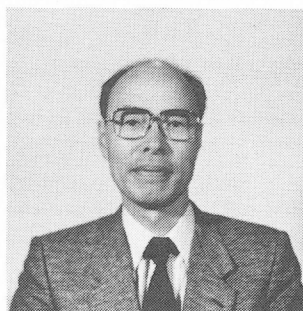


INFLUENCE OF CHLORIDES ON SCALING DETERIORATION OF
HARDENED CEMENT PASTES

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SYNOPSIS

This paper describes the scaling deterioration of hardened cement pastes subjected to freezing and thawing in salt solutions such as NaCl, CaCl₂, MgCl₂ and sea water. The various factors affecting to the scaling deterioration such as kind of solution, concentrations, drying and air entraining were investigated in connection with the microstructural features. The severest scaling was observed on the non AE pastes in NaCl, CaCl₂ solutions and sea water caused by the damage of Ca(OH)₂ and the collapse of CSH. The rate of scaling decreases with freeze-thaw cycle on the non AE pastes in MgCl₂ solution and on the AE pastes in CaCl₂ solution and sea water due to the dense layer formed near the surface. However, very porous portion was observed at adjacent to the dense layer. The cavities in dried AE paste are filled with new compound and the shell of air voids becomes denser and thicker. Consequently, the dried AE paste is much more resistant to surface scaling than non dried one.

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1. INTRODUCTION

It is well known that the concrete subjected to deicing salts or sea water is severely deteriorated due to the combined attack of salt solution and frost in a cold region. The properties of paste matrix affect mainly to the deterioration of such concrete. When hardened cement paste is exposed to deicing salts or sea water, the hydration products react chemically with chlorides and sulphates. As a result, the microstructure of paste matrix is changed. Moreover, the hydration products are damaged due to the freeze-thaw action of capillary water. Consequently, the texture becomes loose. The freeze-thaw deterioration of concrete in a saline environment is due to the chemical and physical change of microstructure in hardened cement paste. Therefore, it is essential to make clear the relation between the macroscopic phenomena such as scaling or strength variations and the microstructural change of hardened cement paste in order to elucidate the mechanism of the deterioration.

Macroscopic approaches have been mainly adopted in the studies on the deterioration of concrete materials subjected to chlorides and freeze-thaw action. There are a great number of researches mainly concerned with the scaling deterioration of concrete pavements and bridge slabs subjected to deicing salts and freeze-thaw action in other countries such as Verbeck and Klieger[1], Hartmann[2], Cordon[3] and Browne et al.[4]. In this country, studies on the scaling deterioration of concrete subjected to sea water and freeze-thaw have been conducted[5][6][7]. On the other hand, the microstructural studies in this area have been carried out only by Hochstetter[8] and Kayyali et al.[9] using a scanning electron microscope.

The present writers have reported on the deterioration of hardened cement paste subjected to freeze-thaw action in $MgCl_2$ solution[10]. This paper describes the scaling deterioration of hardened cement paste in connection with the microstructural and chemical changes to elucidate the mechanism of deterioration of concrete subjected to freezing and thawing in saline environments. The influence of salt solutions, concentrations, drying and entrained air on the scaling deterioration of hardened cement paste subjected to deicing salts such as $NaCl$, $CaCl_2$ and $MgCl_2$, and sea water was investigated in connection with the microstructural features using a scanning electron microscope SEM, an energy dispersive x-ray microanalyzer EDXA, an x-ray diffraction XRD and a differential thermal analyzer DTA.

2. EXPERIMENTAL PROCEDURE

Ordinary portland cement was used. The initial solid phase V_{so} of paste was 40% (W/C 56%) in general, although V_{so} 35% and 45% (W/C 70%, 45%) were also used for $MgCl_2$ 3% solution. Air content was 4% for AE paste. The specimen size was 40 x 40 x 160 mm. The specimens were cured in water at $20^\circ C \pm 1^\circ C$ for 7 days. Some of them were dried in air at $30^\circ C$ and 65% RH for 3 days as a preliminary treatment. Freeze-thaw tests were performed in salt solutions, sea water or fresh water both for the non dried and dried specimens. $NaCl$, $CaCl_2$ and $MgCl_2$ solutions with the concentrations of 3, 6, 10 and 20% were used as the salt solutions. The minimum cooling and the maximum heating temperature were set at $-20^\circ C$ and $+5^\circ C$ respectively. One freeze-thaw cycle took 12 hours. The surface weight loss was measured and the samples were taken from the fractured surfaces of scaling and sections. The microstructures of fractured surface were observed with SEM. The chemical change was investigated using XRD, DTA and EDXA.

3. INFLUENCE OF SOLUTIONS ON SCALING DETERIORATION

3.1 Chemical Changes of Hydration Products

Fig.1 shows the XRD result of hardened cement pastes exposed to freeze-thaw

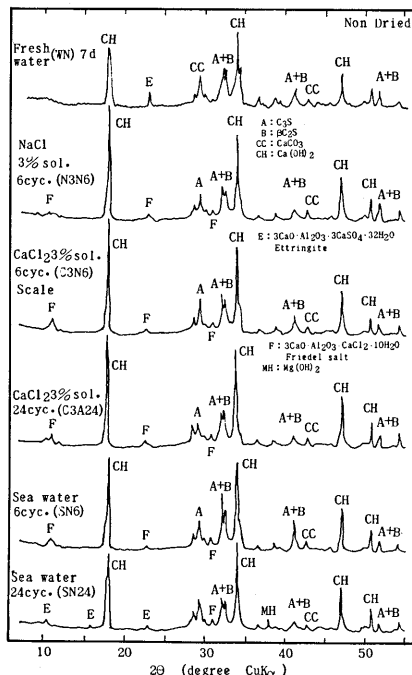


Fig.1 Change of hydrates due to F-T in salt solutions

cycles in salt solutions. There were no significant differences in XRD patterns at 6 cycles of freeze-thaw for the specimens immersed in NaCl, CaCl₂ 3% solution and sea water. Friedel's salt (3CaO·Al₂O₃·CaCl₂·10H₂O) could be detected at this stage. The XRD patterns at 24 cycles of freeze-thaw did not differ from that at 6 cycles, although the peak intensity of Friedel's salt at 24 cycles was slightly stronger than at 6 cycles in CaCl₂ 3% solution. The peak intensity of Ca(OH)₂ became weaker and that of Mg(OH)₂ appeared evidently at 24 cycles in sea water. At the same time, the secondarily produced ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) was detected other than Friedel's salt.

Fig.2 shows the result of DTA which illustrates the difference of compound between surface and inner portion after 24 cycles of freeze-thaw in the salt solutions. There was no such difference of the DTA curves between surface and inner portion in the case of CaCl₂ solution. The peak of Ca(OH)₂ was small at the scale and the endotherm of Mg(OH)₂ was recognized only at the surface portion in the case of MgCl₂ solution. This indicates that Mg²⁺ ions did not diffuse into the inner portion due to the formation of dense surface layer of Mg(OH)₂.

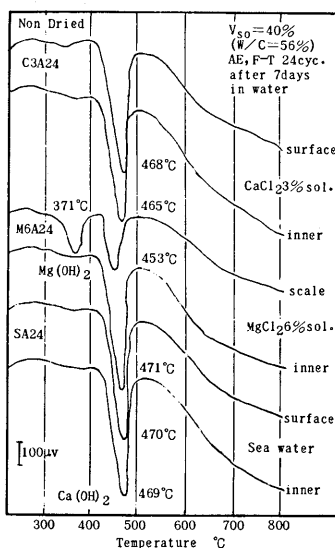


Fig.2 Difference of compound between surface and inner portion (DTA).

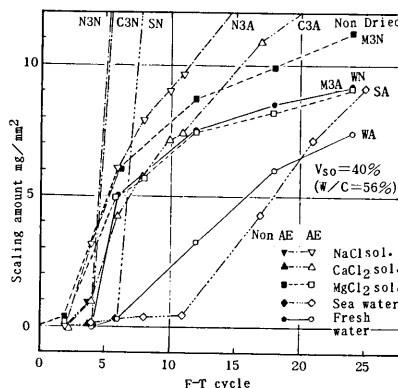


Fig.3 F-T cycle~scaling amount relationship (Difference due to chlorides).

3.2 Differences due to Kind of Solution

Fig.3 shows the differences of scaling due to solutions. In the case of NaCl solution, the microstructure near the surface layer was extremely porous and a large amount of ettringite was detected. The CSH was collapsed at 1-2 mm portion from the surface (Photo 1) and the $\text{Ca}(\text{OH})_2$ was damaged at the surface and inner portion (8-10mm). There were both comparatively sound and damaged $\text{Ca}(\text{OH})_2$ (Photo

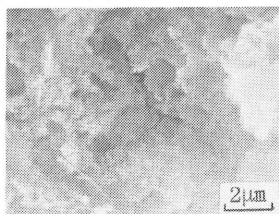


Photo 1 Collapse of CSH at surface portion in NaCl 3 % sol.

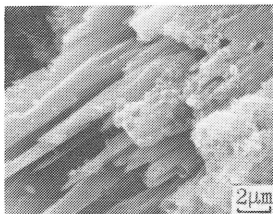


Photo 2 Damage of $\text{Ca}(\text{OH})_2$ at surface portion in CaCl_2 3 % sol.

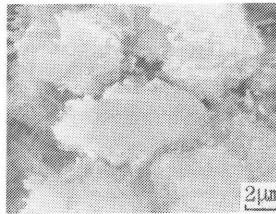
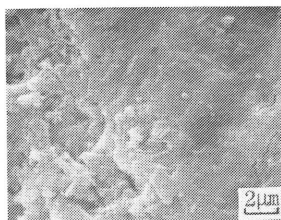
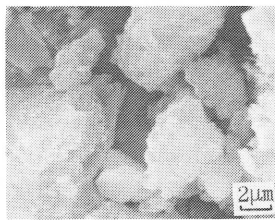


Photo 3 Disintegration of CSH at surface portion in sea water.

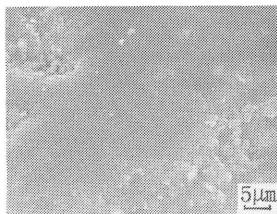


(a) Dense morphology of surface portion.

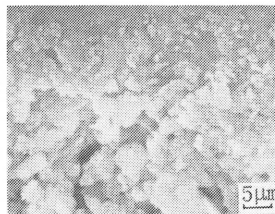


(b) Porous state at around 1 mm from surface.

Photo 4 CaCl_2 3 % solution.

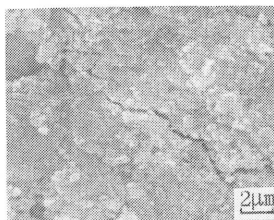


(a) Dense state at surface portion

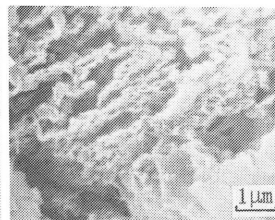


(b) Porous portion adjacent to dense layer.

Photo 5 MgCl_2 3 % solution.



(a) Dense state at surface portion



(b) Damage of CSH, $\text{Ca}(\text{OH})_2$ at inner portion

Photo 6 Sea water.

2), and ettringite was scarcely observed at the surface portion in 1-2mm thickness in CaCl_2 solution. At the inner portion, the $\text{Ca}(\text{OH})_2$ dissolved and the CSH collapsed same as in the case of NaCl solution. The microstructure at the surface portion was porous and the disintegration of CSH(I) particles was observed in the non AE specimens immersed in sea water as shown in Photo 3. And the collapse of CSH(III) and the damage of $\text{Ca}(\text{OH})_2$ were recognized. At the inner portion, the damages of a great number of $\text{Ca}(\text{OH})_2$ crystals and the granular disintegration of CSH(III) were also observed.

In the microstructure at the fractured surface of AE specimens immersed in CaCl_2 solution, the surface was dense and the surface portion within 1 mm showed the sound morphology as shown in Photo 4(a). However, very porous portion was observed adjacent to the dense layer as shown in Photo 4(b). In the case of MgCl_2 both for the AE and non AE specimens, the dense layer of $\text{Mg}(\text{OH})_2$ was produced near the surface as shown in Photo 5(a) and the extremely porous portion was formed adjacent to the dense layer (Photo 5(b)). Such morphology was not observed in the case of fresh water. The microstructure of fractured surface in the scale was dense at the edge and there were many small granular particles at

the central part of fractured surface of the scale, which was not observed in the specimens immersed in fresh water. In the case of AE specimens immersed in sea water, the surface portion became partly denser (Photo 6(a)) and other portion became more porous as a whole. The CSH and Ca(OH)_2 were damaged and the structure became loose at the inner portion (Photo 6(b)).

4. INFLUENCE OF CONCENTRATIONS ON SCALING DETERIORATION

4.1 Chemical Changes of Hydration Products

Fig.4 shows the result of XRD after 24 cycles of freeze-thaw in the salt solutions. The peak intensity of $\text{Ca}(\text{OH})_2$ was stronger and that of Friedel's salt was weaker at the scale than at the inner portion in the case of CaCl_2 6% solution. The peak intensity of Friedel's salt in the case of CaCl_2 10% solution was almost same as the scales in other cases. On the contrary, the peak intensity of $\text{Ca}(\text{OH})_2$ was stronger. This indicates that $\text{Ca}(\text{OH})_2$ was newly produced at the surface in this case. The peak intensity of $\text{Ca}(\text{OH})_2$ became weaker and that of Friedel's salt was stronger in the case of CaCl_2 20% solution same as in the case of CaCl_2 6% solution. Moreover, a double salt, $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ was detected in this case. At the scales after 24 cycles of freeze-thaw in MgCl_2 6% solution,

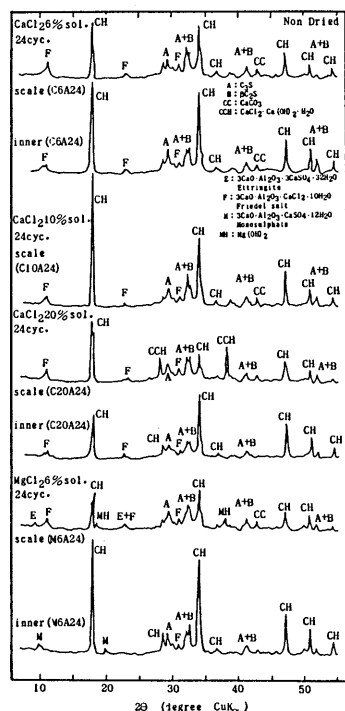


Fig. 4 Difference of compound between scale and inner portion.

ing on the concentrations of CaCl_2 solutions at the surface portion. While the such difference was small at the inner portion. The amount of Ca(OH)_2 at the scale decreased remarkably in the case of MgCl_2 solution. This was caused by the leaching of Ca(OH)_2 due to the substitution between Mg^{2+} and Ca^{2+} ions which resulted the deposition of Mg(OH)_2 at the surface portion.

the peak intensity of $\text{Ca}(\text{OH})_2$ was extremely weak in comparison with the inner portion. In addition, the monosulphate diminished, and the ettringite appeared. The peak of Friedel's salt became stronger and $\text{Mg}(\text{OH})_2$ was also produced.

Fig.5 shows the result of DTA which indicates the differences of compound between the scale and inner portion. The amount of residual $\text{Ca}(\text{OH})_2$ varied extremely depend-

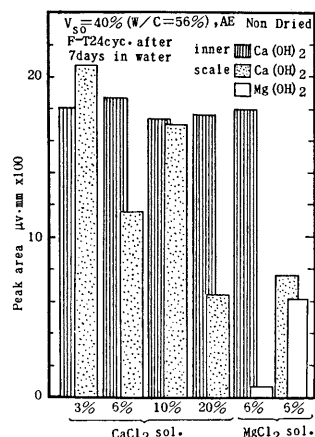


Fig.5 Comparison of compound at scale and inner portion (DTA).

4.2 Differences due to Concentrations

Figs.6 and 7 show the scaling deterioration exposed to the freeze-thaw cycles in CaCl₂ and MgCl₂ solution respectively. The scaling amount was the lowest in 20% solution. The reason is considered that the diffusion of Cl⁻ions is inhibited due to the formation of new compound in cavities and in microcracks, and the freezing temperature becomes lower due to higher concentration of the solution.

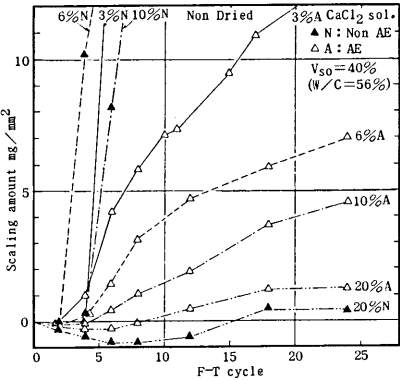


Fig. 6 F-T cycle~scaling amount relationship (concentration of CaCl₂ sol.).

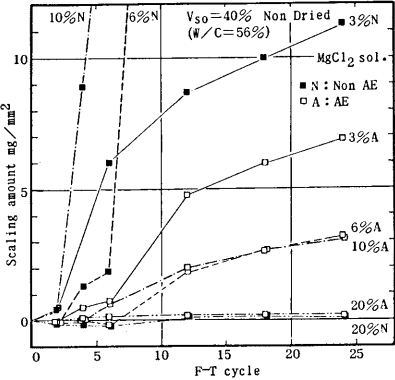


Fig. 7 F-T cycle~scaling amount relationship (concentration of MgCl₂ sol.).

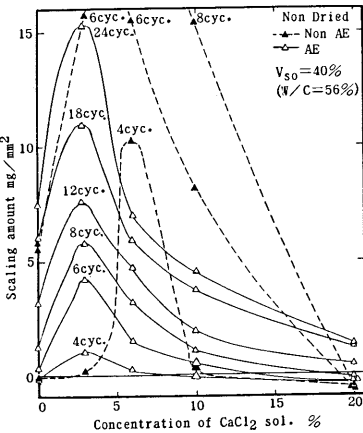


Fig. 8 Concentration~scaling amount relationship (CaCl₂ sol.).

Fig. 8 shows the relation between the concentration and the scaling amount in CaCl₂ solutions. The maximum scaling occurred at 5-6% of concentration for the non AE and at 3% for the AE specimens. The same result was obtained in MgCl₂ solutions which was not illustrated here. According to the studies on concrete by Verbeek and Klieger [1], 2-4% of concentration gave the severest scaling in NaCl or CaCl₂ solution. The scaling was the largest at relatively lower concentration as mentioned above. The reason is considered as follows: the freezing temperature is higher at lower concentration, consequently the frozen water amount becomes greater, the degree of saturation rises continuously, since the cavities are not filled up with new compound due to freeze-thaw cycles as in the case of higher concentration.

5. EFFECT OF DRYING ON SCALING DETERIORATION

5.1 Effect of Air Entraining

Air entraining was effective to resist the scaling deterioration for the non dried specimens with greater V_{so} (Fig. 9(a)). It has been pointed out that since the degree of saturation is higher at small V_{so} or in salt solutions[11][12], air entraining shows rather unfavorable effect to resist the deterioration.

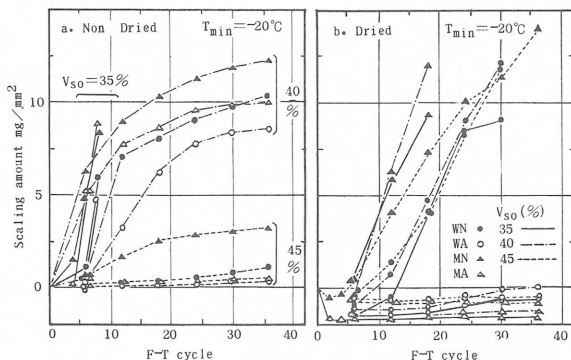


Fig.9 F-T cycle—scaling amount relationship (effect of drying).

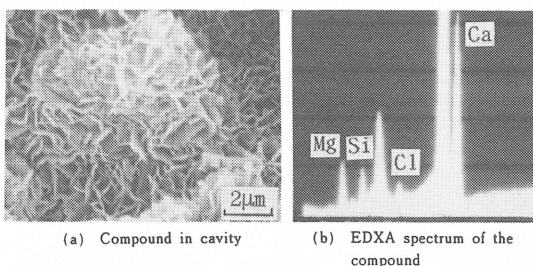


Photo7 Cavity filled up with compound at surface portion ($V_{so}=40\%$, $MgCl_2$ 3 % sol.).

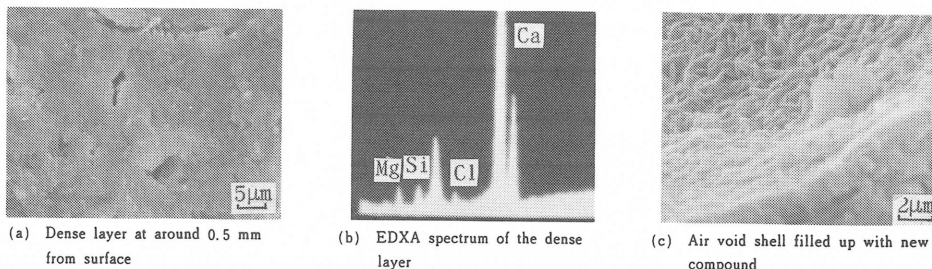


Photo8 Dense layer and air void shell at surface portion ($V_{so}=35\%$, $MgCl_2$ 3% sol.).

(a)(b)). The new compounds were observed at the portion between two layers. The void surface of entrained air was covered with the new compound and the shell of air voids became denser and thicker as shown in Photo 8(c). These compounds are considered to be $Mg(OH)_2$, $CaCO_3$ or a solid solution of these two with CSH.

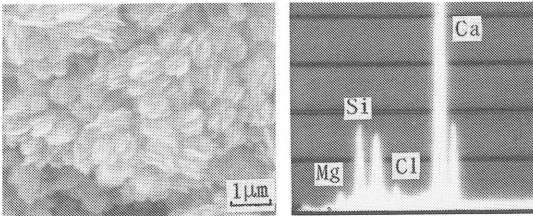
When hardened cement paste is subjected to drying, the CSH increases the resistance to splitting[14] and the texture of paste matrix becomes denser due to carbonation shrinkage[15]. The cavities are filled with new compounds and it results in lower porosity[16]. The shell of air voids becomes denser and thicker. Consequently, air entraining effect increases significantly. Therefore, the dried AE paste is much more resistant to surface scaling than the non dried one.

On the other hand, the dried AE specimens were remarkably resistant to scaling compared with the non AE as shown in Fig.9(b). The AE specimens with V_{so} 35% were particularly sound. The increase in scaling resistance due to drying is reported in the studies on concrete[1][7][13].

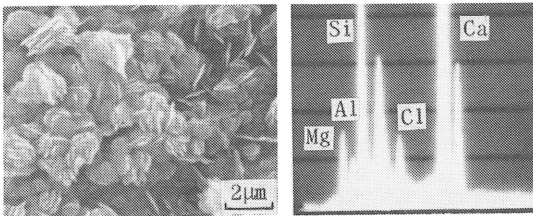
The dense layer with $Mg(OH)_2$ and $CaCO_3$ was formed in thickness of 30-40 μm at the surface portion of non AE specimens. However, the portion adjacent to the dense surface layer was extremely porous, although the granular disintegration was less than the non dried specimens. The dense layer at surface portion was formed in thickness of 100 μm for the AE specimens with V_{so} 40%. Although the portion adjacent to the dense layer was slightly porous, it was observed that larger cavities (Photo 7) and the inside of air void shells were covered with the new compound. In the case of V_{so} 35%, there were observed two dense layers. One was 50 μm in thickness on the surface layer, and the other was 150 μm in thickness at 0.5 mm from the surface (Photo 8

5.2 Differences due to Kind of Solution

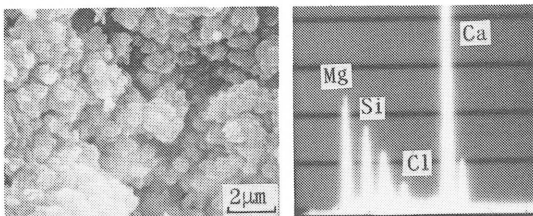
The scaling deterioration was remarkably small for the AE pastes regardless of the kind of salt solution as shown in Fig.10. On the other hand, the non AE pastes subjected to salt solutions were initially in process of absorption. Then the deterioration proceeded almost at the constant rate after beginning of scaling. These rate of deterioration was smaller than the non dried specimens in NaCl, CaCl₂ solution and sea water (Fig.3). However, the deterioration was the greatest for the dried pastes subjected to MgCl₂ solution, although the deterioration decreased with freeze-thaw cycle for the non dried pastes.



(a) Compound filling up cavities at surface portion
(b) EDXA spectrum of the compound
Photo 9 NaCl 3 % solution.



(a) Compound filling up cavities at surface portion
(b) EDXA spectrum of the compound
Photo 10 CaCl₂ 3 % solution.



(a) Compound filling up cavities at surface portion
(b) EDXA spectrum of the compound
Photo 11 Sea water.

cavities at the surface portion were filled up with the new compound as shown in Photo 10(a). This compound contained Ca 73.2%, Si 18.5% and Cl 2.6%. Fibrous and large granular compound were produced in the cavities at the distance of 6-8 mm from the surface, which constituent elements were similar to the compound at the surface portion (Photo 10(b)). In the case of sea water, the cavities were filled up with the granular compound at the distance of 1 mm from the dense surface layer which was consist of Mg(OH)₂ and CaCO₃ (Photo 11(a)). This compound contained Mg, Si, Cl and Ca (Photo 11(b)) which percentages were 16.9, 12.1, 2.6 and 68.3% respectively. The newly formed compound was observed at the inner

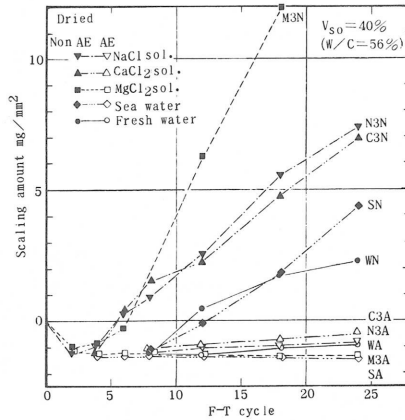


Fig.10 F-T cycle~scaling amount relationship (difference among chlorides).

In the case of non AE pastes immersed in MgCl₂ solution, the portion adjacent to the dense layer was porous. While, the cavities at the surface portion were filled with newly formed compound in the case of AE pastes immersed in NaCl, CaCl₂ solution and sea water, although the deterioration was hardly observed. In NaCl solution, the cavities at the distance of 1 mm from the surface were filled up with the granular compound (Photo 9(a)). This compound was consist of Ca 86.7%, Si 9.3% and Cl 1.4% (Photo 9(b)). And the new compound covered the cavities and AE voids at the distance of 6-8 mm from the surface.

In the case of CaCl₂ solution, the

portion at the distance of 6-8 mm from the surface. The main constituent elements were Ca 96.2%, Si 2.1%, Cl 1.0% and Mg 0.7%. Since Al and Fe were not detected. It was postulated that this compound was CaCO_3 .

5.3 Differences due to Concentrations

The relations between freeze-thaw cycles and scaling amounts, and between concentrations of CaCl_2 and scaling amounts are shown in Figs.11 and 12. The scaling amounts were so small for the AE pastes that the effect of concentration on scaling could not be exactly discussed. However, it can be estimated that the maximum scaling occurred at approximately 3% solution. While the maximum peak of deterioration can be seen apparently at 6% solution for non AE pastes. This result agrees with that for the non dried pastes subjected to CaCl_2 or MgCl_2 solution (Fig.8).

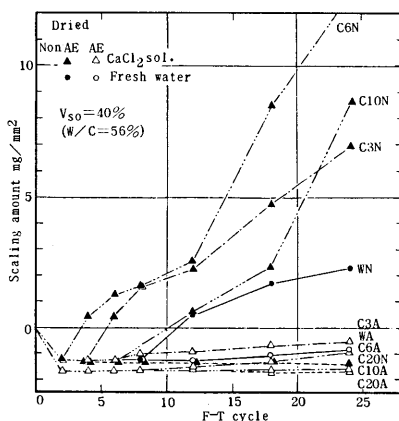


Fig.11 F-T cycle~scaling amount relationship
(difference due to concentration of CaCl_2 sol.).

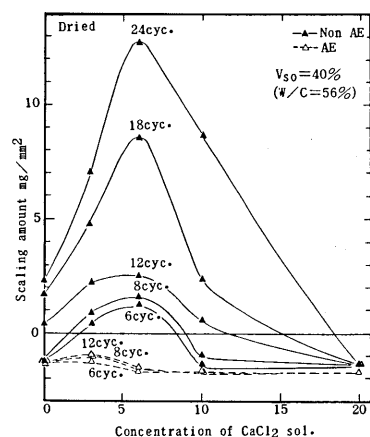


Fig.12 Concentration~scaling amount relationship
(CaCl_2 sol.).

6. CONCLUSION

The effect of salt solutions and concentrations on the scaling deterioration of hardened cement pastes subjected to freezing and thawing was discussed in connection with the microstructural features. As a result, it was found that the scaling deterioration was remarkably different due to the kind of solution and their concentrations. The effect of drying was also studied. It was pointed out that the reduction in scaling deterioration for the dried pastes was caused by the microstructural changes due to newly formed compound. The conclusion of this paper is summarized as follows:

- (1) The degree of deterioration is depending on the kind of solution. The deterioration tends to become greater in NaCl or CaCl_2 solution than in others even for AE pastes. On the contrary, the effect of air entraining is remarkable for the pastes subjected to sea water.
- (2) The non AE pastes in NaCl , CaCl_2 solution or sea water are extremely deteriorated. The Ca(OH)_2 dissolves or collapses. The CSH(I) disintegrates at the surface portion, and the CSH(III) collapses or fails to be granular particles.
- (3) The dense layer is formed at the surface portion of 1 mm thickness and the portion adjacent to the dense layer becomes extremely porous in the case of

AE specimens immersed in sea water or CaCl_2 solution and of non AE specimens immersed in MgCl_2 solution which deterioration decreases with freeze-thaw cycle.

(4) The maximum damage of scaling occurs at the concentration of 3% solution of CaCl_2 or MgCl_2 for the AE pastes and of 6% solution of CaCl_2 for non AE pastes. This result is identical with that for the dried specimens.

(5) The dried AE pastes are hardly deteriorated until 24 cycles of freezing and thawing regardless of the kind of salt solution. This is mainly due to the microstructural changes in the pastes such as the dense surface formed by the new compound, the reduction of large cavities at the porous portion filled up with the compound, and the growth in thickness of air void shells.

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