# Performance evaluation on chlorine ion immobilizing ability of concrete using calcium aluminate aggregate and additive

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ABSTRACT Japan is facing the sea on every side. It has been reported that there are many deteriorated concrete structures due to salt damage. In recent years, in order to improve the resistance to salt-damage, materials have been research and developed using calcium aluminate. In this research, we focus on the aggregate (CaO  $\cdot$  Al<sub>2</sub>O<sub>3</sub> aggregate) and admixture (CaO · 2Al<sub>2</sub>O<sub>3</sub>) for making the specimens for improving resistance of salt damages. Compressive strength test, permeability of chloride ion and observation of aggregate interface on SEM were carried out, using concrete on different replacement of calcium aluminate materials. In order to confirm the composition of the product, a cement paste specimen using the calcium aluminate material was prepared and the hydration product was clarified using XRD. As a result of XRD test, it was found that the calcium aluminate materials react with water and calcium hydrate (Ca(OH)<sub>2</sub>) which is a cement hydration product. And the calcium aluminate materials (especially CA aggregate) added with salt, it was found that chloride ion was immobilized as Friedel's salt and hydration product was generated on the aggregate interface. We can see many hexagonal plate at the aggregate interface on observation of the aggregate interface by SEM. It was confirmed that the products are Friedel's salt and hydration products form calcium aluminate materials from previous studies. Although according to water permeability test, the interface of aggregate may be densified by these hydration products. It is suggested that the densification of the aggregate interface may decrease the permeability inside the concrete. Furthermore, the effect of shielding salt is expected under the severe salt environment on long term.

# 1 INTRODUCTION

# 1.1 Background

Japan is facing the sea. Many cases of salt damage caused by flying salt in the structure near the coasts have been reported. It is known that when the salt damages progresses, the durability and performance of the structure are remarkably impaired. One common countermeasure against salt damage is the use of Blast furnace slag cement which is a shielding effect of chloride ion penetration. Measures after service include a surface coating method in which the concrete surface is covered with a coating film waterproof material, a desalination method, an electric corrosion prevention method. It is said that low heat Portland cement has low salt damage resistance as commonly used cement, and countermeasures at the time of construction are required. In recent years, in order to improve resistance to salt damage, development and research of aggregate  $CaO \cdot Al_2O_3$  (hereinafter referred to as "CA aggregate") mainly composed of calcium aluminate and admixture CaO · 2Al2O3 (hereinafter referred to as "C A2") has been made. They react with cement hydrate Ca(OH)<sub>2</sub> (hereinafter "CH") and chemically immobilize chloride ion as Friedel's salt to improve chlorine immobilization resistance. It is thought that salt tolerance is improved by using these as admixtures.

# 1.2 The purpose

In this study, we checked the strength and characteristics of concrete aggregate using ordinary Portland cement, low heat Portland cement substituting chlorine-immobilized material. Furthermore, when chloride ions penetrate into the concrete, improvement of strength and substance permeability by confirming densification of the interior aggregate interface inside the concrete is confirmed.

# 1.3 About chlorine fixing material "CA aggregate"

Figure 1 shows the appearance of CA aggregate and Table 1 shows chemical composition table of CA aggregate. CA aggregate is prepared with clinker generated in the process of manufacturing alumina cement (lime source and cement produced by dissolving





Figure 1. CA aggregate.

Figure 2. After pre-wetting.

alumina source). As can be seen from Figure 1, since there are many holes produced in the manufacturing process, it has the feature of being porous. The CA aggregate reacts with CH generated by the cement to produce hydrocalumite ( $3CaO \cdot Al_2O_3 \cdot Ca (OH)_2 \cdot 12$ H<sub>2</sub>0, density 2.02 (g/cm<sup>3</sup>)). From reaction formula [1]. It is known that this hydrocalumite immobilizes chloride ions which cause salt damage as Friedel's salt ( $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ , density 2.09 (g/cm<sup>3</sup>)). From reaction formula [2]. From this, it is thought that there is an effect of suppressing chloride ions from penetrating into concrete.

$$\begin{aligned} & \operatorname{CaO} \cdot Al_2O_3 + 3Ca(OH)_2 + 10H_2O \\ & \to 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O \end{aligned} \tag{1}$$

$$\begin{array}{l} Cl^{-} & CaO \cdot Al_2O_3 + 3Ca(OH)_2 + 8H_2O + 2Cl^{-} \\ \rightarrow & 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 11H_2O \end{array} \tag{2}$$

Figure 2 shows the appearance of dried aged aggregate after pre-wetting. Since the aggregate of CA has the property of reacting with water, it is considered that the product was precipitated by pre-wetting. Figure 3 shows the results of powder X-ray diffraction measurement of crushed CA aggregate. Figure 4 shows the measurement results of the powder precipitated on the surface of CA aggregate after pre-wetting. Comparing unhydrated CA aggregate powder with powder on the surface after pre-wetting. It was confirmed that the amount of CA aggregate decreased due to the hydration reaction and that hydrogarnet which is a hydration product by CA aggregate was precipitated. It is considered that CH was not present due to reaction with CA aggregate only, and hydrogarnet was precipitated instead of hydrocalumite.

# 2 CONFIRMATION OF HYDRATION PRODUCT

# 2.1 Confirmation of hydration reaction of cement paste using crushed CA aggregate

### 2.1.1 Test outline and method

In this test, a cement paste specimen was prepared using powdered CA aggregate. Powder X-ray diffraction was carried out for the purpose of comparing the hydration product confirmation and the ability to immobilize salt by cement type. The formulations

Table 1. CA aggregate powder chemical composition.

	Density					
$Al_2O_3$	CaO	MgO	SiO <sub>2</sub>	FeO	S	(g/cm <sup>3</sup> )
55.6	31.7	4.2	4.6	0.9	0.18	2.89



Figure 3. Result of crushed CA aggregate.



Figure 4. Result of powder precipitated on the surface.

used in this test are shown in Table 1. Regarding the materials used, ordinary Portland cement (OPC) and low-heat Portland cement (LPC), which were considered to have low salt damage resistance, were used for cement. As the chlorine-immobilized material, CA aggregate pulverized beforehand by a pod mill and the powdered was used. In order to confirm the change of the hydrated product due to the supply of the chloride ion, the mixing water is mixed by mixing with a 3% salt water (hereinafter referred to as salt water mixing) and mixing with tap water (hereinafter referred to as water mixing). For the curing method, sealed curing was carried out by allowing to stand in a thermostatic chamber (room temperature 20°C, humidity 60%).

### 2.1.2 Outline of specimen

Figure 5 shows the appearance of the specimen prepared in this test. With the mix proportion shown in Table 2, cement, powder of CA aggregate and water for mixing were placed in a bowl and mixed by stirring to prepare a paste specimen. In order to confirm the change of the hydration product over time, at the age of 1, 3, 7 and 28 days, the paste specimen was immersed in acetone to stop hydration and then pulverized in a mortar. Hydrate was observed by powder X-ray diffraction.



Figure 5. The appearance of specimen.

Table 2.	Mix	proportion.
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W/C	Cement type	CA addition amount	Mixing water		
50	OPC		water		
	OFC	50/	3% salt water		
	LDC	570	water		
	LPC		3% salt water		



Figure 6. OPC (Mixing water : water).

### 2.1.3 Test results and discussion

Figure 6 to 9 show measurement results by powder X-ray diffraction (hereinafter referred to as "XRD") by time of various paste specimens. In Figure 6 and Figure 8 in which tap water is used for the mixing water, the peak of CA is confirmed before mixing. As time goes by, the peak decreases and it turns out that hydrocalumite is produced instead. In addition, in the case of mixing with 3% concentration of salt water shown in Figure 7 and Figure 9, as in the case of kneading with tap water, the peak of CA increases with the lapse of time from kneading is decreasing. As a difference from the case of kneading with tap water, hydrocalmite was not confirmed and only Friedel's salt was confirmed. These are thought to be due to the reaction of the theoretical formulas shown in the above-mentioned formulas [1] and [2]. As the cause of the difference in hydration products, the effect due to the type of cement is not confirmed. Therefore, according to the past research, the aggregate itself has hydration reaction material properties, and hydrocalumite is produced under the condition that CH is



Figure 7. OPC (Mixing water : 3% salt water).



Figure 8. LPC (Mixing water : water).



Figure 9. LPC (Mixing water : 3% salt water).

supplied as cement hydrate. Furthermore, it was confirmed that when chloride ions were present, Friedel's salt could be generated to fix chloride ions. It is believe that the reaction itself is carried out uniformly regardless of the type of cement. However, since there is a difference in the XRD peak intensities of the hydrates produced depending on the type of cement, it is assumed that the reaction amount of the CA aggregate changes according to the supply amount of CH derived from cement.

#### **3** SUBSTANCE PERMEABILITY

### 3.1 Using material and specimen specifications

#### 3.1.1 About mix proportion name

Regarding the mix proportion name, it is set as follows: The notation of the acronym "N, L, BB" indicates the type of cement. The next number of cement type indicates the usage rate of CA aggregate. When the expression "CA2" next to the contamination ratio of the CA aggregate is present, it indicates that CA<sub>2</sub> is added. When there is a notation "- S" next to the mixing ratio of CA aggregate or CA2 addition, it indicates that the mixing water is salt water. As for the fresh properties, it was confirmed that the slump was lowered in the formulation using CA aggregate for OPC. Due to the reason that the aggregate is porous, it is conceivable that the cement paste caught in the hole of the aggregate itself. It was suggested that the slump was stable in the formulation using LPC, and there was a possibility that there was a difference in fresh properties depending on the type of cement.

#### 3.1.2 About mix proportion

Table 3 shows the mix proportion and fresh properties of the concrete used in this test. The chemical components of each cement and salt immobilization material are shown in Table 4.

#### 3.2 Implementation test and method

#### 3.2.1 Compressive strength test

A cylinder of  $\phi 100 \times 200$  mm was used as the specimen. After curing, a compressive strength test was conducted in accordance with JIS A 1108. In the measurement of the compressive strength, the compressive strength was calculated from the average value of three pieces of data in consideration of the variation.

#### 3.2.2 Vacuum water absorption test

As pretreatment of test specimens, concrete specimens of  $\phi 100 \times 200$  mm were cut to width of 50 mm at 21 and 49 days of age. After sealing again for 7 days, it was left standing in a drying oven at 40°C for 7 days from age 28 and 56 days. It was confirmed that the amount of mass decrease by drying was 1% or less of the total mass and was used in the following tests.

Vacuum water absorption test was conducted with the purpose of verifying the influence of whether or not CA aggregate is used on substance permeability. Figure 10 shows the state during the vacuum absorption test, Figure 11 shows the state of measuring the water absorption depth.

The side of the specimen was covered with aluminum tape, aligned in a plastic container, and water was poured into the container to half of the height of the specimen (2.5 cm). Thereafter, a vacuum degassing treatment was performed in a state in which the inside of the vacuum desiccator was 150 Pa or less. In order to prevent the lower surface of the specimen from coming into contact with the container, a splint was placed in the lower part, and it was floated about 1 cm from the

Table 3.	Mix	pro	portion.
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name	Cement type	W/C Unit amount (kg/m3)						Fresh properties		
		(%)	W	C	S	G	CA	CA2	Slump (cm)	Air (%)
NO		50	170	340 340	852	951	-	-	7.5	4.7
N0-S							-	-	6.0	4.0
N100	N					-	1007	-	3.5	4.4
N100-S	1					-	1007	-	4.0	5.4
LO					854	954	-	_	10.5	3.2
L0-S							-	-	11.0	3.9
L100						-		-	13.0	3.2
L100-S	L					_			10.0	4.7
L100-CA2				316	864	-	1010	20	10.0	3.7
L100-CA2-S						-	l .	20	10.0	4.2
BB0	BB			340	847	945	-	-	8.5	3.3
BB0-S							-	-	8.5	3.3

Table 4. Materials chemical composition.

		Chemical composition (mass%)								
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO3	Fe <sub>2</sub> O <sub>3</sub>	MgO	R <sub>2</sub> O	FeO	S	
N	64.09	20.45	5.15	2.09	3.04	0.89	0.57	-		
L	63.08	26.18	2.73	2.33	3.11	0.95	0.41	-	_	
CA	31.70	4.60	55.60			4.20		0.90	0.18	
CA <sub>2</sub>	23.96	0.64	67.73	0.01	7.09	0.27	0.21			



Figure 10. Vacuum absorption tester.



Figure 11. Depth measurement.

bottom of the container. After maintaining the vacuum state for 3 hours, the specimen was split and the penetration depth of water into the specimen was measured. The measurement points were five points at the center of the specimen, and the average of the measured values was taken as the water absorption depth.



Figure 12. Specimen the simple permeability test.



Figure 13. Test specimen after splitting.

# 3.2.3 Simple permeability test

Simple permeability test was conducted with the purpose of verifying the influence of whether or not CA aggregate is used on substance permeability. Figure 12 shows the state of the specimen during the simple permeability test, and Figure 13 shows the test specimen after splitting. The plastic cup was fixed using a silicone sealing material on the upper surface of the specimen so that there is no water leakage in the specimen, and the initial weight was set as the initial weight. 100 cc of water was poured into the container and drained at the time of measurement to measure the amount of water reduction and the weight of the specimen. After the measurement, 100 cc of water was again poured into the container, and the measurement was repeated. The water absorption was calculated from the increment of the weighed test body weight and the initial weight. After repeating the measurement for a certain period of time, the specimen was split and the penetration depth of water into the specimen was visually confirmed.

### 3.2.4 Air permeability test

Air permeability test was conducted with the purpose of verifying the influence of the presence or absence of CA aggregate on substance permeability. A test specimen was set in the test cell, and an air pressure of 0.2 N/mm<sup>2</sup> was applied to the pressure vessel. Based on the past research, the air permeability coefficient was calculated from the obtained air permeability. The larger the air permeability coefficient, the easier it is for gas to pass.



Figure 14. Results of the compressive strength test.



Figure 15. Water absorption depth.

# 3.3 *Experimental result*

# 3.3.1 Compressive strength test

Figure 14 shows the results of the compressive strength test at 28 days of age. In the formulation using limestone, neither N, L or BB showed large difference in strength between water mixing and salt water mixing. N formulation increased strength by using CA aggregate. However, in the L formulation, there was no change in strength in formulation using limestone and CA aggregate respectively. The reason why no difference in strength was observed in the formulation of L is that, L produces less CH than N. Therefore, the amount of hydrocalumite produced is small, and it is considered that the periphery of the aggregate did not densify. When CA2 was added to the formulation of L, the strength decreased. However, in saltwater drilling, strength is greatly increased as compared with water-kneading. This is considered because the ability to immobilize chlorine was increased by using CA aggregate and CA<sub>2</sub> in combination. Also, even when L with a small amount of CH production is used, it is possible that the interior of the concrete is densified by the fixed chloride ion.

# 3.3.2 Vacuum water absorption test

Figure 15 shows the water absorption depth at 28 days of age. As for the formulation using N, the result that the water absorption depth is large in the order of N100 > N0-S > N0 > N100-S was confirmed. As compared



Figure 16. The water absorption rate (OPC).



Figure 17. The water absorption rate (LPC).

with N0 formulation, the absorption of N100 formulation showed an increase in water absorption depth of about 15%. In the N 100 - S formulation, a decrease in the water absorption depth was observed about 10%. For the formulation using L, it was confirmed that the water absorption depth was large in the order of L0-S >L100 > L0 > L100-S. Compared to the N formulation, the water absorption depth is large in various formulations. L is thought to be due to a smaller amount of CH production than N and a small amount of product due to the reaction. Regarding L0 formulation, the water absorption depth increased by about 10% in both L0-S formulation and L100 formulation. Both N and L results show that the water absorption depth is the smallest in 100-S formulation. This is considered to be due to the densification of the transition zone part by the formation of hydrocalumite and Friedel's salt due to reaction of CA aggregate with chloride ion.

#### 3.3.3 Simple permeability test

Figures 16 and 17 show the water absorption rate by the simple permeability test on the test specimen of 28 days old. In this test, measurements were taken up to 144 hours from the start of the test. Figures 18 show graphs in which the water absorption rates at the time of 144 hours from the start of the test are arranged for each compounding. As for the results on the 28th day of age, it was confirmed that the water absorption rate is larger in the order of 0 > 100 > 100 - S > 0-S in both N and L formulations. Consider the cause of the lowest



Figure 18. The water absorption rate.

water absorption of N0-S formulation and L0-S formulation. It is conceivable to modify the cement paste portion by chloride ions. For the formulation using N, it was confirmed that the water absorption ratio decreased by about 25% in the N100 formulation and about 50% in the case of the N100-S blended with respect to N0. The reason for this is considered that the volume expanded due to the formation of hydrocalumite and Friedel's salt on the surface of the CA aggregate, and the water absorption rate became lower due to the densification of the transition zone part. For the formulation using L, it was confirmed that the water absorption ratio decreased by about 20% in the L100 formulation and by about 60% in the case of the L100-S blended with respect to L0. As can be seen from the comparison of the bar graphs in Figure 18, as a relation regarding the height of the water absorption rate, a large difference of 28 days as the material age was not confirmed except for the decrease in the water absorption rate of L100.

The results of this test did not correlate with the vacuum absorption test results described above. The following points are conceivable as the cause. In the vacuum water absorption test, a vacuum degassing treatment is performed in a state in which the inside of the vacuum desiccator is 150 Pa or less. Therefore, water is likely to penetrate into pores in the specimen. Therefore, when compared with the results of the simple permeability test, it is considered that the water absorption depth of the N100 formulation and the L100 formulation using porous CA aggregate was increased. Although it suppresses the penetration of water under natural gravity, it seems that it shows that it is easy for water to penetrate even in the densified cement paste part by absorbing by vacuum degassing treatment.

#### 3.3.4 Air permeability test

Figure 19 shows the air permeability coefficient at 28 days of age. In the formulation using N, the permeability coefficient was large in the order of 100 > 100-S > 0 > 0-S. The N100 compounding has the s mallest amount of air passing. It is considered that the product due to the reaction of the CA aggregate with CH and water densified the aggregate interface and the amount of passing air became small. However, it



Figure 19. Air permeability coefficient.

shows the result that the amount of passing air is large in compounding with chloride ion. In the formulation using L, the air permeability coefficient was large in the order of > 0-S > 100 > 100-S. It can hardly be said that densification by hydration products was confirmed by this test. No correlation was found between the results of the vacuum absorption test and the simple permeability test in both N and L formulations.

# 4 OBSERVATION OF AGGREGATE INTERFACE

#### 4.1 Outline of experiment and equipment used

In order to observe the interface of CA aggregate, observation was carried out using digital microscope. Furthermore, in order to observe the product at the CA aggregate interface, observation was carried out using a scanning electron microscope.

4.1.1 Observation results with digital microscope Figure 20 shows the observation results of the aggregate interface of L0 formulation and Figure 21 formulation of L100. Comparison of L blending using limestone and L100 blending using CA aggregate In the L0 formulation, the aggregate interface is clear, whereas in the L100 formulation, a white gel-like substance can be confirmed near the aggregate interface. This white gel may be a product such as hydrocalumite due to hydration of CA aggregate or alumina gel due to precipitation from aggregate. When this component is an alumina gel, it is possible that the reaction of aggregate surface is hindered by CA aggregate covered with gel, and the amount of hydrocalumite produced may be reduced.

#### 4.1.2 *Observation results by scanning electron microscope*

Figure 22 and 23 show the observation results of scanning with a scanning electron microscope containing L100-S. In the formulation of L100-S, acicular substances and spherical substances were observed in the vicinity of the aggregate. In addition, it was confirmed that the periphery of the CA aggregate was covered with numerous polygonal plate-like crystals. It is similar to the crystal form of Friedel's salt reported in the past resarch It is thought that it is necessary to conduct elemental analysis in the future and confirm the composition of the product specifically.



Figure 20. Results of the aggregate interface (L0).



Figure 21. Results of the aggregate interface (L100).



Figure 22. Results of scanning (L100-S).

# 5 CONCLUSION

The results obtained in this study are summarized below.

 The CA aggregate has reactivity with water. Therefore, there is a possibility that hydrogarnet has been generated at the aggregate interface from the stage of pre-wetting accompanying kneading.



Figure 23. Results of scanning (L100-S).

- 2) The CA aggregate generates hydrocalumite under the condition that CH is supplied as cement hydrate. It was confirmed that in the presence of chloride ion, it has the ability to generate Friedel's salt and immobilize chloride ion.
- 3) By using the aggregate of CA, it was confirmed that the slump was reduced by blending. This is thought to be due to the fact that the cement paste is intruded into the hole of the aggregate due to the feature that the CA aggregate is porous.
- 4) In formulation using OPC, compressive strength increased by using CA aggregate. However, in the formulation using LPC, no change in strength was observed. The reason why the difference in strength was not observed in the formulation of L is considered to be because the amount of CH production is smaller than that of N and the amount of hydrocalumite produced is small and the surrounding aggregate is not densified.
- 5) By using the CA aggregate, the water absorption depth in the vacuum water absorption test increased. This is probably because water is likely to penetrate the pores in the specimen by the vacuum deaeration treatment. It is considered that the absorption zone depth decreases in the formulation containing the intrinsic chloride ion and the transition zone part densifies due to the product of the CA aggregate reacting with the chloride ion and precipitating.
- 6) In the simple permeability test, the results showed the lowest water absorption rate for the mix proportion subjected to salt water kneading using

limestone. However, in the vacuum water absorption test, the water absorption depth was large. Although this suppresses the penetration of water under natural gravity, it seems that it shows that it is easy for water to penetrate even in the densified cement paste part by absorbing by vacuum degassing treatment.

7) Observation of the CA aggregate interface by microscope or scanning electron microscope confirmed the existence of product at the aggregate interface.

# 6 FUTURE ISSUES TO BE EXAMINED

In order to accurately clear that the CA aggregate immobilizes chloride ions in concrete, it is necessary to consider by EPMA mapping and so on.

It is necessary to analyze the elements in XRD and EDS and analyze the product at the aggregate interface concretely. Furthermore, it is necessary to confirm the difference in product amount depending on the type of cement.

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