

# Chloride ion penetration behaviour in concrete containing an expansive additive and a calcium-aluminate-based additive

Shinya ITO<sup>1</sup>, Takeshi IYODA<sup>2</sup>

<sup>1</sup> Denka Co.Ltd., 2209, Omi, Itoigawa-city, Niigata 949-0393, Japan

<sup>2</sup> SHIBAURA INSTITUTE OF TECHNOLOGY, 3-7-5, Toyosu, Koto-ku, Tokyo 135-8548, Japan

shinya-ito@denka.co.jp

**Abstract.** The effect of the material characteristics on the infiltration behaviour of chloride ions in concrete containing a combination of an expansive additive and a calcium-aluminate-based additive has been investigated. The same level of salt resistance as that of blast furnace slag cement was exhibited even for a small addition amount. In addition, the permeation behaviour of chloride ions was largely influenced by the immobilisation capacity and pore network. When these changes were dominant, the results suggested that the characteristics based on the Fick diffusion equations may not necessarily reproduce the actual permeation behaviour of chloride ions.

## 1. Introduction

In Japan, there is a large amount of airborne salt from the ocean, and degradation of reinforced concrete structures because of salt damage has been reported nationwide owing to spraying of antifreeze agents in winter. Salt damage is generally indicative of steel corrosion in concrete owing to infiltration of chloride ions. For general-purpose materials, blast furnace cement and common additives, such as fly ash, are used. In recent years, an additive has been developed in which  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  ( $\text{CA}_2$ ) of calcium aluminate is admixed with cement to react with  $\text{Ca}(\text{OH})_2$  (CH), which is a cement hydrate, to form a hydrate with an immobilisation function, and free chloride ions, which cause corrosion of steel, are chemically immobilised as Friedel's salt. It has been reported that the additive exhibits high salt damage resistance at low dosage. In addition, if excessive cracks occur in the concrete structure, chloride ions directly reach the reinforcing rebar, which increases the possibility of premature deterioration. Therefore, it is important to suppress crack occurrence as a salt damage countermeasure. In addition, by incorporating an expansive additive in concretes, it is possible to suppress excessive cracking by introducing a shrinkage reduction effect or a chemical pre-stressing effect. Therefore, it can be expected that the external permeation path of chloride ions can be minimised by using  $\text{CA}_2$  and an expansive additive in combination, and the permeation rate of chloride ions can be suppressed by the immobilisation function even in the cured body. Although the basic characteristics and salt damage resistance of concretes containing  $\text{CA}_2$  and an expansive additive in combination have been reported in previous studies, it is essential to establish a method to reflect the results to check the durability of concrete for practical use. For commons additives, such as blast furnace slag and fly ash, the characteristic values for durability inspection are clearly indicated in the concrete standard statement of the Society of Civil Engineers based on a vast amount of data, but they

cannot be directly applied to concrete containing CA<sub>2</sub> or an expansive additive. In this study, we investigated the material characteristics of concretes containing CA<sub>2</sub> and an expansive additive, and we then investigated the effect of the material characteristics on the chloride ion infiltration behaviour for durability examination.

## 2. Materials and methods

### 2.1 Composition of materials and concrete

Ordinary Portland cement (OPC) and blast furnace cement B (BB) were used as the cements. CA<sub>2</sub> was prepared by calcining at 1750 to 1850 °C. A CaO/Al<sub>2</sub>O<sub>3</sub> molar ratio of 0.5 was used with calcium carbonate and aluminium oxide as the raw materials. The obtained clinker was pulverised by gradual cooling. A lime–ettringite composite was used as the expansive additive. The chemical composition and densities of CA<sub>2</sub> and the intumescent materials are given in Table 1. Sand (density 2.62 g/cm<sup>3</sup>) produced by Kimitsu City, Chiba Prefecture was used as the fine aggregate, and limestone crushed stone (density 2.70 g/cm<sup>3</sup>) produced by Tsukumi City, Oita Prefecture was used as the coarse aggregate. The concrete mix proportions are given in Table 2. The cement, CA<sub>2</sub>, and the expansive additive were regarded as a binder (B, Table 2).

**Table 1.** Chemical compositions and densities.

	Chemical composition (%)					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>	
OPC	64.1	20.5	5.2	2.1	3.0	3.16
CA <sub>2</sub>	24.0	0.6	67.7	0.01	7.1	2.96
Ex	70.6	1.0	7.2	18.5	0.8	3.10

**Table 2** Concrete mix proportion

No.	W/B (%)	s/a (%)	Unit weight (kg/m <sup>3</sup> )					
			W	C	CA <sub>2</sub>	Ex	S	G
N	55.0	48	170	309	—	—	864	965
N+CA <sub>2</sub>				289	20	—		964
N+CA <sub>2</sub> +Ex				269	20	22		964
BB				310	—	—		859

### 2.2 Test materials and measurement methods

#### 2.2.1 Permeation characterisation of the chloride ions

A salt water immersion test was performed to evaluate the permeation characteristics of chloride ions. In the salt water immersion test, a 100 mm × 100 mm × 400 mm prismatic specimen was cured in water at 20 °C for 28 days. The five surfaces other than the 100 mm × 400 mm surface were coated with epoxy resin and immersed in 10% aqueous NaCl solution at 20 °C with one surface exposed to epoxy resin. At the specified age of the specimen, the depth from the exposed surface to the coloured part was measured by sequentially splitting and spraying silver nitrate solution (0.1 N) on the split surface.

#### 2.2.2 Chloride ion profile

After 48 weeks aging of the immersion material, the test piece was cut at intervals of 1 cm in the depth direction from the permeation surface of the specimen. The total chloride ion content was analysed in

accordance with JIS A1154, and the chloride ion profile in the depth direction was constructed. The soluble chloride ions were extracted with warm water at 50 °C, and the amounts of free and fixed chloride ions were determined.

### 3. Results and discussion

#### 3.1 Evaluation of the chloride ion permeability

##### 3.1.1. Salt immersion test

The chloride penetration depths of the concrete specimens soaked in 10% strength NaCl solution are shown in Figure 1. The penetration depth of the reference sample N aged for 48 weeks was about 30 mm. The penetration depths of the N+CA<sub>2</sub> and N+CA<sub>2</sub>+Ex samples were about 20 and 16 mm, respectively, and the penetration of chloride ions tended to be suppressed by the use of additives. In addition, the difference in the penetration depth compared with BB was several millimetres, and there was not a large difference in the penetration depth in the immersion period. It was presumed that this was because of the fact that hydrates with an immobilisation function, such as hydroculmite (HC), were produced by adding CA<sub>2</sub> immobilised chloride ions as Friedel's salts, thereby suppressing penetration of chloride ions into the concrete. When the expansive additive was used in combination with CA<sub>2</sub>, the penetration depth of chloride ions was equal to or less than that of the CA<sub>2</sub> sample. In addition, if the expansion ratio was within the range of the expansion ratio of shrinkage-compensating concrete, there was no effect on the immobilisation capability of chloride ions of the CA<sub>2</sub> sample, and a synergistic effect on improving the salt shielding property was obtained by the combination of the expansion material and expansive additive.

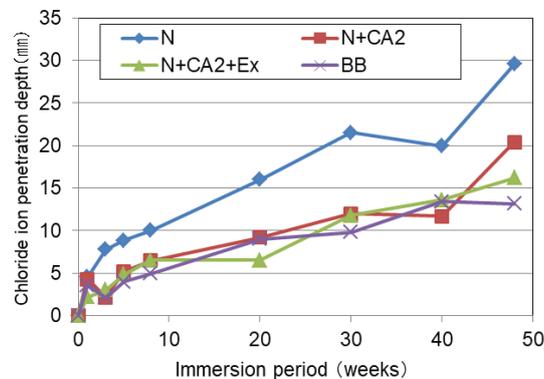


Figure 1. Salt immersion test results.

##### 3.1.2 Chloride ion profile

The chloride ion profiles of the different concrete samples are shown in Figures 2–5. The apparent diffusion coefficients and amounts of superficial chloride ions calculated by Fick's diffusion equations based on this chloride ion profiles are given in Table 3, along with the maximum total chloride ion content in each concrete and the free/immobilised chloride content ratios. The amounts of surface chloride ions estimated from the salinity profiles by Fick's diffusion equations were higher for the N+CA<sub>2</sub>, N+CA<sub>2</sub>+Ex, and BB samples compared with the N sample as a reference. For the distribution of the chloride ion amount in the depth direction from the penetration surface, the difference in the chloride ion amounts between the surface layer and inside the cured body was large, except for the N sample, and the chloride ion amount decreased with increasing depth. The tendency was remarkable for N+CA<sub>2</sub>+Ex and BB in which CA<sub>2</sub> and the expansive additive were used in combination. The apparent

diffusivities of the N+CA<sub>2</sub>+Ex, N+CA<sub>2</sub>, and BB samples were smaller than that of the N sample, by about 42% for the N+CA<sub>2</sub> sample, about 54% for the N+CA<sub>2</sub>+Ex sample, and about 69% for the BB sample. This confirmed that chloride ion diffusion was suppressed by using the combination of CA<sub>2</sub> and the expansive additive compared with using CA<sub>2</sub> alone. In this study, salt water immersion was performed for 48 weeks. Therefore, it is considered that the first layer (0 to 10 mm) of the permeation surface, which exhibited the maximum total salt content, was saturated with chloride ions present in the concrete. For the N sample, because the ratios of free/immobilised chloride ions in the depth direction from the penetration surface direction were not significantly different between the surface layer and inside the sample, it is considered that the permeated chloride ions moved and were immobilised at a constant ratio. In contrast, for the N+CA<sub>2</sub> and N+CA<sub>2</sub>+Ex samples, the immobilisation ratios of the surface layer and inside the sample were different, and it was inferred that immobilisation and adsorption preferentially occurred. In addition, for the BB sample, although the amount of immobilisation was small, penetration of chloride ions into the surface layer was greatly suppressed, suggesting that the pore structure was such that ion penetration was difficult. Therefore, it was considered that the permeation behaviour of chloride ions can be expressed by Fick's diffusion equations for the N sample in which fixation/adsorption and ion permeation proceed at relatively constant rates. However, it is suggested that it is difficult to appropriately describe the permeation behaviour of ions by Fick's diffusion equations for a material that possesses the fixing function, such as CA<sub>2</sub>, or a material with pore structures that influence ion permeation, such as blast furnace cement.

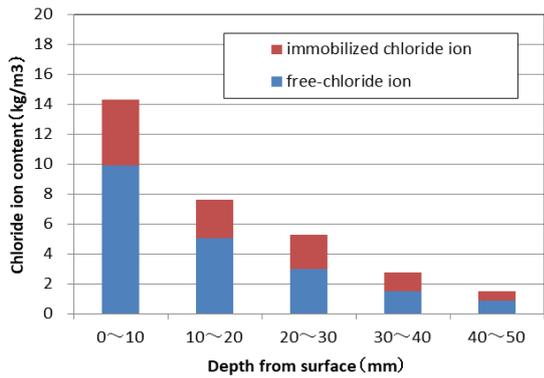


Figure 2. Chloride ion profile for N.

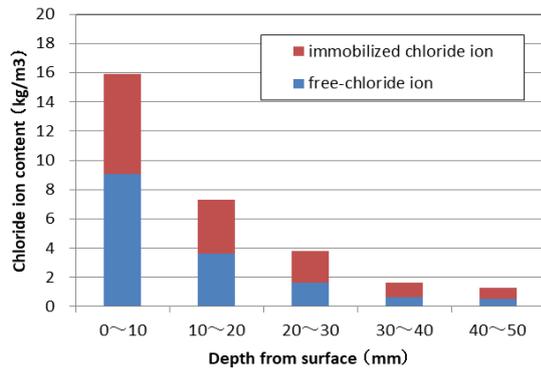


Figure 3. Chloride ion profile for N+CA<sub>2</sub>.

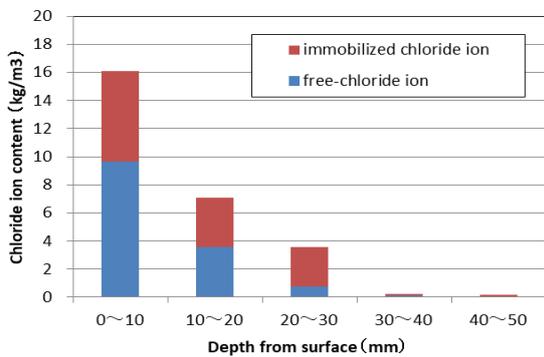


Figure 4. Chloride ion profile for N+CA<sub>2</sub>+Ex.

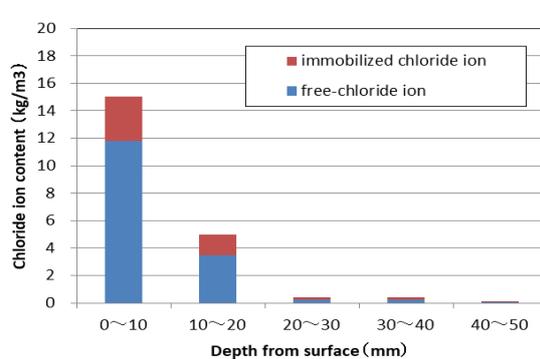


Figure 5. Chloride ion profile for BB.

**Table 3.** Chloride ion contents and free/immobilised chloride ion ratios for the four samples.

	Fick's diffusion equation		Total chloride ion content (kg/m <sup>3</sup> )	Ratio (%)	
	Apparent diffusion coefficient (m <sup>2</sup> /s)	Chloride ion content at the concrete surface (kg/m <sup>3</sup> )		Free-chloride ion	Immobilized chloride ion
N	1.02E-11	16.4	14.3	69%	31%
N+CA <sub>2</sub>	5.88E-12	19.8	15.9	57%	43%
N+CA <sub>2</sub> +Ex	4.72E-12	20.9	16.1	60%	40%
BB	3.13E-12	22.1	15.0	79%	21%

### 3.2 Material characteristics and penetration behaviour of chloride ions

The results suggested that the penetration behaviour of chloride ions inside the hardened bodies and the distribution of free chloride ions differed in the concrete formulations, and that the values calculated with Fick's diffusion equations may not necessarily reproduce the actual infiltration behaviour of chloride ions, except for the N sample. Therefore, we focused on two material properties: the hydrate and the pore structure.

#### 3.2.1 Hydrate

The immobilisation performance of chloride ions in each sample was determined. The hydrate was verified by powder X-ray diffraction (XRD) using the paste test specimens with the mix proportions given in Table 4. Curing of the paste test specimens was performed for 7 days in water. The results are shown in Figure 6. Compared with the case of no mixing, the intensity the CH peak (10°–11.5°) of the cement hydrate decreased when CA<sub>2</sub> or CA<sub>2</sub> and the expansive additive were mixed with ordinary cement. This means that CH was consumed by the hydration reactions of CA<sub>2</sub> and AFm(C) of HC and mono-carbonate or hemi-carbonate formed. The reason why HC and AFm(C) were mixed in the reaction of CA<sub>2</sub> can be attributed to the small amount of mixed components in the cement. In addition, the same hydrate formed when the combination of CA<sub>2</sub> and the expansive additive was used. No peak was observed for ettringite, which is the hydrate of the expansive additive. It was presumed that this was because the SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio was reduced by the combined use with CA<sub>2</sub>. To confirm the hydrate change after salt immersion, the paste test specimens with the same mix proportions were immersed in 10% aqueous NaCl solution for 2 months. The results of XRD measurements after immersion are shown in Figure 7. The peaks of HC and AFm, which were observed before salt immersion, disappeared after salt immersion, and they changed to Friedel's salts regardless of the mix proportion. Therefore, HC and AFm have the function of immobilising HC and AFm as Friedel's salts when chloride ions are present, and it is considered that AFm also has immobilising ability even when it is AFm(C), such as mono-carbonate and hemi-carbonate. Thermal analysis was also performed using paste specimens with the same mix proportions to quantify the amount of Friedel's salt after salt immersion. The amount of Friedel's salt was determined by taking the mass reduction from 247 to 387 °C obtained by thermal analysis using the pure synthesised Friedel's salt as 100% and comparing it with the mass reduction rate of the paste in the same temperature region. The amount of Friedel's salt for each sample determined by thermal analysis is shown in Figure 8. From the results, compared with the N sample, the amount of Friedel's salt was 1.5 times higher for the N+CA<sub>2</sub> sample, 1.45 times higher for the N+CA<sub>2</sub>+Ex sample, and 1.2 times higher for the BB sample, and the immobilisation capacity of chloride ions was remarkably increased in the CA<sub>2</sub> blended system. In addition, the expansive additive did not significantly influence the immobilisation ability of chloride ions.

**Table 4.** Mix proportions of the pastes.

	W/B (%)	
N	55	OPC:100%
N+CA <sub>2</sub>		OPC:93.5% + CA <sub>2</sub> :6.5%
N+CA <sub>2</sub> +Ex		OPC:86.4% + CA <sub>2</sub> :6.5% + Ex:7.1%
BB		BB: 100%

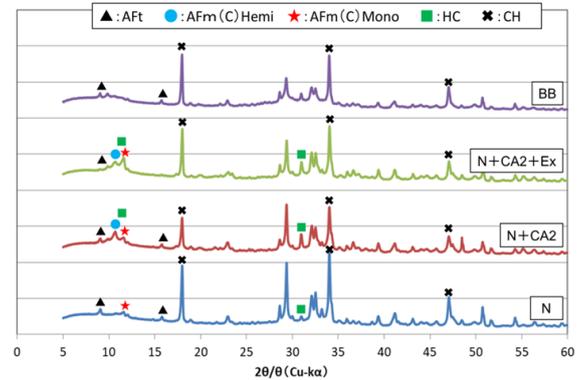


Fig.6 Hydrate before immersion

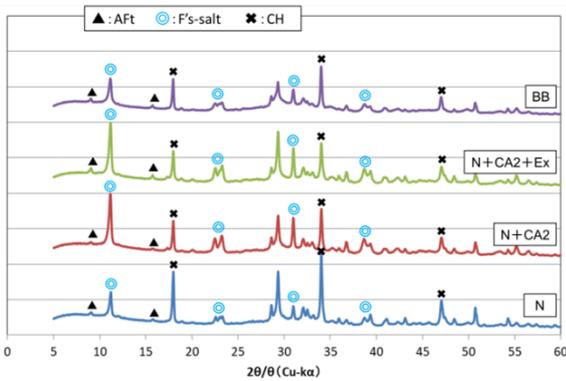


Fig.7 Hydrate before immersion

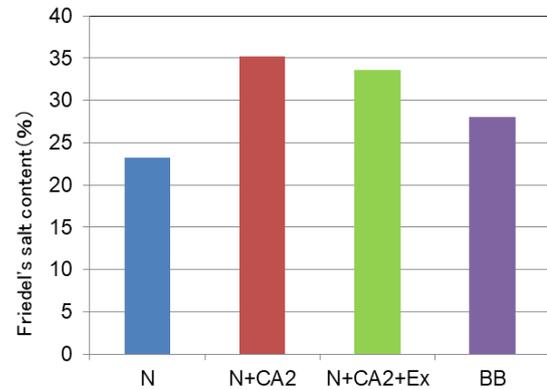


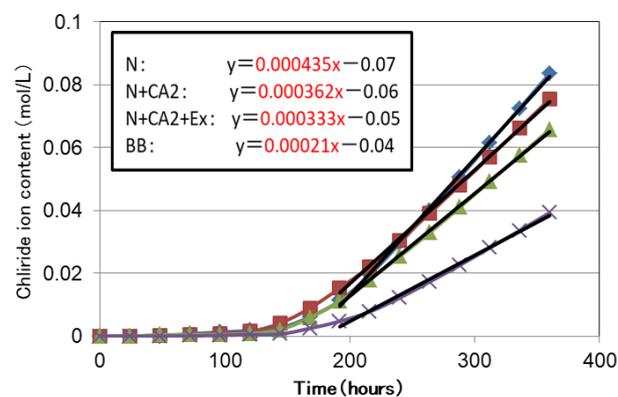
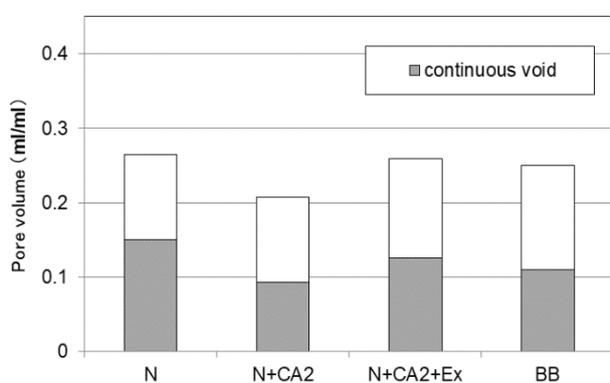
Fig.8 Friedel's salt content

### 3.2.2 Pore structure

The influence of the pore structure was investigated, including the migration path of ions, total pore amount, continuous pore amount, and pore network. First, the ratio of the total pore amount to the continuous pore amount measured by the mercury intrusion method using the paste test specimens after salt water immersion was investigated (Figure 9). The continuous pore amount was determined by press-fitting mercury twice up to a maximum pressure of 410 MPa, and the mercury press-fit amount at the time of re-pressurisation was the continuous pore amount. From the results, the continuous pore volume of N+CA<sub>2</sub>+Ex was the smallest prior to salt immersion and that of N+CA<sub>2</sub> was the smallest after salt immersion. From these results, it is considered that the pores tended to be slightly reduced by using CA<sub>2</sub>. The absolute value of the total pore amount was in the range 0.3–0.4 ml/ml before salt immersion and 0.2–0.3 ml/ml after salt immersion. In addition, there was a tendency for the continuous pore volume to slightly decrease after salt immersions for the composites containing CA<sub>2</sub> and BB. It was presumed that the effect of densification caused by the change in the hydrate, such as formation of Friedel's salt, affected the continuous pore volume. However, the absolute amount ranged from about 0.09 to 0.15 ml/ml, and it was presumed that the difference was not sufficiently large difference for permeation of chloride ions to greatly change.

Next, the pore network was investigated. The steady-state electrophoresis test is a technique for evaluating pore networks. It is specified in the “Method for Testing the Effective Diffusion Factor of Chloride Ions in Concrete by Electrophoresis (JSCE-G-571)” standard of the Japan Society of Civil Engineers. It determines the effective diffusion factor from the amount of ions eluted to the anode side by applying a voltage of 15 V to the hardened concrete to accelerate penetration of chloride ions. The results of the steady-state electrophoresis tests for the concrete samples given in Table 2 are shown in

Figure 10. The amount of chloride ions eluted to the anode was in the order  $N > N+CA_2 > N+CA_2+Ex > BB$ , which is the same as the salt immersion test results described in the previous paragraph. However, when the respective behaviours were compared, the chloride ion permeation behaviours were clearly different between the sample containing  $CA_2$  and the BB sample. Here, we will consider the pore structure inside the cured body on the basis of the results obtained from the steady-state electrophoresis test. In the steady-state electrophoresis test, chloride ions are forced to move to the anode side by a potential gradient, and the eluted amount of chloride ions is measured. That is, the ions eluted on the anode side pass through the continuous pores in the cured body, and the eluted amount in the same time depends on the pore network, which is the complexity of the continuous pores. In addition, because the permeation and migration behaviour of chloride ions clearly differed between the immersion method and electrophoresis method for the sample containing  $CA_2$ , it is considered that the immobilisation function of chloride ions by  $CA_2$  is not reflected by the steady electrophoresis method. Here, from the relationship between the energisation time and the chloride ion concentration on the anode side shown in Figure 10, the cumulative amount of ions since the elution amount of ions became a steady state was approximated by the least squares method. Then, assuming that the slope of the approximate straight line is an index representing the pore network, expressed in proportion to The N sample. The elution rate of chloride ions to the anode side were in the order  $N > N+CA_2 > N+CA_2+Ex \gg BB$ . In addition, based on the N sample, the pore network ratios were  $-52\%$  for the BB sample,  $-17\%$  for the  $N+CA_2$  sample, and  $-25\%$  for the  $N+CA_2+Ex$  sample. That is, the pore structures tended to be more complicated using the expansive additive and  $CA_2$  than using  $CA_2$  alone. Therefore, a synergistic effect can be obtained by using the expansive additive and  $CA_2$  from the viewpoint of suppressing permeation and migration of chloride ions.



**Figure 9.** Pore volumes of the four samples. **Figure 10.** Steady-state electrophoresis test results.

### 3.2.3 Summary of material characteristics and penetration behaviour of chloride ions

The summary of study on the effect of material characteristics and penetration behaviour of chloride ions are shown in Table 5.

**Table 5.** Summary of material characteristics and penetration behaviour of chloride ions

	Fixation ability	Total pore volume	Continuous pore volume	Pore network ratios	Chloride ion suppression effect
N	100%	0.26ml/ml	0.15ml/ml	-	-
N+CA2	150% ◎	0.26ml/ml	0.15ml/ml	-17%	○
N+CA2+Ex	145% ◎			-25%	◎
BB	120% ○	○	○	-52%	◎

#### 4. Summary

The material characteristics of concrete containing a combination of  $CA_2$  and an expansive additive were investigated as a basic study for durability examination, and the effect of chloride ions on the permeation behaviour was investigated. The following results were obtained.

- (1) By dividing the amount of chloride ions into immobilised and free chloride ions based on the chloride ion profile obtained by the salt immersion test, the proportions greatly differed depending on the material characteristics.
- (2) The calculated and measured amounts of surface chloride ions calculated by Fick's diffusion equations differed, except for ordinary concrete. For a material that possesses the immobilisation function, such as  $CA_2$ , or a material that influences the pore structures, such as blast furnace cement, it is difficult to appropriately describe the penetration behaviour of chloride ions by Fick's diffusion equations.
- (3) In the evaluation test using paste samples, the same hydrate was produced using  $CA_2$  alone and using the combination of the expansive additive and  $CA_2$ , and Friedel's salt production when chloride ions were present was also equivalent. The combined use of  $CA_2$  and the expansive additive had no influence on the immobilisation ability of the chloride ions.
- (4) The total and continuous pore volumes of each paste specimen were determined by the mercury intrusion method, and there was no significant difference in the permeation of chloride ions.
- (5) For the pore network calculated on the basis of the steady-state electrophoresis test, the reduction rate of the pore network was larger when the combination of  $CA_2$  and the expansive additive was used compared with  $CA_2$  alone. It was inferred that the pore structure changed by introduction of expansion strain.
- (6) Although the reduction rate of the pore network using  $CA_2$  was smaller than that of the BB sample, the higher immobilisation rate suggested that the same degree of resistance to salt damage was exhibited, albeit with a small total addition rate.

#### *References*

- [1] Kazuhiro Tahara, Kenji Yamamoto, Koji Ashida, Morioka-Machi: Capacity of cemented cement hardened with CaO and  $2Al_2O_3$  to Fix Chloride Ions, Cement and Concrete Papers, No. 64, pp. 428-434 (2010)
- [2] Morioka, Wajin Tawara, Kenji Yamamamoto, and Aki Araki: Diffusion inhibiting effect of chloride ion of  $CaO \cdot 2Al_2O_3$  and its mechanism, concrete technology series No.89 of Civil Engineering Society, Report No.2 of the Study Subcommittee on Physical Property Change and Performance Evaluation of Concrete Using Admixture Materials (333 Committee) Report No.2, pp.443-448 (2010)
- [3] Kowa Tsuji and Kentaro Suhara: Performance Evaluation of Expanded Concrete, Technical Journal Publishing (2011)
- [4] Ryoshi Yoshida, Kishiji: Separation and extraction of continuous pores and ink bottle pores by stepwise injection of mercury, discoloration of samples by mercury injection, Summary of lectures at the annual academic lecture of the Japan Society of Civil Engineers, Vol. 62, 5-043 (2007)
- [5] Ryo Yoshida, Ryoji Kishi: Study on Differences in Mercury Injection Processes in Cement Pastes with Different Water Cement Ratios and Curing, Report on Annual Articles of Concrete Engineering, Vol. 29, pp. 729-734 (2007)