

Chemical Deterioration of Hardened Cement Pastes Immersed in Calcium Chloride Solution

Hiroaki Mori¹, Ryuichiro Kuga¹, Shoichi Ogawa¹ and Yoshimori Kubo²

¹*Taiheiyo Cement Corporation, Research & Development Center,
2-4-2, Osaku, Sakura, Chiba Prefecture 285-8655 Japan
Hiroaki_mori@taiheiyo-cement.co.jp
Ryuichiro_Kuga@taiheiyo-cement.co.jp
Shoichi_Ogawa@taiheiyo-c.co.jp*

²*Kanazawa University, Kakumachou, Kanazawa, Ishikawa Prefecture 920-1192 Japan
ykubo@t.kanazawa-u.ac.jp*

ABSTRACT

In this study, several cement pastes were immersed in CaCl₂ solutions and the most seriously damaged specimens were analyzed in detail using XRD and EPMA in order to consider the mechanisms of chemical deterioration due to CaCl₂. Cement pastes damaged by CaCl₂ attack showed lifting and cracking on the exposed surface and finally formed a layered crack. The damaged part was composed of multiple layers of thin cement pastes. Furthermore, it was found through XRD analysis that the damaged part included a large amount of complex salts of 3CaO·CaCl₂·15H₂O. The degree of the damage seems to be related with the amount of Ca(OH)₂ in the cement pastes. It is considered that the occurring of horizontal cracks is determined by the amount of 3CaO·CaCl₂·15H₂O formed near the surface and the total porosity of hardened cement pastes which relieves the expansive pressure.

Keywords. CaCl₂, Chemical Deterioration, Hardened Cement Paste, 3CaO·CaCl₂·15H₂O, EPMA

INTRODUCTION

After the prohibition of the studded tires in 1991, NaCl and CaCl₂ have been mainly used as de-icing salts in cold and snowy regions of Japan. The usage of de-icing salts is increasing year after year. The effect of the chloride derived from de-icing salts on concrete structures may be larger than that of salts from seawater, since they are generally scattered on concrete roads and bridges as highly concentrated solutions and granulated solids. Some papers have discussed the deterioration of concrete structures due to de-icing chemicals and the prevention measures thereof. It is well known that de-icing salts can penetrate into concrete structures and accelerate the corrosion of steel reinforcements. De-icing salts also promote Alkali-silica reaction and a surface scaling due to freezing and thawing cycles (Shi, 2009). In addition, some researchers have pointed out that highly concentrated CaCl₂ and MgCl₂

solutions cause chemical degradation, swelling, as well as cracking in concrete (Torii, 1992) (Collepari, 1994).

In terms of the deteriorative chemical effect of CaCl_2 , recent studies have suggested that hardened cement pastes expand and the strength of the paste decrease. For mortars and concretes, the deterioration is accompanied by intensive scaling.

It is considered that the degradation was caused by the formation of a hydrated calcium oxychloride as shown by $\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ (Monosi, 1989). Several immersion tests were conducted in order to investigate the effect of mixture proportion and immersion conditions on deterioration caused by CaCl_2 attack. There is little data available concerning the mechanisms and conditions of 3-1-15 formation in hardened cement pastes and the progress of the deterioration is not fully understood.

In this article, several cement pastes were immersed in highly concentrated CaCl_2 solutions and the most seriously damaged specimen was analyzed using X-ray diffraction analysis and an electron probe X-ray micro analyzer. The purpose of this work is to consider the formation mechanisms of the 3-1-15 and to explain the progress in deterioration of the hardened cement pastes.

MATERIALS AND TEST PROCEDURES

Materials and Specimens. Three types of Portland cement and two types of blended cement were used in this study. Portland cements include ordinary Portland cement (OPC), high early strength Portland cement (HPC) and low heat Portland cement (LPC). Blended cements include blast furnace slag cement (BB) and silica fume cement (SF), which were respectively prepared by adding 40 % blast furnace slag and 15 % silica fume to OPC. The two mineral admixtures were: blast furnace slag with a specific gravity of 2.89, total SO_3 of 1.84 %, Blaine fineness of $4380 \text{ cm}^2/\text{g}$ and silica fume with a specific gravity of 2.25, BET specific surface of $9.4 \text{ m}^2/\text{g}$. Chemical compositions and physical properties of Portland cements are given in Table 1.

The water to binder ratio (W/B) was almost always 0.6 throughout the investigation and two different W/B (0.45 and 0.35) were adopted for the ordinary Portland cement. The cement pastes were mixed using a Hobart mixer according to the procedure of JIS R 5201, except that no sand was added. Entrained air reducer was added such that its mass was equalled 0.01 mass% of binder. Every other hour cement pastes were remixed by hand and were cast in 40 mm by 40 mm by 160 mm steel molds after bleeding water was not observed. Two days after casting, specimens were removed from the molds and cured in saturated lime water.

Table 1. Chemical compositions of Portland cement

Cement Type	Chemical composition (mass %)												Density (g/cm^3)	Blaine (cm^2/g)
	Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5		
OPC	0.62	21.4	5.28	2.66	65.0	1.46	2.08	0.29	0.48	0.27	0.09	0.24	3.16	3480
HPC	1.12	20.3	5.06	2.50	65.5	0.93	2.87	0.26	0.28	0.31	0.08	0.38	3.14	4640
LPC	0.75	26.3	2.68	3.04	63.1	0.61	2.57	0.22	0.35	0.31	0.02	0.30	3.22	3340

Immersion Tests. Cement paste specimens were cut into 40 mm cubes. Five plane faces except for an exposure surface were sealed by epoxy resin. After the initial curing period of

28 days, the specimens were immersed in a 30 w/w% aqueous solution of CaCl_2 for 12 weeks and the solutions were exchanged every four weeks. The storage containers were stored at room temperature (20 °C) and low temperature (5 °C). Some specimens were also immersed in a saturated NaCl solution for reference. The solutions were prepared by DI water and chemical reagents; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaCl. Some specimens were subjected to wet-dry cycles (W/D); they were immersed in 5 °C CaCl_2 solution for 4 days, followed by drying for 3 days at 20 °C, R.H.60 % room. After 12 weeks the specimens were continuously immersed in the same solutions for one year. Table 2 shows the combination of specimens and immersion test conditions. The name of specimens is expressed as (Cement type W/B)-(temperature)-(solution type). Every four weeks the weight of specimens was measured. Chloride penetration depth was measured by spraying a 0.1 mol/L AgNO_3 solution on the splitting surface of specimens.

Compressive strength, amount of Ca(OH)_2 and total pore volume of hardened cement pastes after a curing period of 28 days were measured. The amount of Ca(OH)_2 was estimated by thermogravimetric analysis (TG-DTA) and the total pore volume of cement pastes was measured by mercury intrusion porosimetry. The results were summarized in Table 2.

Table 2. Immersion conditions, analysis and properties of cement pastes

Symbol	Cement Type	W/B (%)	Immersion test				Compressive strength (N/mm ²)	Amount of Ca(OH)_2 (%)	Total pore volume (vol. %)
			30w/w% CaCl_2			Saturated NaCl			
			5°C	20°C	Wet/Dry	5°C			
OPC60	OPC	60	○, XRD, Cl	○, EPMA, XRD	○	○, XRD, Cl	40.8	18.7	36.2
HPC60	HPC		○	—	—	—	45.1	20.1	34.0
LPC60	LPC		○	—	—	—	37.2	11.5	40.9
BB60	BB		○, XRD, Cl	○	○	○, XRD, Cl	41.3	8.2	33.8
SF60	SF		○	—	—	—	40.8	10.6	36.2
OPC45	OPC		45	○	—	—	○	56.8	14.9
OPC35	OPC	35	○	—	—	○	81.5	12.2	21.8

Cl: Chloride content measured according to JIS A 1154

X-ray Diffraction. In order to detect hydrates and reaction products in the cement paste which was sampled near the exposure surface, the powder method of X-ray diffraction was adopted. The sample used for XRD analysis was obtained by crushing a 5 mm layer of the hardened cement paste beginning at the exposure surface. X-ray source of $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) was used. The scan step size was 0.02 °. Scan speed was 0.13 sec/step. The $2\theta\text{CuK}\alpha$ ranged from 5 ° to 65 °. The X-ray tube voltage and current were fixed at 35 kV and 350 mA respectively. In order to avoid the transformation of hydrates and reaction products, washing with solvents and drying treatment were not conducted.

XRD analysis was conducted in both samples; OPC60 and BB60 immersed in CaCl_2 solution stored at 5 °C. A complex salt of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ phase was identified by finding the diffraction peaks of 10.6 ° and 21.3 ° (Kuga, 2012).

Electron Probe X-ray Micro Analyzer. The most damaged specimen, OPC60, was immersed in CaCl_2 at 20 °C for 8 weeks and examined by electron probe X-ray analyzer. After drying under vacuum for one week, the specimen was mounted in epoxy resin and cut into halves using a diamond saw. The cut sample was mechanically polished in the following order: #100 waterproof abrasive paper coated with 150 micron SiC, #400, #800, #1000 and #1200 paper coated with 6.5 micron SiC. Analysis area was 20 mm x 25 mm near the

immersed surface. The characteristic X-rays of Cl, Si, Ca and S were simultaneously measured by 5 wavelength-dispersive spectroscopy detector channels. Analytical conditions were 15 kV accelerating voltage, 50 nA beam current, and 50 μm pixel size. Also, three small areas (A, B, C) of the specimen were analysed precisely; A was the damaged area near the exposed surface, B was next to the damaged area and C was the area not penetrated by Cl. Analysis area was 0.4mm x 0.4 mm or 0.4 mm x 0.8 mm. Figure 1 shows the analysis areas by EPMA.

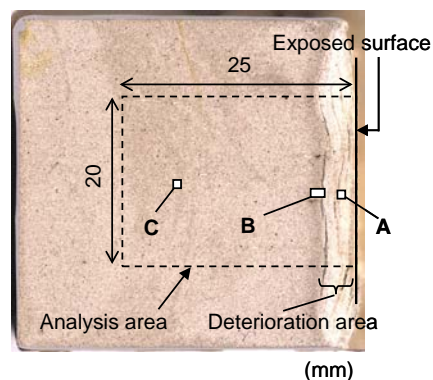


Figure 1. Analysis area by EPMA

RESULTS AND DISCUSSION

Visual Changes of specimens.

Photo 1 shows the external appearances of OPC60, HPC60 and LPC60 immersed in CaCl_2 solutions at 5 °C for 12 weeks. Photo 2 shows their external appearances after continuous immersion for one year without exchanging the solution. HPC60 subjected to CaCl_2 exhibited the greatest degree of damage. After 12 weeks of immersion, the exposed surface swelled and spalled, and the deteriorated area consisted of a laminated structure composed of cement paste layers. For OPC60 comparable deterioration was observed with several millimetres spalling on the immersed surface after one year. LPC60 was the least damaged among three specimens and showed a little spalling and cracking on the exposed surface.



Photo 1. External appearances after 12 weeks (OPC60, HPC60 and LPC60)



Photo 2. External appearances after 1 year

For BB60 and SF60 only a little surface spalling was observed and the degree of damage was smaller than that of LPC60. OPC45 and OPC35 immersed in CaCl_2 for 12 weeks showed a slight degree of damage and after one year immersion, and surface spalling occurred just as in OPC60. On the other hand, specimens subjected to wet-dry cycles (W/D) and immersed in saturated NaCl showed few signs of damage on the surface.

Weight Changes. Figure 2 and Figure 3 illustrate weight changes of specimens during immersion tests. Figure 2 shows weight changes of all specimens immersed in CaCl_2 solutions at 5 °C and Figure 3 shows weight changes of OPC60 and BB60 subjected to different immersion conditions. The weight of specimens immersed in CaCl_2 decreases

gradually up to about 8 weeks, after which surface spalling and cracking are observed, as well as an abrupt increase in weight. BB60 and SF60 immersed in CaCl_2 and all specimens subjected to wet-dry cycles exhibited no weight gain throughout the immersion tests. On the other hand, all specimens immersed in saturated NaCl experienced a steady weight gain which became constant after 10 weeks.

Spragg and coworkers have investigated water absorption in different de-icing and different concentration solutions (Spragg, 2011). They demonstrated that specimens immersed in NaCl absorbed much more water than those in CaCl_2 and that water absorption in saturated CaCl_2 was very little. The weight changes in specimens include liquid absorption in solution, liquid transferring by osmotic pressure, and hydrate dissolution by chemical reaction.

The time at which weight gain begins corresponds exactly with occurrence of surface spalling and cracking. Therefore, it is considered that the weight gain in specimens immersed in CaCl_2 is mainly caused by the penetration of solutions into the surface deteriorated area. However, reasons for the weight loss of specimens immersed in CaCl_2 are not fully understood.

Chloride Penetration Depth. Figure 4 shows chloride ion penetration depths of each specimen after immersion for 4 weeks, 8 weeks and 12 weeks and discoloration depths before spraying a 0.1 mol/L AgNO_3 solution. The chloride ion penetration depth of specimens immersed in 5 °C CaCl_2 increases in the order, HPC60, OPC60 and LPC60. The penetration depth at 12 weeks of blended cement pastes such as BB60 and SF60, and of lower W/B specimens such as OPC45 and OPC35 were lower than that of HPC60 or OPC60. In this study the penetration of the chloride ion at 20 °C are earlier than that at 5 °C and the rate of chemical deterioration due to CaCl_2 was accelerated. Discoloration depth does not necessarily correspond to the chloride penetration depth. It would appear that the final degradation degree of specimens depends on whether cracks occur on the exposure surface.

In immersed condition of W/D, discoloration or deterioration near the exposed surface was not observed while the chloride penetration depth was almost the same as that of continuously immersed specimens in 5 °C CaCl_2 solutions. There are several of interpretations of the effect of wet-dry cycles on deterioration of specimens. Some

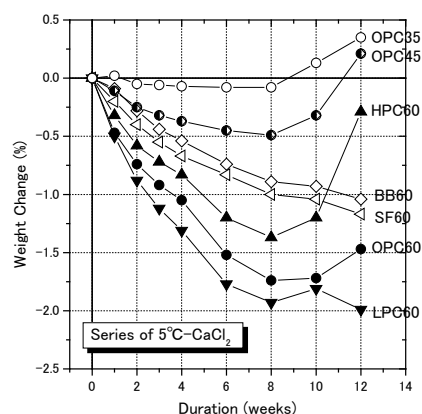


Figure 2. Weight change

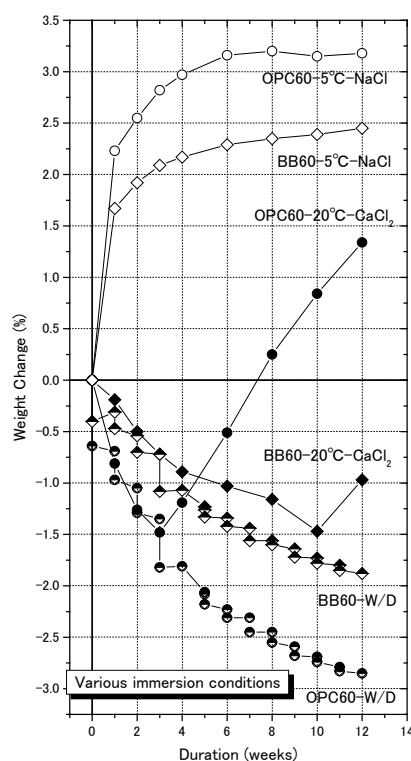


Figure 3. Weight change

researchers suggested that wet-dry cycles accelerate the degree of deterioration, others reported that the W/D condition reduces it. A decrease in the amount of $\text{Ca}(\text{OH})_2$ near the surface by carbonating in drying condition comes to prevent the progress of chemical deterioration by CaCl_2 .

In all specimens the chloride ion penetration depths in NaCl solutions were greater than in CaCl_2 solutions.

Discoloration or deterioration near the exposed surface was not observed. The reason for this will be discussed in the next section.

The addition of mineral admixtures such as blast furnace slag and silica fume reduced the amount of $\text{Ca}(\text{OH})_2$ and simultaneously inhibited the chloride ion penetration. For this reason, resistance to CaCl_2 attack of concrete mixtures containing mineral admixtures were effectively improved (Collepari, 1994). The result of this study agrees with that obtained by Collepari et al. On the contrary, for the lower W/B specimens such as OPC45 and OPC35, damages by CaCl_2 attack were not prevented. Finally, surface spalling occurred whereas chloride ion penetration into cement paste was reduced.

The CaCl_2 attack is accompanied by the formation of a hydrated calcium oxychloride according to the following reaction:



We suggest that the disruptive chemical attack in hardened cement pastes is due to the volume change in formation of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ showed in equation (1) (Kuga, 2012). The expansion pressures caused by formation of 3-1-15 are expected to be relieved, when some pores and voids exist in hardened cement pastes. In blended cement pastes and LPC60, which contain relatively lower amount of $\text{Ca}(\text{OH})_2$, the expansion pressures caused by formation of 3-1-15 will decrease. As a consequence of this, cracks in the surface hardly occurred. On the other hand, OPC45 and OPC35 have a denser pore structure in cement paste matrix and expansion pressures caused by the formation of 3-1-15 phase are not relieved. Cracks occurring on the surface and fluid penetration into the cracks were repeated and the deterioration goes on inside of specimen. From the above consideration we suggest that whether surface cracks occur or not depends on the amount of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ which may cause expansion pressure, and the total porosity which lowers expansion pressure.

Reaction Products. Figure 5 shows the X-ray diffractograms of OPC60 immersed in CaCl_2 solutions at 5 °C while those of BB60 are shown in Figure 6. Each figure illustrates four diffraction patterns of pastes before immersion, after immersion for 4 weeks, 8 weeks and 12 weeks. Ettringite (Ett), Calcium aluminate mono carbonate hydrate (Mc), Calcium aluminate hemi carbonate hydrates (Hc) and Calcium hydroxide (CH) were observed in OPC pastes before immersion.

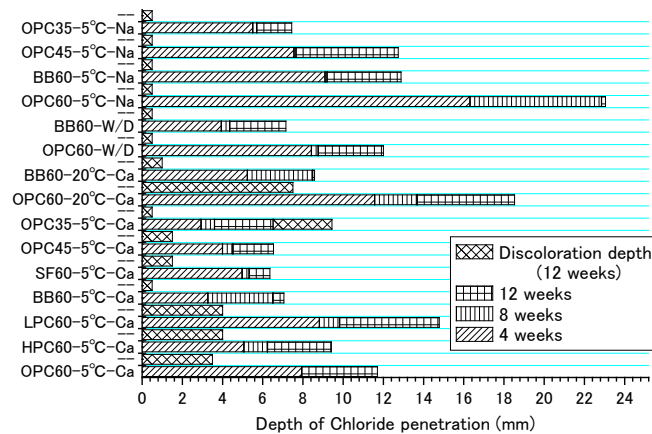


Figure 4. Depth of chloride penetration

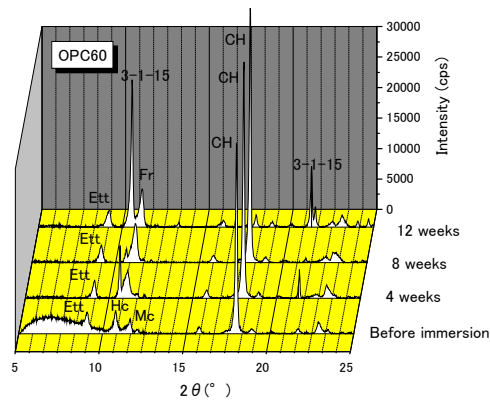


Figure 5. XRD patterns of OPC60

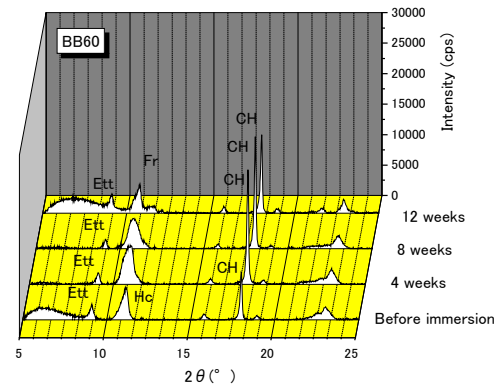


Figure 6. XRD patterns of BB60

For OPC60 immersed in CaCl_2 solutions, the diffraction peaks of Mc and Hc disappeared and other diffraction peaks of Friedel's salt (Fr) and $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ newly appeared. After immersion for 12 weeks, 3-1-15 phase's peaks became clear and the intensity peaks of CH decreased significantly. Friedel's salt generated from Mc or Hc by replacing CO_3^{2-} with Cl^- and CH was consumed with formation of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ phase. For BB60 the diffraction peaks of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ were not confirmed while the peaks of Friedel's salt appeared. In some literature 3-1-15 phase's peaks appeared in mortar with 40 % blast furnace slag. The amount of $\text{Ca}(\text{OH})_2$ in BB60 is lower than that of OPC60 and the depth of chloride penetration is also small. So the formation of 3-1-15 phase may be limited near the immersion surface.

For OPC60 and BB60 immersed in NaCl solutions, the formation of 3-1-15 phase and disappearance of CH were not confirmed while the peaks of Friedel's salt appeared. It was reported that all mortar specimens immersed in saturated NaCl solution for 2 years have no chemical deteriorations or visual changes (Smolczyk, 1968). Damidot calculated the phase diagram of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaCl}_2-\text{Na}_2\text{O}-\text{H}_2\text{O}$ system at 25°C and has shown that NaCl , Fr, CH and 3-1-15 are capable of coexisting as a solid phase (Damidot, 1994). However, when the cement pastes were immersed in NaCl solution, the lack of calcium in pore solutions did not lead to the formation of 3-1-15 phase.

Analysis of Damaged Parts. Photo 3 (a) and (b) showed a cross section of OPC60 immersed in CaCl_2 at 20°C for 8 weeks and enlarged part of the damaged area. The area from the immersed surface to a depth of 5 mm discoloured into black. The damaged parts consisted of cement paste layers which were about 0.2 mm in width and were significantly softened as if the parts were easily ground down by hands.

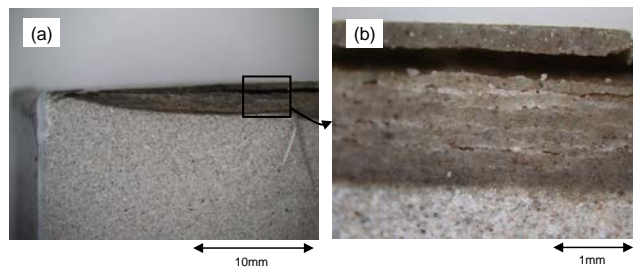


Photo 3. Damaged area near the surface

For the above samples the XRD analysis was conducted and it was observed that the peaks of Friedel's salt (Fr) and $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ phase appeared

distinctly and the peaks of CH decreased significantly. It would appear that the amount of $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ is very large.

Figure 7 shows the four elements' concentration profiles which are made from the results of wide spread area analysis by EPMA. At depths not greater than 5 mm Cl concentration is about 10 mass% and other oxide (CaO, SiO_2 and SO_3) concentrations are lower than those inside. However, only the CaO concentration at a depth of approximately 5 mm is higher than that inside.

Figure 8 shows the back scattered electron image and four elements' concentration profiles on position A shown in Figure 1. There were several cracks which were parallel to the immersed surface and the cracks were filled with high luminance substances.

According to the above results of XRD analysis the substances were considered to be $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ phase. Cracks occurred at even intervals of 100 μm to 150 μm and the damaged parts seemed to be laminated structures consisting of cement paste layers and 3-1-15 layers alternately.

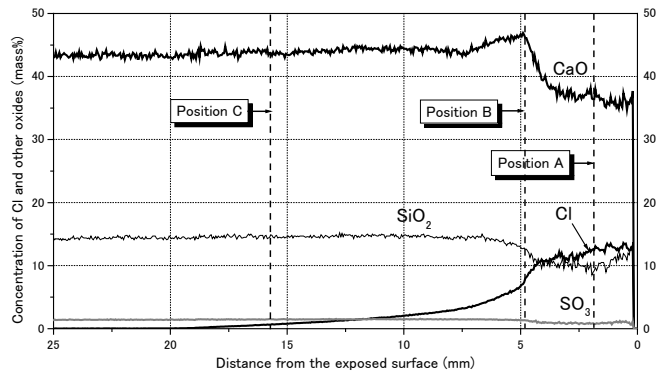


Figure 7. Concentration profile of 4 elements

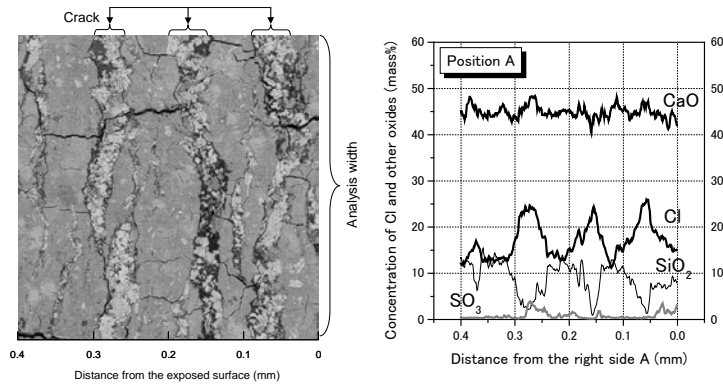


Figure 8. BSE image and concentration profile

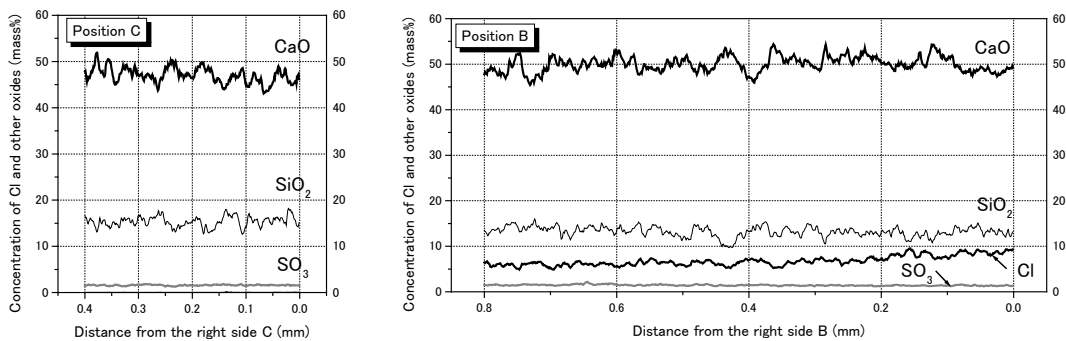


Figure 9. Concentration profile (Analysis area B and C)

From Figure 8 it can be stated that inside a crack observed in the back scattered electron images Cl concentration is high and SiO₂ concentration is very low. The Cl/Ca mole ratio inside a crack is calculated to be 0.8. This result indicates that 3CaO · CaCl₂ · 15H₂O (Cl/Ca=0.5) coexist with chemical compositions of CaCl₂ solution (Cl/Ca=2.0).

Figure 9 shows four elements' concentration profiles on position B and C shown in Figure 1. Cl concentration on B, which is nearly 7 ~9 mass%, is significantly larger than the amount of bound chlorides in hydrated cement pastes that is estimated at about 1.5 mass% in the case of immersion in high concentration of chloride solutions. It may be concluded that a large amount of chloride ions are concentrated in pore solutions of cement pastes.

Figure 10 shows a mapping of Cl/Ca mole ratio on position B. Since there are cracks next to the analyzed area, the right side of position B was directly affected by the concentrated CaCl₂ solutions. At depths not greater than 100μm from the right side there exists several small parts with about 0.5 to 0.6 of Cl/Ca dispersedly. In view

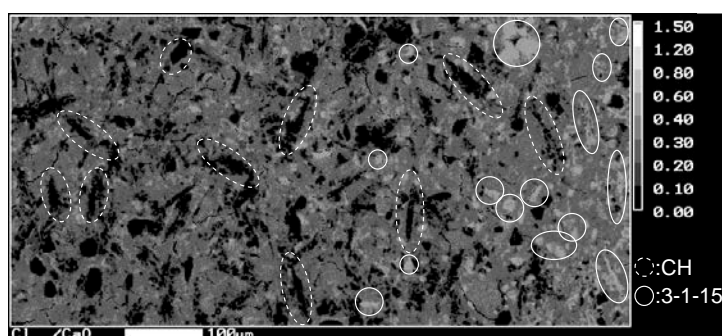


Figure 10. Mapping of Cl/Ca ratio (Analysis area B)

of the Cl/Ca mole ratio it is likely that 3CaO · CaCl₂ · 15H₂O was formed in the small part. Because the shape of 3-1-15 phase's formation parts is similar to that of calcium hydroxide's precipitation, 3-1-15 seems to be formed substituting for Ca(OH)₂ in cement pastes.

From the above consideration we suggest that the process of deterioration by CaCl₂ attack is as follows.

- 1) As chloride ions penetrate from the exposed surface to inside, Cl concentration in pore solution increases. In this stage, 3CaO · CaCl₂ · 15H₂O is not formed in cement pastes because Ca concentration in pore solution is low.
- 2) Ca ions penetrate into the inside of cement pastes. If Ca concentration is higher than some value and Cl/Ca mole ratio is lower than value of 0.5, 3-1-15 is formed at depths not greater than 100 μm from the surface cracks. Because the formation of 3-1-15 consumes a large amount of calcium, it follows that calcium hydroxide disappears from the hydrated cement pastes. It seems reasonable to suppose that 3-1-15 mainly formed at the sites where calcium hydroxide precipitated originally.
- 3) If the expansive 3-1-15 forms a small horizontal crack near the exposed surface, CaCl₂ solution is directly supplied to the surface of cracks. Ca concentration near the sites increases and further amount of 3-1-15 phase is formed.

In order for cracks which are parallel to the immersed surface and the laminated structure to be formed, it is necessary that a large amount of 3-1-15 to be formed at depths of not greater than 100 μm than the nearest exposed surface and cement paste layers should be spread out outside. The reason why a large amount of 3-1-15 was formed at depths of not greater than 100 μm is thought to be a decrease in pH at the nearest area by way of CaCl₂ penetration.

The damaged parts consisted of cement paste layers and were greatly softened as if the parts were easily ground down by hands. The reason for this is considered to be that the cement pastes were divided into sections after the formation of 3-1-15 and these granulated cement pastes were directly affected by CaCl_2 solutions. It may be that the transformation of deteriorated parts such as decalcification of C-S-H occurred after $\text{Ca}(\text{OH})_2$ disappearing from cement pastes. This topic needs further consideration.

CONCLUSIONS

The main results of this study are as follows.

- 1) Cement pastes damaged by CaCl_2 attack showed lifting and cracks on the exposed surface and then formed a layered crack. The damaged part was significantly softened and seemed to be a laminated structure that was composed of cement paste layers and 3-1-15 layers alternately.
- 2) The degree of damage seems to be related with the amount of $\text{Ca}(\text{OH})_2$ in the cement pastes. Whether a layered crack occurs or not depends on the amount of $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ and total porosity of hardened cement pastes which relieves the expansive pressure.
- 3) It is considered that if the expansive 3-1-15 forms a small horizontal crack near the surface, high concentration CaCl_2 solution would be directly supplied through the cracks. And then a larger amount of 3-1-15 will be formed in the cracks, extending cracks width and lifting the cement paste layer. The thickness of the cement paste layer was about 100 μm , and it corresponded with the depth where the 3-1-15 was observed in the cement paste without cracks.

REFERENCES

- Colleparidi, M., Coppola, L., and Pistolesi, C. (1994). "Durability of Concrete Structures Exposed to CaCl_2 Based Deicing salts", *Proceeding 3rd international Conference on durability of concrete, ACI SP-145*, pp.107-120
- Damidot, D., Birnin-Yauri, U. A., and Glasser, F. P. (1994). "Thermodynamic Investigation of the $\text{CaO-Al}_2\text{O}_3\text{-CaCl}_2\text{-H}_2\text{O}$ System at 25°C and the Influence of Na_2O ", *il Cemento*, Vol.4, pp.243-254 (1994)
- Monosi, S., Alvera, I., and Colleparidi, M. (1989). "Chemical Attack of Calcium Chloride on the Portland Cement Paste", *il Cemento*, Vol.2, pp.97-104
- Shi, X. et al. (2009). "Deicer Impacts on Pavement Materials; Introduction and Recent Developments", *The Open Civil Engineering Journal*, Vol.3, pp.16-27
- Smolczyk, H. G. (1968). "Chemical Reactions of Strong Chloride-Solutions with Concrete", *Proceedings 5th International Symposium on Chemistry of Cement*, Vol.3, pp.274-280
- Spragg, R. P. (2011). "Wetting and drying of concrete using aqueous solutions containing deicing salts", *Cement & Concrete Composites*, No.33, pp.535-542
- Torii, K. et al. (1992). "Deterioration of cement mortars immersed in NaCl and CaCl_2 solution", *Proceedings of the Japan Cement Association, Cement & Concrete*, No.46, pp.504-509 (in Japanese)