

C-1-5 Effect of silane-based surface impregnation on complex deterioration of reinforced concrete subjected to penetration of salt water

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***ABSTRACT:** Concrete structures constructed in cold regions have been heavily deteriorated by the supply of de-icing salts. The deterioration mechanism is often considered as the combination of the chloride-induced steel corrosion and the cyclic freezing and thawing of concrete. Moreover, the concrete could be affected by the alkali silica reaction (ASR) if the reactive aggregates are contained in the concrete. In order to clarify the complex deterioration mechanism of reinforced concrete structures subjected to the salt water penetration and to confirm the repair or protection effect of the silane-based surface impregnation applied for such structures in the severe environment, the experimental investigations were carried out. Reinforced concrete (RC) specimens, a part of them contained ASR reactive aggregates, were subjected to the salt water penetration under the cyclic freezing and thawing condition, followed by the high humidity and high temperature storage for accelerating ASR expansion of concrete. As a result, it was found that the scaling of concrete was accelerated by the freezing and thawing with the penetration of the salt water, which promoted the steel corrosion in concrete. The highest scaling rate was measured in the case of concrete containing premix chlorides and reactive aggregates subjected to the 3% salt water penetration. The treatment with the silane-based surface impregnation delayed the initiation of the concrete scaling although the scaling rate after the initiation was higher than the case of the non-impregnated specimens.*

***KEY-WORDS:** Concrete, silane-based surface impregnation, chloride penetration, reactive aggregate, cyclic freezing and thawing.*

INTRODUCTION

Frost damage and ASR are serious deterioration mechanisms of concrete structures respectively. Moreover, in the cases of scattering NaCl as a de-icing salt at a cold climate area, complex deterioration of these mechanisms can be observed [1, 2]. Supply of NaCl could promote not only scaling of the concrete surface but also ASR expansion due to the penetration of Na^+ . Complex deterioration mechanism and the following steel corrosion tendency in concrete due to the penetration of Cl^- supplied by the de-icing salt has not been enough clarified yet although some past papers reported the possibility of the rapid progress of the deterioration.

As a remedial measure against the complex deterioration, surface protection methods are applicable. Among the surface protection methods, the silane-based surface impregnation method, which has been applied in many cases, would be an effective option. However, the repair effect against the complex deterioration cases has not been clarified yet and the conditions for application to achieve the repair effect should be investigated. So, in this study, the accelerated deterioration test due to the cyclic freezing and thawing with the supply of salt water followed by the storage in the condition for promoting ASR was carried out using reinforced concrete specimens containing the reactive aggregate. The objectives of this study are that to confirm the deterioration mechanism of concrete and the steel corrosion due to the complex deterioration and to clarify the effect of silane-based impregnation to suppress the deterioration progress.

EXPERIMENTAL PROGRAM

Mixture proportions of concrete and materials

Mixture proportions and basic properties of concrete adopted in this study were shown in Table 1. Water to cement ratio (W/C) of concrete was 55% for all mixture proportions. Concrete named N contained only non-reactive aggregate and concrete named R contained reactive aggregate and non-reactive aggregate in the ratio of 7:3. Concrete named RCI is supposed to be damaged by the complex deterioration. This concrete contained reactive aggregate and NaCl as the source of alkali. In order to adjust the total alkali contents as $R_2O = 10.0 \text{ kg/m}^3$ for accelerating the deterioration, a corresponding amount of NaCl was dissolved in the mixing water.

Ordinary Portland cement (density: 3.16 g/cm^3 , specific surface area: $3280 \text{ cm}^2/\text{g}$, R_2O : 0.56%) was used. As the fine aggregate, non-reactive fine aggregates (S1, density: 2.56 g/cm^3) and reactive aggregate (S2, density: 2.56 g/cm^3) were used. As the coarse aggregate, non-reactive aggregate (G1, density: 2.55 g/cm^3 , G_{max} : 15 mm) and reactive aggregate (G2, density: 2.68 g/cm^3 , G_{max} : 15 mm) were used.

Table 1. Mixture proportions and properties of concrete.

Name	W/C (%)	s/a (%)	Unit mass (kg/m^3)									Slump (cm)	Air (%)	F'c 28D (N/mm^2)
			C	W	S1	S2	G1	G2	NaCl	WRA*	AEA*			
N	55	48	324	178	848	—	887	—	—	1.5	0.02	9.0	4.0	45.1
R			324	178	249	581	276	644	—	1.5	0.02	7.0	3.5	47.9
RCI			324	178	243	565	276	644	15.4	1.0	0.01	10.5	4.2	45.9

*WRA: water reducing agent, AEA: air entraining agent

Preparation of specimens

Specimens prepared in this study were $100 \times 100 \times 300 \text{ mm}$ RC prisms with a steel bar $\phi 13$ SR235 (JIS number) at the 25 mm depth from the exposed surface as shown in Fig. 1. All specimens were cured in the wet 20°C condition. Brass chips were pasted to concrete surfaces for the measurement of concrete expansion after the curing for 28 days and five surfaces except the exposed surface (the bottom surface of the mold) were coated by epoxy resin. The measurement of the concrete expansion was conducted by means of a contact gauge against the standard length of 200 mm in the longitudinal direction of the specimens.

Moreover, $100 \times 100 \times 100 \text{ mm}$ cubic concrete specimens were prepared for measuring the impregnation depth and the scaling during the cyclic freezing and thawing. These specimens were subjected to the same condition of the curing and the coating of epoxy resin as the RC specimens.

Table 2. Impregnation depth of silene-based impregnation material.

Name of concrete	Surface water absorption rate (%)	Depth (mm)
N	7.6	4.7
R	7.7	3.5
RCI	8.0	3.0

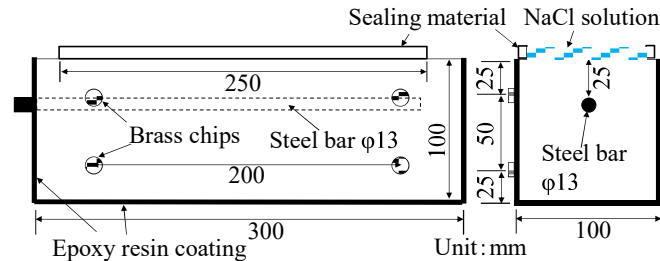


Fig.1. Outline of RC specimen.

After finishing epoxy resin coating and the brass chips pasting, the specimens were dried out for achieving the surface moisture content of 8% and the silene-based impregnation was applied to the half of the all specimens. The amount of application was 200 g/m^2 as the standard level. The measured impregnation depth to each kind of concrete and the surface moisture content are shown in Table 2. The measurement of the impregnation depth was conducted by following JSCE-K 571-2013. The prepared number of the specimens applied the silene-based

impregnation and non-applied case was two respectively. All specimens were cured in the wet condition at 20 °C for one week followed by the freezing and thawing with the supply of salt water.

Acceleration of deterioration and various tests

In order to save and supply NaCl solution, the 8 mm height base was installed on the exposed surface using sealing material as shown in Fig. 1. As the concentration of NaCl solution, 3 % was selected for promoting the scaling referring to the results of the past papers [3, 4].

The cyclic freezing and thawing was carried out controlling temperature in a thermostatic chamber in conformity to ASTM C 672. Freezing process was -18 °C for 16 hours and thawing process was 23 °C for 8 hours. One cycle of freezing and thawing was totally 24 hours and after 30 cycles, the specimens were moved to the accelerated ASR condition. During the accelerated ASR, the specimens were wrapped by the wet cloth in a sealed vinyl bag at 40 °C condition for 30 days.

The scaling was measured after the every seven cycles of the freezing and thawing by using the cubic specimens. At the period of the finishing the cyclic freezing and thawing or the accelerated ASR, the expansion rate of concrete and the half-cell potential, polarization resistance and concrete resistance were measured respectively. All specimens were moved to a 20 °C room the day before the measurement of the concrete expansion rate and the electrochemical indexes for evaluating the steel corrosion. The concrete expansion was measured by using a contact gage.

As a reference electrode for these electrochemical monitoring, saturated silver chloride (Ag/AgCl) was used. As a counter electrode, titanium mesh was used. These electrodes were attached to the center part of the exposed surface through a wet absorbent cotton to measure the average values over the length of the steel bar. The Polarization resistance was measured by the rectangular wave electric current polarization method, as the difference of impedances at 800 Hz and 0.1 Hz of electric current frequency. Resistivity was obtained as the impedance at 800 Hz of electric current frequency.

Scaling due to freezing and thawing

Variation curves of amount of the cumulative scaling during 30 cycles of freezing and thawing are shown in Fig.2. The names of the specimens indicate the concrete name shown in Table 1 followed by “N” or “S”. “N” and “S” means non-application and application of silane-based impregnation respectively.

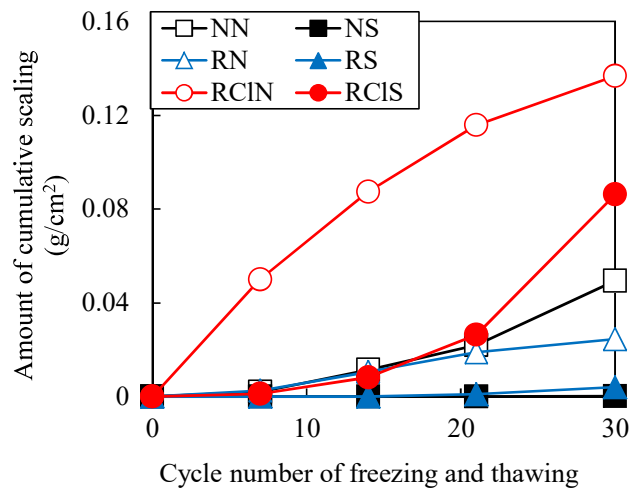
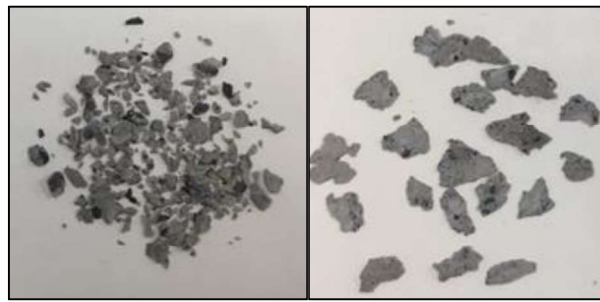


Fig.2. Variation curves of amount of cumulative scaling.

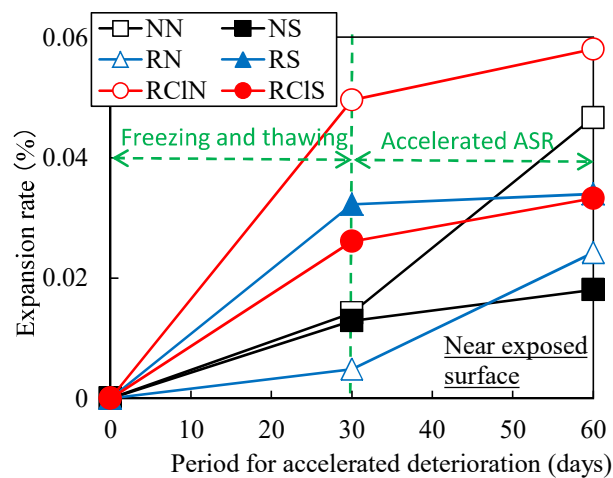


(a) RCIN (b) RCIS
Fig. 3. Scaling of RC specimens after 30 cycles of freezing and thawing.



(a)RCIN (b)RCIS
Fig.4. Pieces of scaling sampled from RC specimens.

According to Fig. 2, RCIN shows the largest amount of the cumulative scaling at the period of 30 cycles as the result of the earliest initiation of the scaling from the beginning of the acceleration test. RCIS shows the rapid increase of the scaling after the elapse of 20 cycles of freezing and thawing. It can be said that RCI concrete contained much amount of the premixed NaCl, which could promote the progress of the scaling before the Cl^- ions penetrate from the exposed surface. The form of scaling observed in RCIN and RCIS was quite different from each other as shown in Fig. 3 although the Cl^- content in concrete would be similar regardless of whether the silane-based impregnation was applied or not. The situation of RCIN was localized deeper loss of area as shown Fig. 3 (a) and the situation of RCIS was surface delamination of wider area. Moreover, the form of scaling pieces collected from the RC specimens was also different from each other. Pieces from RCIN were like crashed fine ones whereas pieces from RCIS were like flakes.



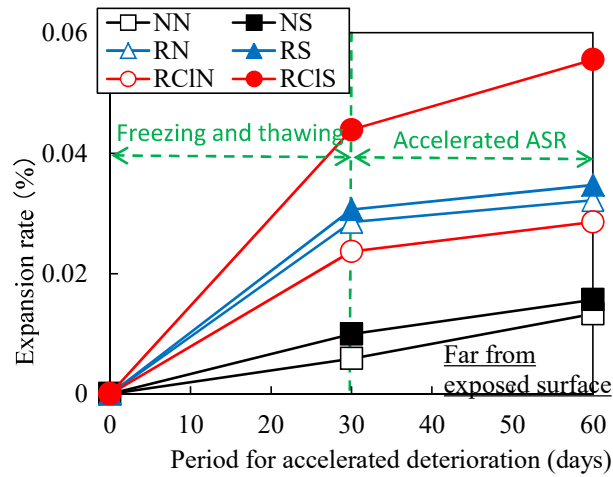


Fig.5. Variation curves of concrete expansion with time.

Endo et al. investigated the scaling of concrete applied silane-based impregnation under the freezing and thawing environment [5, 6], which reported that the application of the silane-based impregnation could suppress the increase of scaling at the early stage of the deterioration although the rapid increase of the scaling was observed after the suppressed deterioration period as shown in this study. The reason of this was considered that the water pressure from the inside of the impregnation layer of concrete surface grew due to the low water permeability of the impregnation layer. The similar situation would promote the delamination of the impregnation layer of the specimens in this study in addition to the effect of the plenty of premixed Cl^- in concrete.

In Fig. 2, NS and RS show almost no scaling, which would be caused by the effect of the silane-based impregnation for the prevention of the penetration of NaCl solution from the exposed surface.

Concrete expansion

Variation curves of the concrete expansion rate with time during the period of the accelerated deterioration are shown in Fig. 5. The horizontal axis of this Fig. expresses the period after the end of the curing. The left Fig. shows the concrete expansion rate measured near the exposed surface as shown in Fig. 1 and the right Fig. shows the data measured at the point far from the exposed surface. From these Figs, RCIN and NN, which generated larger amount of scaling, show relatively large expansion near exposed surface, while in the case of the expansion measured at the point far from the exposed surface, the effect of the kind of the aggregate or the amount of alkali seem to be significant. The main reason of the concrete expansion during the period of freezing and thawing would be the damage of concrete micro structure and water absorption due to the cyclic freezing and thawing rather than the ASR expansion since the maximum temperature during the period of freezing and thawing was 23 °C.

In the cases of the specimens using concrete “R” without the premixed Cl^- , ASR will progress with the penetration of NaCl from the outside of concrete. However, the expansion caused by ASR would be minor because the relatively small amount of the scaling could not accelerate the penetration of NaCl solution into concrete. On the other hand, in the cases of the specimens using concrete “RCI”, enough amount of alkali for the progress of ASR was supplied as the premixed NaCl. RCIN shows larger concrete expansion near the exposed surface due to the occurrence of the scaling from the early stage of the freezing and thawing while the ASR expansion pressure at the point far from the exposed surface would be released by the scaling. RCIS shows the concrete expansion tendency contrary to that of RCIN, which may be caused by the suppression of the scaling at the early stage of the deterioration due to the application of silane-based impregnation.

Electrochemical evaluation of steel corrosion in concrete

Variation curves of half-cell potential and polarization resistance of steel in RC specimens during the accelerated deterioration test are shown in Fig. 6 and Fig. 7 respectively. Moreover, the variation curves of electric resistivity of cover concrete in RC specimens are shown in Fig. 8.

According to Fig. 6, RCI specimens generally show the base values of half-cell potential which indicate the corrosion state with the dosage of much amount of NaCl into concrete. These specimens initially contained Cl^- of 9.1 kg/m³ that is much higher than the threshold Cl^- content to initiate steel corrosion. RCIS was applied the silane-based impregnation that has the effect of the promoting the water evaporation but such effect cannot be expected

in this study because of the wet environment of the accelerated deterioration conditions.

The half-cell potential of specimen NN is decreasing with the elapsed time. This specimen showed relatively large amount of scaling as shown in Fig. 2, which would promote the penetration of Cl^- and the earlier initiation of steel corrosion compared with the other specimens without the premixed Cl^- . The specimens using “R” concrete show the nobler half-cell potential values which indicate non-corrosion state referring the ASTM C876-91 standard regardless of whether the silane-based impregnation was applied or not.

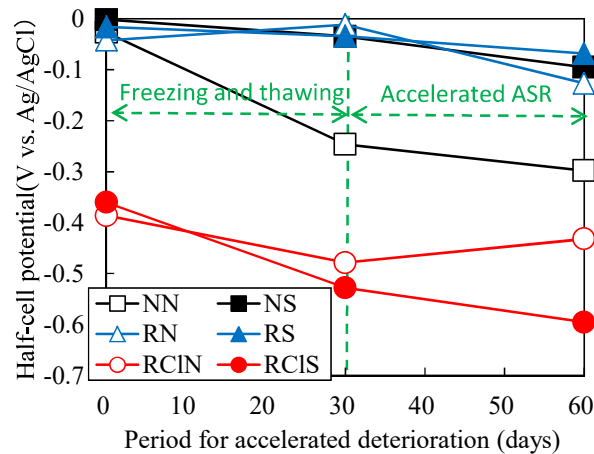


Fig.6. Variation curves of half-cell potential of steel bar in concrete with time.

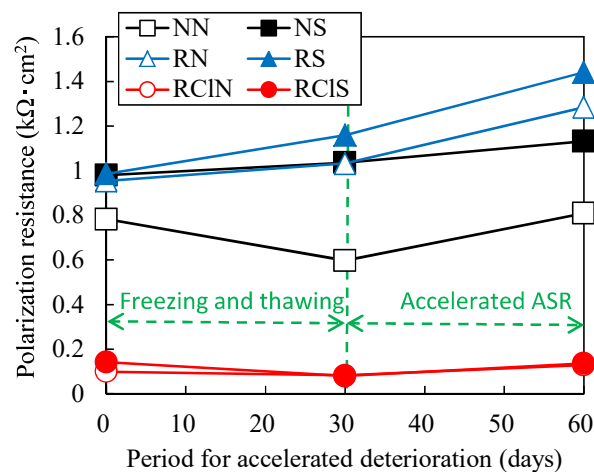


Fig.7. Variation curves of polarization resistance of steel bar in concrete with time.

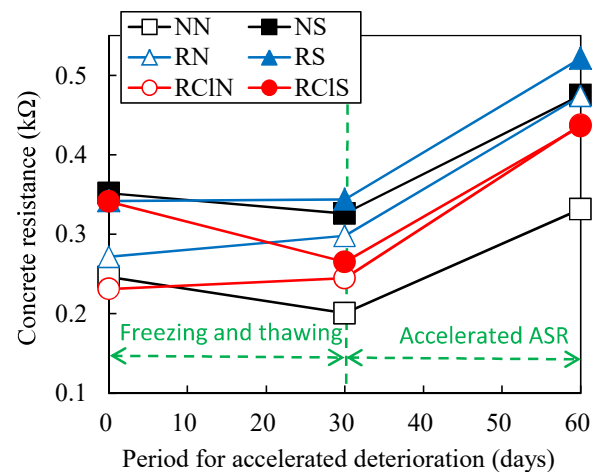


Fig.8. Variation curves of concrete resistance with time.

From Fig. 7, it can be said that the tendency of the measured values of polarization resistance is in accordance with the tendency of the results of half-cell potential, namely, the base half-cell potential cases correspond to the small polarization resistance. Such a small polarization resistance means a high rate of steel corrosion. The specimens using R concrete show the gradual increase of polarization resistance with the elapsed time. In the past research [7], authors suggested that the mild progress of ASR without concrete expansion due to the penetration of NaCl could improve the resistance performance against the ingress of the deterioration factors due to the void filling by means of ASR gel. In this study, the steel corrosion rate would be suppressed by the densification of microstructure of concrete due to the filling effect of ASR gel.

According to Fig. 8, at the beginning time of the accelerated deterioration test, the concrete resistivity values become large with the application of the silane-based impregnation to the specimens. These results explain that the impregnation improved the properties of concrete surface. However, RCIS shows the significant decrease in the concrete resistivity to the similar level of the non-impregnated case RCIN due to the relatively large amount of the scaling during the 30 cycles of freezing and thawing. These results indicate that the surface protection effect could be lost relatively early in the cases that the concrete contains much amount of Cl^- which will promote the scaling seriously.

Moreover, all specimens show the increase in the concrete resistivity with the transfer of specimens to the accelerated ASR environment. This means that the hydration of cement would be promoted in the high temperature wet condition which results in the densification of the micro structure in concrete. However, the concrete resistivity would decrease due to the occurrence of the concrete cracks caused by the ASR expansion of concrete in the future.

The longer term investigation will be done to clarify the complex deterioration mechanism and the protection effect of the silane-based impregnation material.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Concrete named RCl containing reactive aggregate and premixed NaCl to adjust the total alkali content R_2O as 10.0 kg/m^3 showed larger amount of scaling during the cyclic freezing and thawing than the concrete without premixed NaCl.
2. The application of the silane-based impregnation to RCl concrete was effective to suppress the scaling at the early stage deterioration although the amount of scaling rapidly increased when the 20 cycles of freezing and thawing passed. The application of the silane-based impregnation changed the scaling situation of concrete surface. If the concrete didn't contain the alkali, the silane-based impregnation was effective to suppress the scaling.
3. As a result of 30 cycles freezing and thawing followed by the accelerated ASR for 30days, the concrete expansion near the exposed surface would be mainly affected by the scaling and that at the far point from the exposed surface would be mainly affected by the ASR.
4. RC specimens from which large amount of scaling was measured showed the base values of half-cell potential and small values of polarization resistance. Moreover, the polarization resistance of RC specimens using R concrete increased with the time of the accelerated deterioration.
5. The concrete resistivity of RC specimens increased with the application of the silane-based impregnation. However, RCIS shows the significant decrease in the concrete resistivity to the similar level of non-impregnated case RCIN due to the relatively large amount of the scaling during the 30cycles of freezing and thawing.

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