Evaluation of Salt Resistance by Different Mix Proportion on Concrete Using Expansive Materials and Calcium Aluminate Admixture

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ABSTRACT

Japan is surrounded by the sea. So reinforced concrete structures have a problem salt damage by chloride ions from the sea. And in cold climates, salt damage and deterioration of reinforced concrete structures is caused by spraying of anti-freezing agents in winter. In recent years, the method is being developed that using Calcium Aluminate admixture can chemically immobilize the chloride ions as Friedel’s salt thereby decreases the soluble chloride ion concentration. In this study, I perform unsteady-state electrophoresis tests and chemical analysis with XRD by different mix proportion on concrete using Expansive materials to suppress generation of a crack and Calcium Aluminate admixture. As a result, using Expansive materials and Calcium Aluminate admixture has the chloride ion penetration suppress improvement effect which generates an equivalent effect to reduce the water-cement ratio by 10%. In addition, it was suggested that the effect of immobilization function by Calcium Aluminate admixture was different depending on water-binder ratio.

KEYWORDS: *expansive materials, salt resistance, salt damage, fixing chloride ions, Calcium Aluminate admixture*

1. Introduction

In Japan, deterioration of reinforced concrete structures due to salt from the sea and the use of anti-freezing agents in snowfall areas has been widely reported. General countermeasures include the use of blast furnace cement, fly ash and other admixtures, and increasing the cover, but it is difficult to apply these countermeasures to all structures from the viewpoint of cost and workability. However, from the viewpoint of cost and workability, it is difficult to apply to all structures. Therefore, in recent years, calcium aluminate admixture $CaO \cdot 2Al_2O_3$ (hereinafter referred to as CA_2) has been developed, which is mixed with cement to produce hydrocalumite (hereinafter referred to as HC), a hydrate with chloride ion fixation function. In addition, if excessive cracks occur in concrete structures, chloride ions penetrating through the cracks may reach the reinforcing bars, leading to early deterioration. In this paper, we discuss the effects of CA_2 and Expansive materials (hereinafter referred to as Ex) in concrete. It is expected that the combined use of CA_2 and Ex in concrete minimizes the path of chloride ion penetration and suppresses the penetration rate of chloride ions by the immobilization function in the hardened cement. In a previous study, it was confirmed that concrete with W/B=55% using ordinary Portland cement with a small amount of CA_2 had salt penetration resistance equivalent to blast furnace cement Type B. In order to further expand the range of application of concrete using CA_2 and Ex, salt penetration resistance due to admixture was investigated in low heat Portland cement (hereinafter referred to as LPC), high early strength cement (hereinafter referred to as HEC), and ordinary Portland cement (hereinafter referred to as OPC) with W/B of 35%, 45%, 55%, and 65%, mixed with CA2 and Ex. In this study, the effect of admixture penetration behavior of chloride ions were investigated.

2. Experimental and result

2.1 Materials

In this study, OPC, HEC, and LPC were used. The chemical compositions and densities of the CA_2 and expanded materials are shown in Table 1. Crushed sand with a density of 2.60 g/cm³, fineness modulus of 2.62, and water absorption ratio of 1.92% was used as fine aggregate, and crushed stone with a density of 2.70 g/cm³, fineness modulus of 6.64, and water absorption ratio of 0.26% was used as coarse aggregate. The planned concrete mix for this study is shown in Table 2. Cement, CA_2 and expansion materials were considered as binders (denoted as B in the table) and were replaced by cement.

Table 1 Chemical and physical properties of CA_2 and Ex

Component	Chemical composition(mass%)					Density
	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	(g/cm³)
CA_2	24.0	0.6	67.7	0.0	7.1	2.96
Ex	70.6	1.0	7.2	18.5	0.8	3.10

Table 2 Mix Designs of concretes used for chloride penetration resistance

No.	W/B	s/a	Unit weight (kg／m³)					
	(%)	(%)	W	C	CA_2	Ex	S	G
N35	35	44	170	486	—	—	722	955
NCE35				444	20	22	722	954
N45	45	46		378	—	—	796	970
NCE45				336	20	22	795	969
N55	55	48		309	—	—	858	965
NCE55				267	20	22	857	964
N65	65	50		262	—	—	913	948
NCE65				220	20	22	912	947
H45	45	46		309	—	—	860	967
HCE45				267	20	22	859	966
L55	55	48		378	—	—	795	969
LCE55				336	20	22	794	968

2.2 Compressive strength test

The specimens were cured in water for 28 days and then tested for compressive strength in accordance with JIS A 1108. The results are shown in Figure 1. In all cases, the compressive strength of the NCE mixture with CA_2 and Expansion materials was almost the same as that of the N mixture with no admixture. Therefore, it is no adverse effect of mixing CA_2 and Expansion materials on the strength.

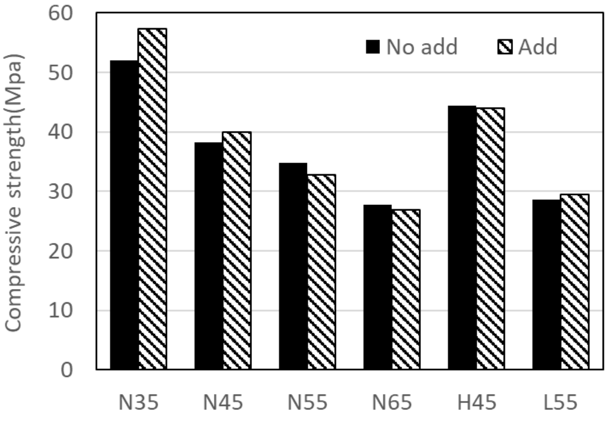

Figure 1. Compressive strength

2.3 Porosity test

The porosity was calculated by the Archimedes method using a specimen of Φ100×50mm cured in water for 28 days using ordinary Portland cement. After the specified curing period, water was poured into the specimens, and decompression by a vacuum pump to make the specimens water-saturated, and then the mass of the water-saturated specimens and the mass of the surface-dry water-saturated specimens were measured. After that, it was dried in a drying oven at 40°C until the mass became constant, and the porosity was calculated. The results are shown in Table 3. The porosity was smaller in the NCE mixture for all W/Bs. This may be due to the increase in the volume of the solid phase when CA_2 reacted with CH to form HC, which filled the voids, and the shrinkage reduction effect of the Expansion materials. In addition, typically the compressive strength of the specimens increased as the porosity decreased, but this relationship was not observed in this test.

Table 3 Total porosity

W/B	35	45	55	65
N	6.89%	9.59%	10.91%	11.66%
NCE	5.83%	9.37%	9.12%	11.14%

2.4 Unsteady-State electrophoresis test

A conventional electrophoresis test apparatus was used. Specimens were prepared using cylindrical molds made of vinyl chloride (Φ100 mm; height: 50 mm). The specimens were subjected to vacuum-saturation pretreatment using saturated calcium hydroxide. Aqueous NaOH (0.3 mol/L) was injected to the anode side of the test apparatus and NaCl solution (0.5 mol/L) to the cathode side. The applied voltage was kept constant at 30 V and current was passed. Once energization was completed, the specimen was removed and split. The chloride ion penetration depth was measured by spraying the exposed surface with silver nitrate solution (0.1 mol/L). The results of the transient electrophoresis test are shown in Figure 2 and 3. Figure 2 shows the results for the concrete without CA_2 and Expansion materials (N mix proportion), and Figure 3 shows the results for the concrete with CA_2 and Expansion materials (NCE mix proportion). From the figures, it can be seen that the chloride ion penetration depth decreases with decreasing W/B both N and NCE mix proportion. This is due to the denser pore structure created by the lower W/B, which physically suppresses the penetration of chloride ions. Figure 4 shows the results of L and H mix proportion, and it is confirmed that even when LPC and HEC are used, the salt penetration resistance is improved by mixing the Expansion materials and CA_2 as well as OPC.

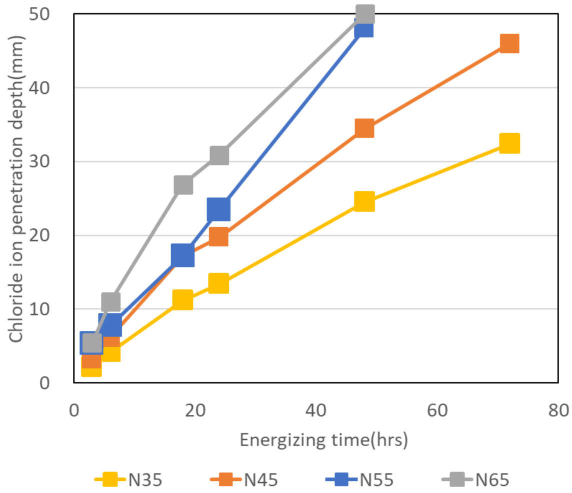

Figure 2. Chloride-ion penetration depth (N mix proportion)

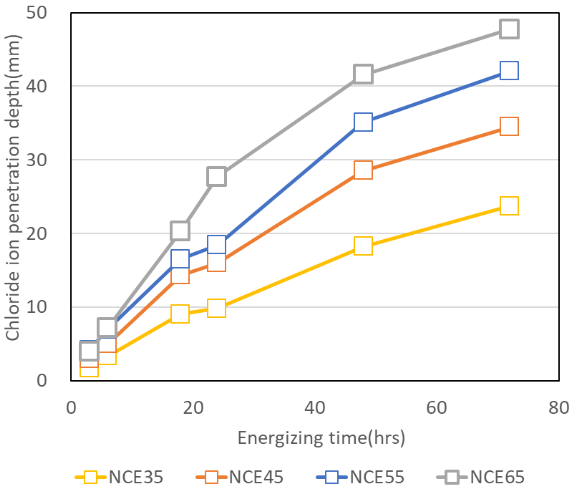

Figure 3. Chloride-ion penetration depth (NCE mix proportion)

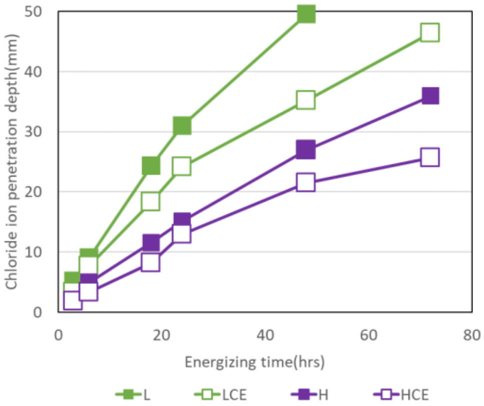

Figure 4. Chloride-ion penetration depth (usingLPC and HEC mix proportion)

Figure 5 shows the results of N and NCE mixtures with W/B of 45% and 55%. It can be seen that the salt penetration behavior of concrete with N45 and concrete with NCE55 are comparable. In other words, the NCE mix proportion with the addition of the Expansive materials and CA_2 have almost the same salt penetration resistance as the N mix proportion without the addition, which have 10% lower W/B. It can be inferred that the addition of the Enpansive materials and CA_2 has the same effect of improving the salt penetration resistance as the reduction of W/C by 10%.

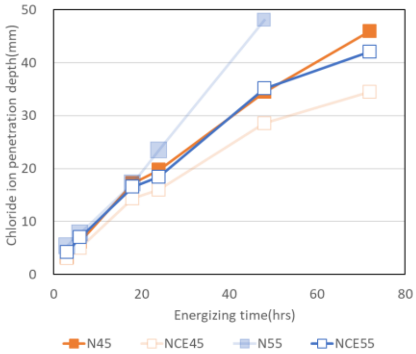

Figure 5. Chloride-ion penetration depth (W/B=45% and 55%)

2.4 Diffusion coefficient

Diffusion coefficient is calculated using formula (1) from the penetration depths determined in the Unsteady-State Electrophoresis Test. The diffusion coefficient is shown in Figure 6.

$$\mathrm{D} = \mathrm{k} \cdot \frac{RT}{zF} \cdot \frac{L}{\Delta\varphi} \tag{1}$$

D：Diffusion coefficient (m^2/s)

k：Chloride Ion Penetration Rate (m/s)

R：The Constant Value for a Gas (＝8.31J/(K･mol)

T：Absolute Temperature (k)

z：Valence of a Chloride Ion (=1)

F：Faraday Constant (=9.65×104J/(V･mol))

L：Height of specimens (mm)

$\Delta\varphi$：Applied voltage (V)

The diffusion coefficients obtained from formula (1) are shown in Figure 4. The diffusion coefficients of the NCE mix proportion were smaller than those of the N mix proportion for all W/B. As mentioned above, it was confirmed that admixture of CA_2 and Expansion materials had the same effect of improving salt penetration resistance as lowering W/C by 10%. In addition, the larger the W/B, the greater the salt penetration resistance improvement effect of mixing CA_2 and Expansion materials.

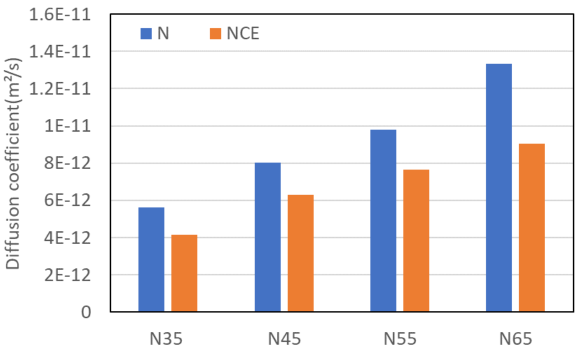

Figure 6. Diffusion coefficients for different concrete mix proportion

3. Chemical Diffraction by Cement Paste

3.1 Difference in HC production due to difference in W/B

In the previous section, it was found that the larger the W/B, the greater the improvement in salt penetration resistance with the mixing Expansion materials and CA_2. The specimens were cured in water at 20°C for 28 days, dried for 24 hours, and then crushed. Afterwards, all the mix proportion were mixed with 10% of aluminum oxide as a standard material, and the hydration products were verified by powder X-ray analysis (XRD). The results are shown in Figure 7. The amount of CH per aluminum oxide was calculated using the peak value of CH near 18° and the peak value of aluminum oxide near 57.5° for each mix proportion by the internal standard method. The peak intensity of calcium hydroxide (CH) in cement hydrates was decreased in NCE mix proportion compared to N mix proportion, regardless of the W/B. On the other hand, it was observed that the peak intensity around 10° to 11.5°. This indicates that CH was consumed by the hydration reaction of CA_2 to produce hydrocalumite (HC) and AFm(C), a monocarbonate-hemicarbonate. Figure 8 shows that the amount of CH produced in the NCE mix proportion is about 40% less than that in the N mix proportion. Next, the total amount of HC, monocarbonate, and hemicarbonate, which have the ability to chemically immobilize free chloride ions as Friedel's salt, is expressed as the chloride ion immobilization capacity using the same method as the CH production capacity in Figure 9. It can be seen that the chloride ion immobilization capacity of the NCE mix proportion is higher than that of the N mix proportion at any W/B. The Cl-immobilization capacity of the NCE mix proportion was about 1.15 times higher than that of the N mix proportion at W/B = 35%, while it was about twice as high at W/B = 65%.

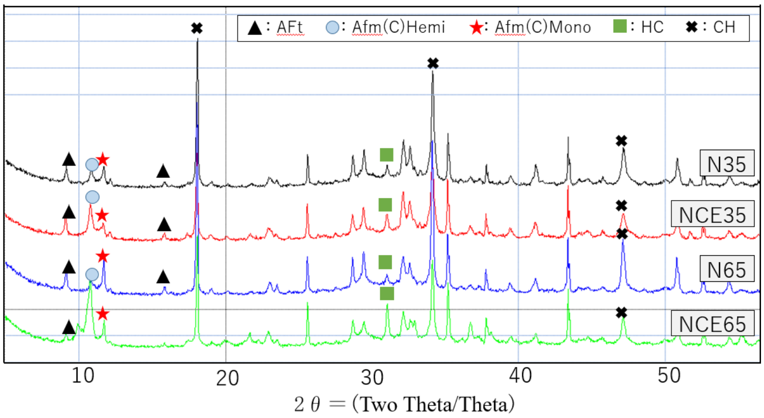

Figure 7. Diffraction results by XRD

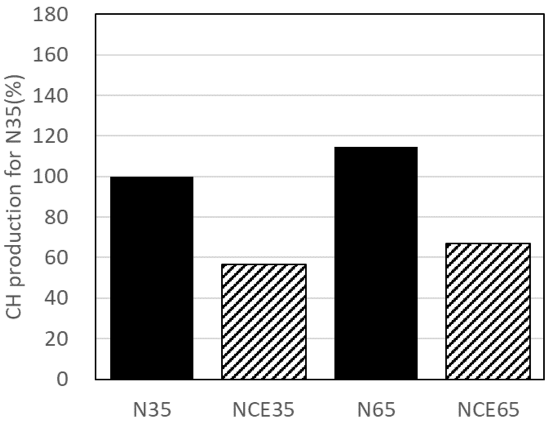

Figure 8. Relative CH content

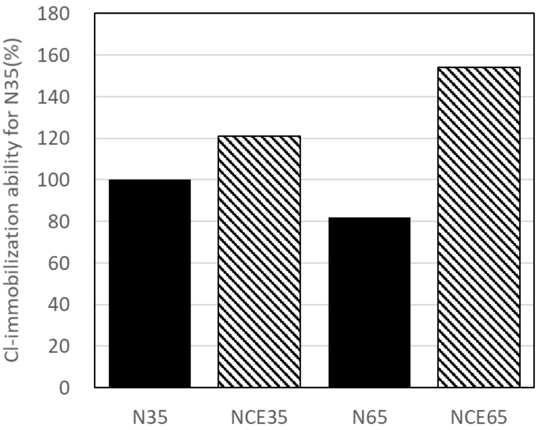

Figure 9. Relative Cl-mobilization ability

3.2 Relationship to Porosity

In the previous section, we focused on the hydration products, but here we will focus on the porosity. Figure 10 shows the relationship between porosity and diffusion coefficient. Reduction in porosity of the W/B=65% was about 0.5 times greater than that of the W/B=35%, but the suppression of diffusion coefficient was about 3 times greater. It can be seen that the amount of suppression of diffusion coefficient against the decrease of porosity is different between the mix proportion with W/B = 35% and W/B = 65%. This is due to the chemical immobilization of large amounts of free chloride ions as Friedel's salt, since the increase in the amount of HC produced by the admixture of CA_2 is greater at higher W/B. The difference in the amount of chloride ions supplied to the inside of the hardened cement due to the difference in porosity is also considered to be one of the factors. When W/B is high, porosity is large and chloride ion penetration is also large. Therefore, it can be inferred that the immobilization capacity of

NCE65 was maximized in the hardened cement. On the contrary, although NCE35 has some immobilization function, it does not exert its immobilization ability due to the lack of chloride ion supply, and it is inferred that the dense porosity physically suppressed the penetration of chloride ions. It can be concluded that the higher the W/C of the concrete, the greater the effect of CA_2 admixture on salt penetration resistance.

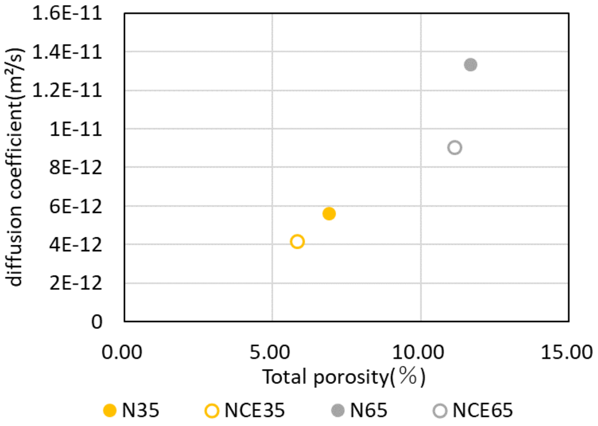

Figure 10 Relationship between porosity and diffusion coefficient

4. Conclusions

In this study, the salt penetration resistance was investigated using various types of cement and W/B of concrete with CA_2 and Expansion materials, and the following results were obtained.

1) The compressive strength did not decrease when mix proportions with Expansion materials, CA_2 and different cement types, and the improvement in salt penetration resistance was also confirmed.
2) The use of CA_2 and Expansion materials is equivalent to a 10% reduction in W/C and improves the salt penetration resistance.
3) Tests using cement paste have shown that the higher the W/B, the more hydrocalumite is produced and the higher the immobilization capacity of chloride ions.
4) It is inferred that the factor of salt penetration inhibition is different for W/B different concrete with using Expansion materials and CA_2

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