

# Effect of prevention for chloride ion using both of CA2 and expansive admixture to low heat Portland cement

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**ABSTRACT:** Salt damage is one of the serious causes of deterioration in reinforced concrete. However, when building mass concrete under salt damage environment, we have to use cement with a heat suppression effect which has low resistance for chloride ion. In this research, we focused on the CA<sub>2</sub> which is admixture for salt damage prevention. CA<sub>2</sub> reacts with calcium hydroxide from cement hydration and makes hydrocalumite. Thus, the soluble chloride ion is reduced. Finally, concrete using CA<sub>2</sub> has high resistance for salt damage. LPC concrete using CA<sub>2</sub> has low resistance for chloride ion than OPC concrete using CA<sub>2</sub>. After that, we had XRD measurement, and we have confirmed that hydration product is different in LPC and OPC when adding CA<sub>2</sub> and expansive admixture. We think that the difference of hydration product is reason for difference of salt damage prevention by difference of ability to immobilize chloride ion.

## 1 INTRODUCTION

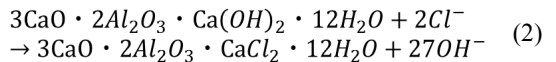
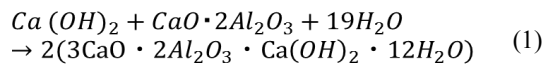
We have to care for thermal crack when building a mass concrete. Thermal crack have the risk of penetrating the structure. If the crack occurs, durability of the structure is declined by penetrating the deterioration factors such as carbon dioxide, chloride ion and water.

To prevent thermal cracks, we use a cement with a heat suppression effect such as low heat Portland cement. In addition, we use expanding admixture for shrinkage prevention. Low heat Portland cement is less alite (C<sub>3</sub>S) and aluminate phase (C<sub>3</sub>A) for heat suppression. However, monosulfate which has potential to immobilize the chloride ion is made from aluminate phase (C<sub>3</sub>A). Thus, low heat Portland cement has low resistance to chloride ion compared with other cements. Therefore, we have less opportunity to use low heat Portland cement under salt damage environment such as harbor.

Recently, CaO · 2Al<sub>2</sub>O<sub>3</sub> (CA<sub>2</sub>) which react with calcium hydroxide from cement hydration and makes hydrocalumite. Its reaction is shown in formula(1). This hydrocalumite immobilize chloride ion as Friedel's salt. Its reaction is shown in formula(2). Thus, the soluble chloride ion is reduce. Finally, concrete using CA<sub>2</sub> has high resistance for salt damage.

In this research, we made and tested concrete using low heat Portland cement, CA<sub>2</sub> and expansive admixture for the purpose of constructing the harbor structure. Using these concrete, we checked the resistance for chloride ion by immersed test in salt wa-

ter and Non-steady-state electrical migration tests. And, we also confirmed compressive strength and resistance for carbonation.



## 2 EXPERIMENTAL OUTLINE

### 2.1 Using material and specimen specifications

Table 1 shows the chemical composition of the bonding admixtures. CA<sub>2</sub> is mainly composed of Al<sub>2</sub>O<sub>3</sub>. The expansive admixture contains many (SO<sub>3</sub>) .

Table 2 shows the mix proportion of concrete. Water-binder ratio (W/B), ratio of coarse aggregate (s/a) and unit water content (W) are constant in all of concrete, and using cements are ordinary Portland cement (OPC) and low heat Portland cement (LPC). In this research, CA<sub>2</sub> and the expansive admixture was replaced with the cement. We also checked the prevention for chloride ion from the difference of addition amount of CA<sub>2</sub> and the expansive admixture. Curing method is water-curing for 28 days.

Table 1. Chemical composition of the binder

	contents(mass%)							Specific surface area [cm <sup>2</sup> /g]	Density [g/cm <sup>3</sup> ]
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	R <sub>2</sub> O		
OPC	64.09	20.45	5.15	2.09	3.04	0.89	0.57	3240	3.16
LPC	63.08	26.18	2.73	2.33	3.11	0.95	0.41	3760	3.24
CA2	23.96	0.64	67.73	0.01	7.09	0.27	0.21	3100	2.96
Ex	70.6	1.0	7.2	18.5	0.8	-	-	2840	3.05

Table 2. Mix proportion of concrete

	Cement type	W/B (%)	s/a (%)	Unit Weight [kg/m <sup>3</sup> ]					
				W	C	CA2	Ex	S	G
L	LPC	50	48	163	326	-	-	876	974
L(0-20)					306	-	20		
L(10-10)					306	10	10		
L(10-20)					296	10	20		
L(15-15)					296	15	15		
L(30-0)					296	30	-		
L(30-20)					276	30	20		
N	OPC				326	-	-	873	971
N(10-0)					316	10	-		
N(10-10)					306	10	10		
N(15-15)					296	15	15		

2.2 Test method

2.2.1 Compressive strength test

After 28 days of water curing, we had a compression test of concrete reference to JIS A 1108-2006.

2.2.2 Non-steady-state electrical migration test

Fig 1 shows experimental equipment for non-steady-state electrical migration test. As a pre-treatment, the specimen is saturated with calcium hydroxide solution in a vacuum. 0.3N of NaOH solution is injected into anode side and 3% NaCl solution is injected into cathode side. DC voltage is set to 30V. After energized a predetermined time for the specimen, the specimen was split in half and sprayed 0.1N silver nitrate solution on the split surface (Fig.1). After that, the part which was colored in white was measured as the penetration depth of chloride ion. Penetration depth is an average of 7 points. After measuring the depth, we calculated diffusion coefficient using NT BUILD 492 at formula(3)-(5).

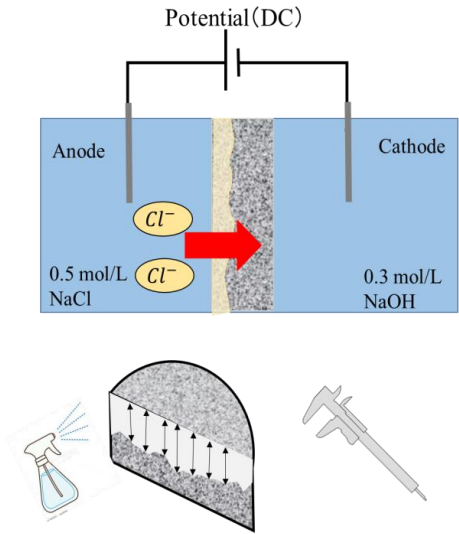


Figure 1. Non-steady-state electrical migration test method

$$D_{nssm} = \frac{RT}{zFE} \cdot \frac{X_d - \alpha\sqrt{X_d}}{t} \quad (3)$$

$$E = \frac{U - 2}{L} \quad (4)$$

$$\alpha = 2 \sqrt{\frac{RT}{zFE}} \cdot \operatorname{erf}^{-1}\left(1 - \frac{2C_d}{C_0}\right) \quad (5)$$

Where,  $D_{nssm}$ : non-steady-state migration coefficient,  $m^2/s$ ;  $z$ : absolute value of ion valence, for chloride,  $z = 1$ ;  $F$ : Faraday constant,  $F = 9.648 \times 10^4 \text{ J/(V}\cdot\text{mol)}$ ;  $U$ : absolute value of the applied voltage,  $V$ ;  $R$ : gas constant,  $R = 8.314 \text{ J/(K}\cdot\text{mol)}$ ;  $T$ : average value of the initial and final temperatures in the anolyte solution,  $K$ ;  $L$ : thickness of the specimen,  $m$ ;  $x_d$ : average value of the penetration depths,  $m$ ;  $t$ : test duration, seconds;  $\operatorname{erf}^{-1}$ : inverse of error function;  $C_d$ : chloride concentration at which the colour changes,  $C_d \approx 0.07 \text{ N}$  for OPC concrete;  $C_0$ : chloride concentration in the catholyte solution,  $C_0 \approx 2 \text{ N}$ .

### 2.2.3 Salt water immersion test

Fig 2 shows the method of salt water immersion test. After 28 days of water curing, the specimen ( $100 \times 100 \times 400 \text{ mm}$ ) was coated with epoxy resin leaving one side surface. Then, the specimen was immersed in NaCl 10% solution. The specimen was split in the age of 1, 2, 4, 8 weeks, and was sprayed 0.1N silver nitrate solution on the split surface. After that, the part which was colored in white was measured as the penetration depth of chloride ion. Penetration depth is an average of seven points.

### 2.2.4 Accelerated carbonation test

$CA_2$  consumes calcium hydroxide, so the concrete addition of  $CA_2$  may be lowered alkali. So, we checked the resistance for carbonation.

Fig 3 shows the method of accelerated carbonation test. After 28 days of water curing, the specimen ( $100 \times 100 \times 400 \text{ mm}$ ) was coated with aluminum tape except one side surface. Then, the specimen was put in the carbonation test chamber. It was kept at temperature was 20 degree Celsius, relative humidity was 60% and concentration of carbon dioxide was 5%. The specimen was split in the age of 1, 2, 4, 8 weeks, and sprayed 1% phenolphthalein solution on the split surface. After that, the part which was not colored in purple was measured as carbonation depth. Depth is an average of seven points.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Compressive strength test

Fig 4 shows the result of compressive strength after

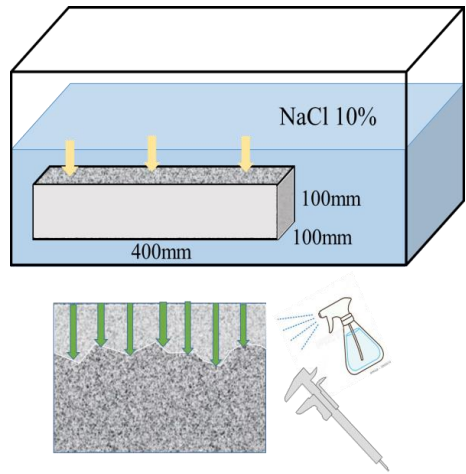


Figure 2. Salt water immersion test method

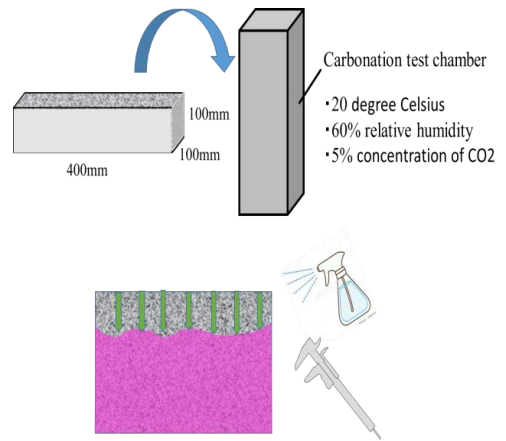


Figure 3. Accelerated carbonation test method

water curing 28 days. The compressive strength of LPC concretes addition of  $CA_2$  and expansive admixture are decreased than only LPC. On the other hand, the strength of OPC concretes addition of  $CA_2$  and expansive admixture are not decreased than only OPC. In this research,  $CA_2$  and the expansive admixture was replaced with cement in binder ratio is constant. Therefore, decreasing in strength is affected that the decreasing of total cement content. However, the compressive strength of OPC addition  $CA_2$  and the expansive admixture is not decreased. As this reason, OPC has enough strength at water curing the 28 days. However, water curing the 28 days is shortage for LPC. So, the strength of only LPC is decreased.

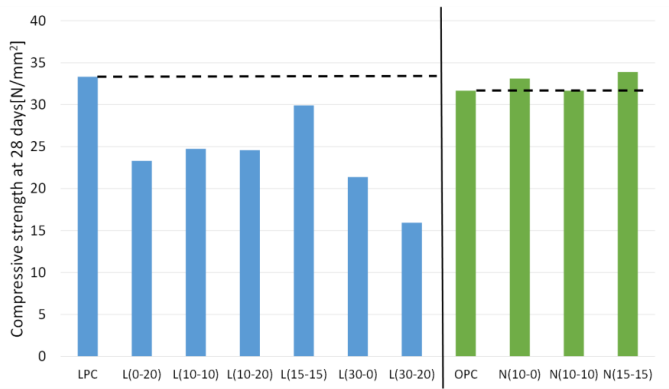


Figure 4. Compressive strength at 28 days

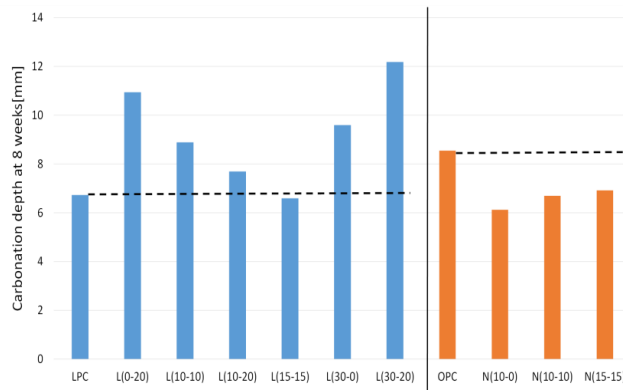


Figure 5. Carbonation depth at eight weeks

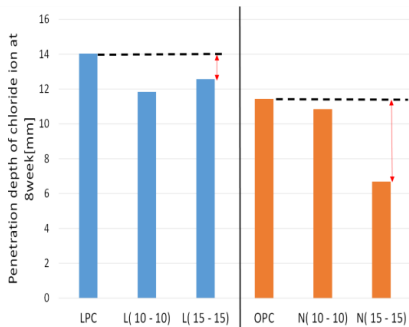


Figure 6. Penetration depth of chloride ion in salt water immersion test at 8 weeks

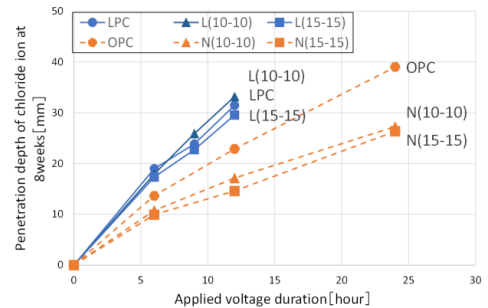


Figure 7. Penetration depth of chloride ion in non-steady-state electrical migration test at 8 weeks

### 3.2 Accelerated carbonation test

Fig 5 shows the depth of carbonation at eight weeks. The resistance to carbonation of LPC concretes addition of  $CA_2$  and expansive admixture are decreased. On the other hand, the resistance to carbonation of OPC concretes addition of  $CA_2$  and expansive admixture are not decreased. In previous studies<sup>1,2)</sup>, concrete addition of  $CA_2$  is densified physically.

This is because hydrocalumite and monosulfate is generated and they fill the void. However, the trend was different in cement type in this research.

### 3.3 Salt water immersion test and Non-steady-state electrical migration test

Fig 6 shows the penetration depth of chloride ion at eight weeks. We show the results of the only 6 types of concrete to compare the cement type difference.

The resistance to chloride ion of LPC concretes addition of CA<sub>2</sub> and expansive admixture are not decreased. On the other hand, the resistance to chloride ion of OPC concretes addition of CA<sub>2</sub> and expansive admixture are improved. The reason for this improvement is that chloride ion was immobilized as a Friedel's salt by addition of CA<sub>2</sub>. Fig 7 shows the result of non-steady-state electrical migration test. Penetration depth of chloride ion is almost same as LPC concretes addition of CA<sub>2</sub> and expansive admixture in spite of conduction time has increased. On the other hand, resistance to chloride ion of OPC concretes addition of CA<sub>2</sub> and expansive admixture are improved. The result of two tests is similar. From the two results, resistance to chloride ion is different in cement type. In addition, non-steady-state electrical migration test can also be evaluated the resistance to chloride ion by immobilization of the chloride ion.

### 3.4 Relationship between SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio and penetration depth of chloride ion

To evaluate resistance to chloride ion, the presence of C-A-H hydration product like hydrocalumite, ettringite and monosulfate that has potential to immobilize the chloride ion is very important. Therefore, Fig 8 shows the relationship between SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio and penetration depth of chloride ion. SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio was calculated from the chemical composition of each admixture. Despite the SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio is not so much changed in the OPC concretes, there was a difference in penetration depth of chloride ion. On the other hand, in spite of the SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio is changed in the LPC concretes, there was not a difference in penetration depth of chloride ion. It shows that there is no relationship between SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio of before reacting and penetration depth of chloride ion after reacting.

### 3.5 Relationship between compressive strength and durability

Fig 9 shows the relationship between compressive strength and carbonation depth. Carbonation depth decreases along the increase of compressive strength. This is not related to the cement type.

## 4 CHEMICAL ANALYSES

From these test results, we find that the concrete addition of CA<sub>2</sub> and expansive admixture is different between LPC and OPC. So, we assumed that the hydration product and hydration speed in LPC and the OPC are different due to the difference in chemical composition content. We made cement pastes with the addition of CA<sub>2</sub> and expansive admixture to the LPC and the OPC to measure the hydration product.

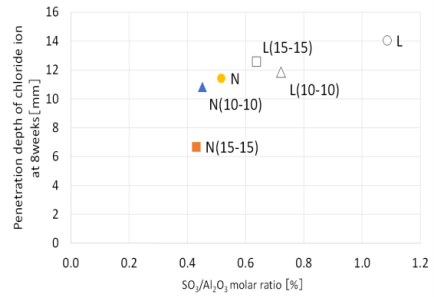


Figure 8. Relationship between SO<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio and penetration depth of chloride ion

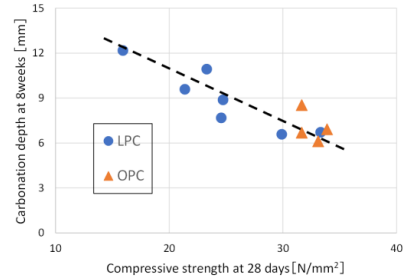


Figure 9. Relationship between compressive strength and carbonation depth

## 4.1 Experimental outline

Fig 10 shows the specimen dimensions and experimental outline. Specimens were sealed curing. Specimen were crushed in every test age, for the purpose of confirming the hydration products, like monosulfate, ettringite, hydrocalumite, calcium hydroxide. Hydration products were measured by X-Ray diffraction (XRD). Further, for the purpose of measuring the amount of calcium hydroxide, Thermogravimetric-Differential Thermal Analysis (TG-DTA). The reason for measuring the amount of calcium hydroxide is because CA<sub>2</sub> consumes calcium hydroxide.

## 4.2 Results and discussions

### 4.2.1 X-ray Diffraction (XRD)

Fig 11 and 12 show the results of XRD. These results are charts of hydration produced for seven days. There are the peak of near 9° and 11° in only OPC. We have identified that the peak of near 9° is ettringite, and the peak of near 11° is hydration product based on carbonate which was produced by the limestone powder contained in the OPC. The case of adding only OPC+CA<sub>2</sub>, the peak near 11° is reduced. Instead, the peak near 10° appeared. This peak has

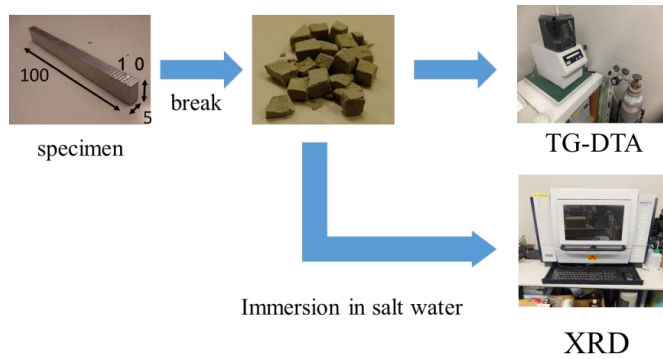


Figure 10. Outline of chemical test

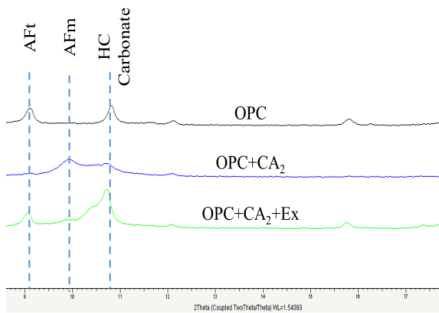


Figure 11. XRD result (OPC+CA<sub>2</sub>+Ex)

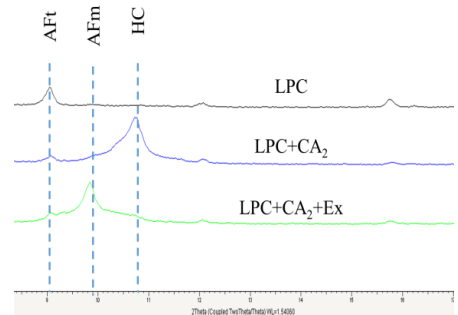


Figure 12. XRD result (LPC+CA<sub>2</sub>+Ex)

been identified as monosulfate. In addition, the case of adding OPC+CA<sub>2</sub>+Ex, there is the peak near 11°. It is close to the peak of hydrocalumite and hydration product of the based on carbonate. Therefore, there is a need for detailed analysis in the Rietveld analysis.

On the other hand, there is the peak near 9° in only LPC. This peak has been identified as ettringite. Next, the case of adding only LPC+CA<sub>2</sub>, the peak of near 9° is decreased, the peak of near 11° is increased. We have identified that the peak of near 11° is hydrocalumite. In addition, the case of LPC+CA<sub>2</sub>+Ex, the peak of near 11° is decreased, the peak of near 10° is increased. We have identified that the peak of near 10° is monosulfate.

#### 4.2.2 Thermogravimetric-Differential Thermal Analysis (TG-DTA).

Fig 13 and 14 shows the result of TG-DTA of the LPC. These results are also a hydration product for seven days as well as the XRD. The amount of calcium hydroxide is reduced in the case of adding CA<sub>2</sub> and expansive admixture to the LPC. Especially, the amount of calcium hydroxide is greatly reduced in the case of adding only CA<sub>2</sub>. It shows the same ten

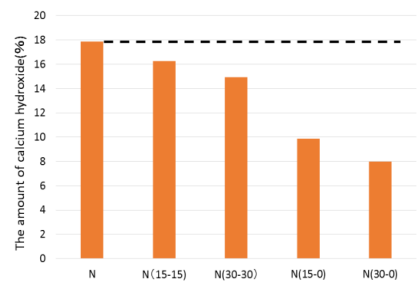


Figure 13. TG-DTA result (OPC+CA<sub>2</sub>+Ex)

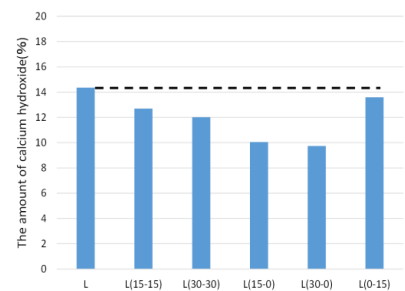


Figure 14. TG-DTA result (LPC+CA<sub>2</sub>+Ex)

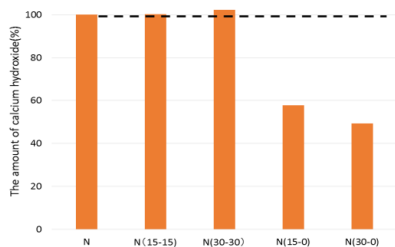


Figure 15.TG-DTA result (OPC+CA<sub>2</sub>+Ex)

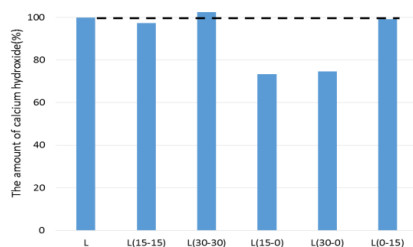


Figure 16.TG-DTA result (LPC+CA<sub>2</sub>+Ex)

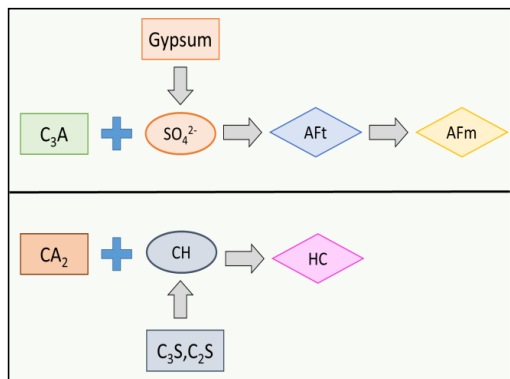


Figure 17.Hydration reaction illustrations (OPC+CA<sub>2</sub>+Ex)

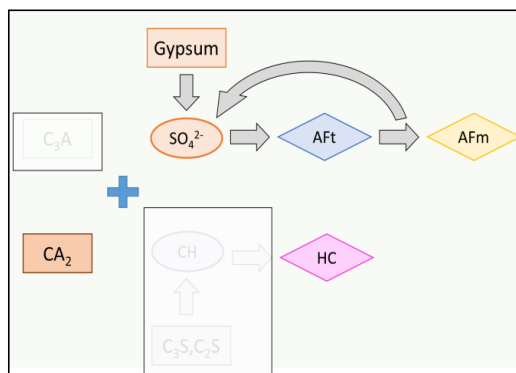


Figure 18.Hydration reaction illustrations (LPC+CA<sub>2</sub>+Ex)

dency as previous studies<sup>1, 2</sup>). However, this decreasing includes in decreasing of cement content. To distinguish weather decreasing of cement content or consumption by CA<sub>2</sub>, we were arranged the result of TG-DTA by per unit of cement. As a method, we divide each cement content in cement content of only LPC, and it was multiplied by the production amount of calcium hydroxide of only LPC. Thus, we calculated the amount of calcium hydroxide generated by LPC. Then, we examined the impact of the addition of CA<sub>2</sub> and expansive admixture.

The graph considering it is Fig 15 and 16. The amount of calcium hydroxide is reduced in the case of adding only CA<sub>2</sub>. On the other hand, the amount of calcium hydroxide is not decreased in case of adding CA<sub>2</sub> and expansive admixture. The amount of calcium hydroxide is not decreased even in the case of adding only the expanding admixture. Therefore, we see that the expansive admixture does not generate the calcium hydroxide. In other words, we see that the CA<sub>2</sub> is not consumed in the case of adding the expanding admixture.

From the above chemical analysis, we have confirmed that the hydration product is different in case of adding only CA<sub>2</sub> to the LPC and case of adding both CA<sub>2</sub> and the expansive admixture in LPC. The reason for this, ettringite is produced by the reaction of SO<sub>3</sub> that contained in expansive admixture and Al<sub>2</sub>O<sub>3</sub> that contained in CA<sub>2</sub>. As shown in formula

(1), we assumed that CA<sub>2</sub> reacts with calcium hydroxide and generates hydrocalumite. However, in the beginning of the hydration, the amount of calcium hydroxide generated from the LPC is low. Therefore, CA<sub>2</sub> reacted with SO<sub>3</sub> which is contained a large amount in the expansive admixture. We show the hydration illustrations at figure 17 and 18.

From Figure 11 and 12, when the addition of CA<sub>2</sub> and expansive admixture to the OPC and LPC, we confirms that the hydration product is different. In the case of adding OPC+CA<sub>2</sub>+Ex, hydration products which has potential to immobilize the chloride ion are hydrocalumite and hydration product of the based on carbonate. In the case of LPC+CA<sub>2</sub>+Ex, monosulfate was produced. We think that the ability which immobilize the chloride ion is different in each. This is the reason why the difference occurs in the penetration depth of chloride ions in the LPC and the OPC.

## 5 CONCLUSION

- 1) Compressive strength of concrete which LPC+CA<sub>2</sub>+Ex was reduced. This is because the reduction of cement content, lack of curing and early demolding.

- 2) Carbonation depth of concrete with the addition of expansive admixture and  $CA_2$  to LPC was increased. We have confirmed the relationship between in compressive strength. However, there is not the relationship between reduction of the pore volume or amount of calcium hydroxide. it is necessary to consider in the future.
- 3) In LPC and OPC, there is a difference in the salt penetration resistance in the case of addition of expansive admixture and  $CA_2$ . It also showed a similar trend in the salt water immersion test and the non-steady-state electrical migration test.
- 4) We confirmed that the hydration product is different in adding only  $CA_2$  and adding  $CA_2$  and expansive admixture in LPC. This is because  $CA_2$  react with  $SO_3$  contained in expansive admixture not react with the calcium hydroxide. Then, the ettringite is generated instead of the hydrocalumite, and monosulfate is produced. On the other hand, we could not identify the

hydration product in OPC. In the future, there is a need for more detailed analysis using, for example, Rietveld analysis to identify the hydration product

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