

D-2-5 Influence of water cement ratio of concrete on repair effect due to surface protection after electrochemical treatment

Bruno Ribeiro

*Graduate School of Advanced Technology and Science, Tokushima University, Tokushima, Japan.
ribeiro@iji-lab.sakura.ne.jp*

Kazuhide Nakayama

*Graduate School of Advanced Technology and Science, Tokushima University, Tokushima, Japan.
nakayama@iji-lab.sakura.ne.jp*

Takao Ueda

*Department of Civil and Environmental Engineering, Tokushima University, Tokushima, Japan.
ueda@ce.tokushima-u.ac.jp*

Akira Nanasawa

*Cement & Special Cement Additives Research Dept., Denka Co., Niigata, Japan.
akira-nanasawa@denka.co.jp*

ABSTRACT: When a surface protection method for concrete is applied after completing an electrochemical repair method, the surface protection material may be deteriorated prematurely due to the supply of high alkaline electrolyte from the inside of the concrete after the electrochemical treatment. The difference in the water cement ratio of concrete may affect the degree of the deterioration of surface protection materials after electrochemical treatment. Therefore, in this study, various kinds of surface protection were applied to reinforced concrete specimens with different water cement ratios after the electrochemical treatment. Using such specimens, the durability of surface protection materials and the repair effect for the steel corrosion in concrete were experimentally investigated. As a result, it was found that concrete with a lower water cement ratio showed higher alkalinity after the electrochemical treatment, which was a severe environment for the surface protection material, and that the chloride removal efficiency was decreased compared with the case of the higher water cement ratio. The reason is that the concrete with the lower water cement ratio contains a greater amount of cement with Na^+ or K^+ which contributes to increase the alkalinity and suppressed the electrochemical migration of Cl^- due to the higher chloride binding capacity of concrete.

KEY-WORDS: Chloride removal effect, protection effect against corrosion, surface protection method, water cement ratio

INTRODUCTION

The desalination and the realkalization are electrochemical corrosion prevention methods, which can be applied as a repair method for chloride-induced steel corrosion and carbonation of concrete in reinforced concrete structures. Unlike traditional repair methods, these methods do not require removing the carbonated or chloride-contaminated concrete. These methods are expected to be applied widely as a repair method for reinforced concrete structures damaged by steel corrosion in the future [1]. However, since these are relatively new repair methods, the long-term data after application is insufficient, therefore, it is necessary to clarify sustainability of the repair effect.

After finishing the electrochemical treatment, the external electrode is removed and in order to prevent the ingress of deterioration factors from the concrete surface, a surface protection method should be applied. But in some cases, it has been pointed out that sufficient performance of surface protection materials may not be obtained. The reason of this is considered that the concrete alkalinity level become higher than the case of non-treated concrete due to the electrochemical penetration of highly alkaline electrolyte and generation of OH^- by cathodic reaction in the vicinity of steel bar [2].

In past papers, various surface protection methods were applied to reinforced concrete specimens after desalination or realkalization were applied and the durability of the surface protection material and the influence of the surface protection on the corrosion prevention effect of steel bar in concrete after the electrochemical treatment were investigated [3, 4]. However, in these studies, the mix proportion of concrete was fixed.

The different water cement ratio (W/C) of concrete may result in the different ion distribution in concrete and may affect the repair effect after the electrochemical treatment. In this study, RC specimens were prepared using concrete with different W/C and various surface protection materials were applied to these specimens after applying the desalination. To evaluate the protection effect against steel corrosion in concrete and the durability of the surface protective materials, electrochemical indexes were measured periodically during the storage at 40 °C in the moist condition.

Table 1. Mix proportions of concrete, fresh properties and compressive strength measured at the age of 28 days

W/C (%)	s/a (%)	G _{max} (mm)	Unit mass (kg/m ³)							Slump (cm)	Air (%)	Compressive strength (N/mm ²)
			C	W	S	G	WRA*	AEA*	NaCl			
45	48	15	389	175	791	871	1.17	0.0125	13.2	11.5	2.0	46.9
60			300	180	820	903	0.5	0.0095		6.5	3.0	37.7

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

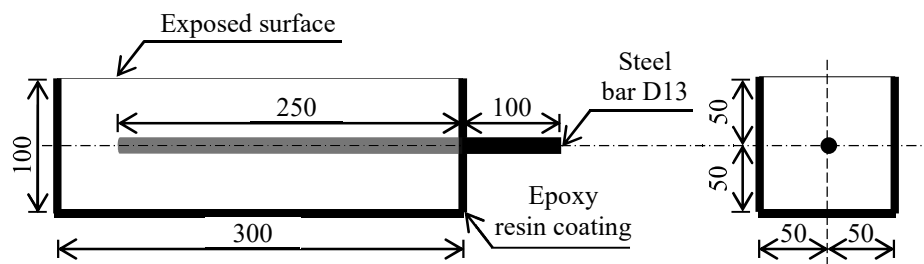


Fig.1. Outline of a RC specimen (unit: mm)

EXPERIMENTAL PROGRAM

Materials and preparation of RC specimen

Table 1 presents the mix proportions of concrete used in this experiment, the results of fresh concrete test and the compressive strength at the age of 28 days. Twenty-four hours after casting, the specimens were demoulded, and they were sealed and placed in a temperature-controlled room (20 °C) for 28 days for curing, prior to the further testing. As W/C of concrete, 45% and 60% were selected supposing PC and RC concrete, respectively. Ordinary Portland cement was used and NaCl was dissolved in mixing water for premixing Cl⁻ of 8.0 kg/m³, assuming a severe corrosion environment to the steel in concrete.

Most of the experimental results were obtained using RC specimens of 100×100×300 mm with a steel bar D13 mm at the central part of the square cross-section in each specimen. After the curing, excepting an exposed surface, the other 5 surfaces were coated with epoxy resin to insulate from the electrical current and deterioration factors (refer to Fig. 1).

Electrochemical treatment and test methods

Before and after the desalination, half-cell potential, polarization resistance and concrete resistance were measured. These measurements were carried out as the average value of the total length of the steel bar in the specimen using a saturated silver chloride electrode (Ag/AgCl) as a reference electrode and titanium mesh for the counter electrode.

For applying desalination, a direct current was supplied between the titanium mesh (anode) and a steel bar (cathode) in the concrete. The current density was 1.0 A/m² and the treatment period was 8 weeks using 0.1 N Li₃BO₃ solution as the electrolyte. During the treatment period, Cl⁻ concentration in electrolyte and potential difference between electrodes of each specimen were measured. In the case of 60% as W/C, non-desalination specimens were prepared and stored in moist 20 °C temperature-controlled room during treated. After applying

desalination, distribution of ions (Cl^- , Na^+ , K^+) concentration and pH values in concrete were measured using specimens for chemical analysis. The cutting method of concrete specimens for chemical analysis is shown in Fig. 2. 8 pieces of 10 mm thick concrete plates were cut out and each plate finely grinded and passed through a 0.15 mm sieve. After air drying for 24 hours, it was mixed and used as analytical samples.

Using these samples, the total Cl^- concentration and water soluble Cl^- concentration were measured by a potentiometric titration method in accordance with JIS A 1154. For measuring, 12.5 g of analytical sample and 25 ml of pure water were stirred for 3 minutes in a 50 mL glass beaker and after settling 5 minutes, the pH value was measured with a pH electrode. The other concentrations of cations in the sample extracted by nitric acid were measured using an atomic absorption spectrophotometer.

The other specimens were stored in a room at a temperature of 20 °C and a humidity of 60% R.H. for controlling the moisture content of the exposed concrete surface as 10% measured using high-frequency moisture meter. After that, 3 types of surface protection material (epoxy resin, polymer cement mortar and silane-based impregnation) for concrete were applied according to the respective application specifications (note that the other five surfaces are coated with epoxy resin after the curing period) and specimens without surface protection (unprotected) were also prepared, as shown the Table 2. In all cases, 2 specimens were used to desalination. Moreover, in the case of W/C of 60%, 2 non-desalination specimens were prepared. The symbols shown in the table indicate the W/C following by the kind of surface protection and the electrochemical treatment. U, S, E and P mean unprotected, silane-based impregnated, and epoxy resin and polymer cement mortar, respectively. D and N mean desalination and non-desalination, respectively.

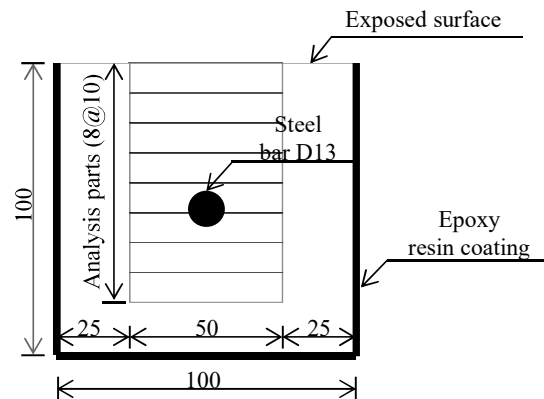


Fig.2. Cutting method of concrete specimens for chemical analysis (unit: mm)

Table 2. List of concrete specimens

W/C (%)	Surface protection material	Symbol	RC specimens	
			Desalination specimens (D)	Non-desalination specimens (N)
45	—(Unprotected)	45%U	2	—
	Epoxy resin	45%E	2	—
	Polymer cement mortar	45%P	2	—
	Silane-based impregnant	45%S	2	—
60	—(Unprotected)	60%U	2	2
	Epoxy resin	60%E	2	2
	Polymer cement mortar	60%P	2	2
	Silane-based impregnant	60%S	2	2

After the application of surface materials, the specimens were stored at 40 °C in moist condition to accelerate the deterioration. After storage for about 150 days, bond strength of epoxy resin coating and polymer cement mortar were measured by the pull-out test following JSCE-K-531-2013. In the case of silane-based impregnated material, the concrete resistance of the surface protection side and contact angle of a water droplet were measured during the storage period. The contact angle of a water droplet of about 2 mm in diameter was measured using images taken by a digital camera.

RESULTS AND DISCUSSIONS

Measurements during the electrochemical treatment and Cl^- concentration distribution in concrete after desalination

The Cl^- concentration in electrolyte and potential difference between electrodes measured during the desalination is shown in Fig. 3. Cl^- concentration in the electrolyte represents the amount of extracted Cl^- from the concrete. When the W/C of concrete is 45%, the potential difference between electrodes becomes larger and the Cl^- concentration in the electrolytic solution becomes smaller than the case of 60%. In the case of lower W/C, the pore structure in concrete becomes dense and the electric resistance value increase, that is why the voltage becomes large to supply a constant current.

The distributions of total Cl^- in the specimens after desalination is shown in Fig. 4. The horizontal axis is the distance from the exposed surface (0 mm) of specimen. Also, in the Fig., the location of the steel bar as the cathode is shown. According to Fig. 4, regardless of W/C of concrete, Cl^- content in concrete can be reduced from the amount of premixed Cl^- as 8.0 kg/m^3 . Especially, significant chloride removal effect is obtained around the vicinity of the steel bar as the cathode. However as previously mentioned, desalination efficiency in the case of 45% W/C is lower than that of 60%. Such tendency was also confirmed in the past paper [5]. The reason were considered that in the case of lower W/C concrete, electrochemically removable Cl^- in pore solution would be less than the case of higher W/C, because of the higher Cl^- binding capacity as the Friedel's salt in the case of the lower W/C case. However, as shown in Fig. 4, the ratio data of water soluble chloride to total Cl^- in concrete after desalination are not much affected by W/C. Even in the case of lower W/C, some degree of free Cl^- ions would remain in the pore solution after desalination.

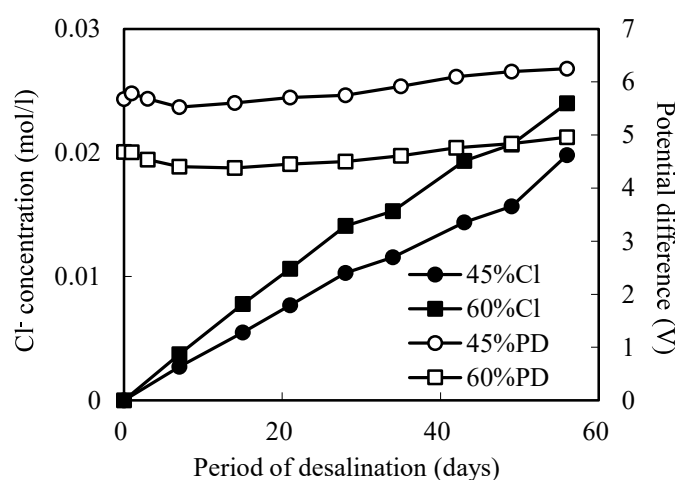


Fig.3. Variation curves of Cl^- concentration in electrolyte and potential difference between electrodes during the desalination

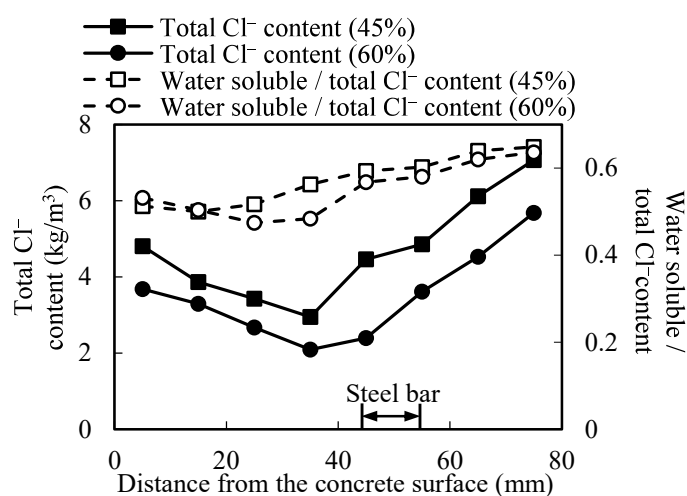


Fig. 4. Distributions of Cl^- content and water soluble / total Cl^- content in concrete after desalination

Distribution of the R₂O and pH value in concrete after desalination

The distribution of R₂O and pH values in the concrete after the desalination is shown in Fig. 5. The amount of R₂O was determined by the equation $R_2O = Na_2O + 0.65K_2O$ (kg/m³) using measured values of Na⁺ and K⁺ content in the concrete. The amount of R₂O and pH value of the non-desalination specimens were 9.67 kg/m³ and 12.45 in the case of 45% W/C, and 9.20 kg/m³ and 12.43 in the case of 60% W/C, respectively. Since the 13.2 kg/m³ of NaCl was added initially, a large amount of Na⁺ was contained in concrete, which migrated due to the electrophoresis and it accumulated at the steel bar as the cathode.

There is a correlation between the distribution of R₂O and the distribution of pH values in concrete. Due to the cathodic reaction during desalination, a high pH value distribution and a large amount of R₂O can be observed in the vicinity of the steel bar. Regarding the influence of W/C, the peak of R₂O amount and pH value in the case of 45% W/C are slightly higher and closer to the exposed surface than the case of 60% as W/C. In the case of 45% as W/C, the amount unit cement is about 90 kg/m³ more than the case of 60% W/C, so the difference in the peak value would be caused by the difference in the amount of R₂O derived from cement. In addition, the denser pore structure and the larger electric resistance in the case of 45% as W/C could suppress the electrophoresis of Na⁺ and K⁺, by which the peak position would be formed at the closer point to the concrete. It has been pointed out that the main factor of deterioration of the surface protection materials applied after the electrochemical treatment would be a high alkali solution in concrete [4]. In the case of lower W/C concrete, a higher alkaline environment could be formed at the closer point to concrete surface and accelerate deterioration of the surface protection materials.

Table 3. Basic properties of surface protection materials obtained by using non-desalination specimens

Types of surface protective material	Bond strength		Impregnation		Contact angle of	
	(N/mm ²)		depth (mm)		a water droplet (°)	
	W/C 45%	W/C 60%	W/C 45%	W/C 60%	W/C 45%	W/C 60%
Epoxy resin with wet wear resistance	3.4	3.7	—	—	—	—
Polymer cement mortar with acrylic resin (PCM)	1.2	1.3	—	—	—	—
Silane-Siloxane type impregnation	—	—	1.8	2.4	129	131

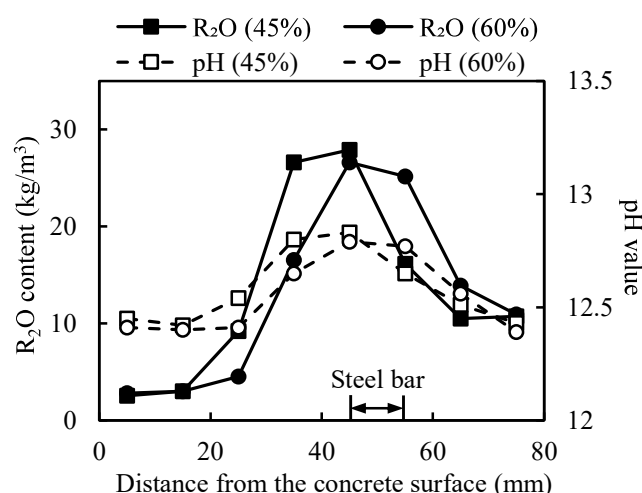


Fig.5. Distribution amount of R₂O and pH value in concrete after desalination

Evaluation of the performance of the surface protection material after desalination

Basic properties of surface protection materials obtained by using non-desalination specimens are shown in Table 3. All of these results were obtained using non-desalination specimens of 100×100×200 mm after curing of surface protection materials for 7 days. The variation curves of the results of the contact angle of a water droplet and the

concrete resistance of the surface protection, both obtained during the accelerated deterioration period, as shown in Fig. 6 and Fig. 7, respectively.

As shown in the Fig. 6, the contact angle of a water droplet of desalination specimens is smaller than that of non-desalination specimen, and in the case of desalination specimens, the contact angle of a water droplet of 45% as W/C is smaller than the case of 60% as W/C. This may be caused by the smaller impregnation depth and the high alkalinity of 45% case, as already mentioned.

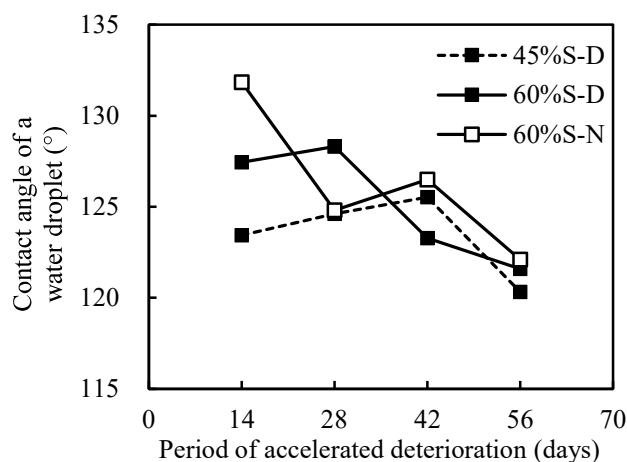


Fig.6. Contact angle of a water droplet

According to the Fig. 7, the concrete resistance of all specimens increase with time. Regardless of W/C of concrete, specimens applied silane-based impregnant show a larger concrete resistance than that of the unprotected specimens. Such increase of concrete resistance would be due to the protective effect of the silane-based impregnant. In the case of unprotected specimens, the concrete resistance of W/C 45% is larger than that 60%. Whereas, when the silane-based impregnant is applied, the concrete resistance of the specimen using concrete of 45% as W/C is smaller than the cases of 60% as W/C at the beginning of the period of accelerated deterioration. This may be caused by the smaller impregnation depth and the high alkalinity of the case of 45% as W/C.

The results of bond strength test of epoxy resin coating and polymer cement mortar is shown in Fig. 8. From Fig. 8, regardless of the type of surface materials, the bond strength of the specimens using concrete of 45% as W/C is smaller than the cases of 60% as W/C, and in the cases of 60% as W/C, the bond strength of desalination specimens is smaller than the cases of non-desalination specimens. The reason of the decrease of the bond strength may be the high alkalinity of concrete after the desalination as shown in Fig.5. However, the all data of the measured bond strength exceed 1.0 N/mm² which is generally required in Japan.

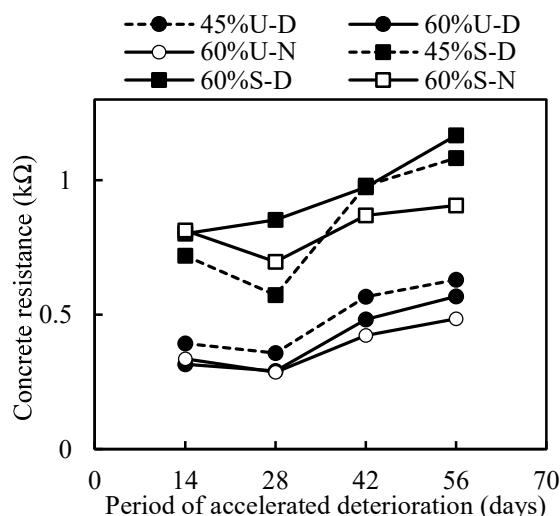


Fig.7. Concrete resistance of the surface protection side

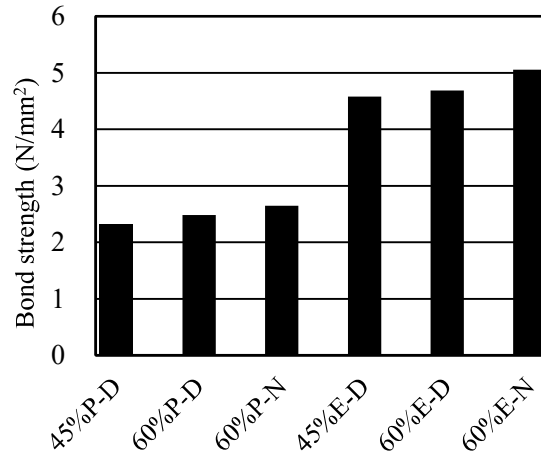


Fig.8. Bond strength of epoxy resin coating and polymer cement mortar

Protection effect against steel corrosion after desalination

(a) Immediately after desalination

The results of half-cell potential, polarization resistance and concrete resistance of RC specimens measured before and after the electrochemical treatment are shown in Table 4. Referring to the criteria of ASTM C 876, regardless of W/C, the half-cell potential before desalination indicates the corrosion of steel in concrete due to the premixing of Cl^- which was 8.0 kg/m^3 . However, after the desalination, the half-cell potential changes to a base value around -1 V due to the cathodic polarization of the steel during the desalination. In general, small polarization resistance values indicates high corrosion rate of steel. However in the previous study [4], the polarization resistance value decreased after the electrochemical treatment, but gradually increased with time, due to the re-passivation of the steel bar. In this study, the polarization resistance values of 45% are larger than the cases of 60%, which may be due to of a dense pore structure than the case of 60%. Concrete resistance values also decrease with applying desalination, especially when the W/C was 60%. It would be due to the coarser pore structure of the case of 60% which accelerated penetration of electrolyte than the case of 45% W/C.

Table 4. Electrochemical indexes before and after desalination

	W/C (%)	Half-cell potential (V vs Ag/AgCl)	Polarization resistance ($\text{k}\Omega$)	Concrete resistance ($\text{k}\Omega$)
Before desalination	45	-0.21	0.146	0.209
	60	-0.291	0.137	0.165
After desalination	45	-1.061	0.005	0.181
	60	-1.044	0.001	0.127

(b) After application of surface treatment

Variation curves of half-cell potential of non-desalination specimens and desalination specimens during the period of accelerated steel corrosion after applying surface protection are shown in Fig. 9 and Fig. 10, respectively. For avoiding the influence of surface protection material, these data are measured from the measurement window (30×30) made at the centre of at the opposite side of the exposed surface, after the application of the surface protection materials.

In Fig.9, the steel corrosion continues even after applying the surface protection materials in the non-desalination specimens. When epoxy resin coating was applied, the half-cell potential decreases due to the lower oxygen permeability and smaller supply of oxygen from the outside of concrete which can be consumed by the corrosion reaction of the steel.

In Fig.10, the half-cell potential values of the all specimens become around -1 V due to the cathodic polarization of the steel during the desalination. However, regardless of the type of surface materials, these values gradually increase with time due to the re-passivation of the steel bar. After 18 weeks, the half-cell potential of the desalination specimens coated with silane-based impregnated and unprotected specimens the half-cell potential apparently recover faster due to the large amount of oxygen supplied from the outside compared with other cases.

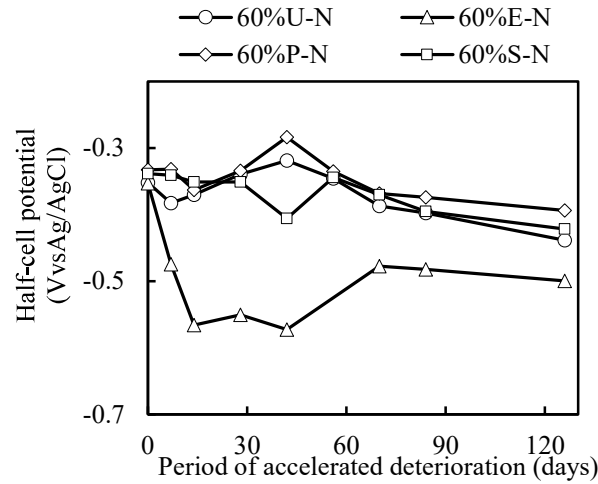


Fig. 9. Variation curves of half-cell potential during the accelerated deterioration period obtained by non-desalination specimens

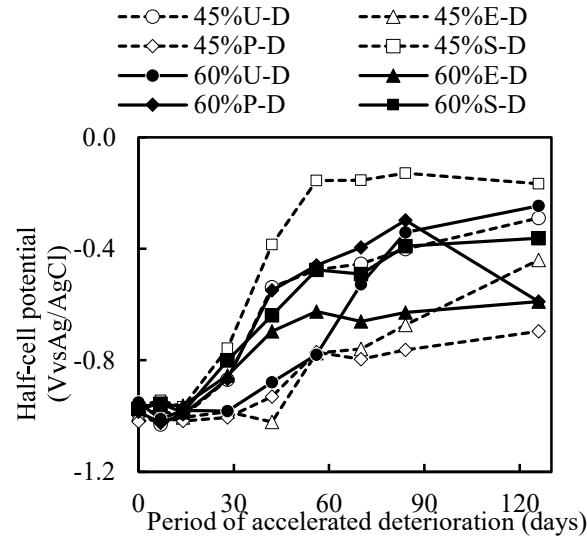


Fig.10. Variation curves of half-cell potential during the accelerated deterioration period obtained by desalination specimens

CONCLUSIONS

The results obtained in this study can be summarized as follows:

1. The desalination efficiency in the case of the concrete 45% as W/C was lower than the case of 60% as W/C. However, the ratio of water soluble Cl^- to total Cl^- in concrete after desalination was not much affected by the difference of W/C of concrete.
2. The application of desalination to concrete of 45% as W/C resulted in the formation of the higher peak of alkali accumulation which was detected at the closer part to the exposed surface, compared with case of 60% as W/C.
3. At the beginning of the period of the accelerated deterioration, the contact angle of a water droplet on the surface of the specimens applied silane-based impregnant after desalination was smaller than the case of non-desalination specimen. The reduction degree of the contact angle in the case of specimen using concrete of 45% as W/C was larger than the cases of 60% as W/C. However, the concrete resistance of the specimens applied silane-based impregnant after desalination remained higher values than the cases of non-desalination cases.

4. The bond strength values of epoxy resin and PCM coating decreased with the application of the desalination. The degree of the bond strength reduction in the cases of specimens using concrete of 45% as W/C was a little larger than the cases of 60% as W/C. However, regardless of the type of surface materials, all the data of measured bond strength exceeded 1.0 N/mm² which is generally required in Japan.
5. After 18 weeks of accelerated deterioration condition, the half-cell potential values of the steel bar of the silane-based impregnated specimens and unprotected specimens recovered to the nobler potential values from the base values measured immediately after desalination than the cases applied epoxy resin coating and polymer cement mortar after desalination.

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