortar. It was confirmed that the air permeability addition amount increased. On the other hand, in the concrete with W/C 30%, the reduction in the air permeability coefficient by adding the C-S-H type hardening accelerator was small compared with W/C 50%.

### 3.3 Consideration of densified pore diameter

Figure 6 shows the porosity per unit mortar and the air permeability coefficient obtained above. It can be confirmed that the air permeability coefficient improves as the porosity improves. This relationship also showed the same tendency in the mix proportion in which the coarse aggregate amount was changed. In the relationship between the porosity and the air permeability coefficient, the tendency differs between the absence of the C-S-H

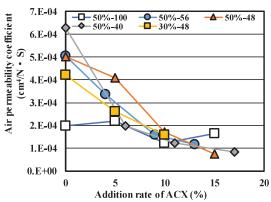
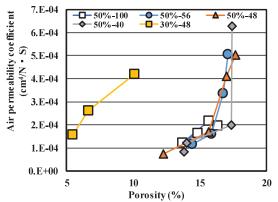


Fig. 7. Air permeability coefficient per unit mortar



**Fig. 8**. Relation between pore volume and air permeability coefficient

type hardening accelerator and the addition of a small amount and a large amount. By adding a small amount of the C-S-H type hardening accelerator, the reduction amount of the pore is small but the decrease amount of the air permeability coefficient becomes large. This tendency was particularly clear at 50%-40, which is the largest amount of coarse aggregate. On the other hand, as the addition amount was increased, the relationship showed that the air permeability coefficient became smaller as the pore decreased, and the same tendency was observed for both mortar and concrete. From all the result of this research the consideration is that small amounts are added. the hydration reaction of the cement from the core particles of C-S-H existing in the transition zone between the coarse aggregate and the cement hardening zone occurs, and when the added amount exceeds a certain level, the pore in the mortar, that is, the capillary pore. It can be inferred that a reforming hydration reaction is occurring. Therefore, in the case of addition of a small amount in the case of a high W/C, since a hydrate is formed in a large pore, the influence on the strength is not large and the substance permeability is improved. On the other hand, it

can be imagined that the strength and durability are affected by densifying the pore of the mortar itself rather than the transition zone portion due to the low W/C state and addition to some extent. From now on, we are considering to be able to evaluate the mechanism of the effect quantitatively from methods such as direct observation using SEM etc.

#### 4. CONCLUSIONS

The results obtained in this research are summarized pelow

- The C-S-H type hardening accelerator, which is a new material, acts on the concentration in the unit water rather than affecting the cement, it is preferable to add the concentration to the unit water amount.
- (2) When the water cement ratio was high, the effect of densifying the pore in the transition zone region was observed in a small amount addition. Densification of the bulk portion is also recognized by the addition of a large amount, so it is considered that the added amount influences the properties of the concrete.

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### PHOTOS AND INFORMATION



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