CORROSION CHARACTERISTICS OF REINFORCEMENT IN CONCRETE STRUCTURES SUBJECT TO ASR AND SEAWATER ATTACK IN MARINE ENVIRONMENT

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Abstract

When concrete with reactive aggregates are exposed to marine environment, both the alkalis and chlorides in seawater may mutually act on it. However, the relation between the progress of ASR and the corrosion of reinforcement in marine environment is not fully understood. The authors carried out the long-term exposure test using the reinforced concrete specimens, which were exposed to two marine conditions, in seawater and splash zone. In the experiment, expansion, amounts of chlorides and alkalis in concrete, electrochemical characteristic and corrosion losses of reinforcement were measured.

The main results are as follows: (1) corrosion of reinforcement was sufficiently influenced by the chloride ion content and the presence of ASR gel around the reinforcement, (2) active formation of ASR gel at alkali content of 3 to 5kg/m^3 tended to suppress corrosion by the buffer effect of ASR gel, although reinforcements tended to corrode at chloride ion content of 1.2 to 3.5kg/m^3.

Keywords: corrosion of reinforcement, ASR, marine environment, combined deterioration, exposure test

1 INTRODUCTION

When concrete structures using reactive aggregates are exposed to seawater or deicing salts, the supplied alkalis are generally believed to accelerate alkali-silica reactions (ASR), while chlorides penetrating into the cracks caused by ASR promote corrosion of the reinforcements, resulting in complicated deterioration [1,2,3]. ASR in concrete may influence the reduction of the OH^- concentration and the increase of the Cl^-/OH^- in the pore solution, and the threshold chloride ion content for initiation of corrosion may decrease. But reports also indicate that when chloride ion content around reinforcements is relatively low—no more than 1kg/m^3—a passive film is regenerated by the buffering effects of the highly alkaline gel formed by ASR [1]. And also, there are some reports suggesting that the corrosion of reinforcement is suppressed by the occurrence of ASR [4,5]. The depression of corrosion in seawater and NaCl solution results from the formation of ASR gel layers surrounding the reinforcements [5].

Based on an investigation of structures afflicted by ASR, the authors have confirmed some cases in which reinforcements retain their soundness even when chloride ion content around the reinforcements exceeds 2kg/m^3 [6]. And, a saline-water spray test with reinforced concrete specimens showed that even when chloride ion content is as high as 3kg/m^3, reinforcements can be passivated [7]. However, this information remains inadequate to reach conclusions regarding the relation between the ASR expansion, chloride ion content of concrete and the corrosion development process of reinforcements.

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To throw light on such issues, the authors exposed concrete specimens in which reinforcements had been installed to two actual marine environments—seawater immersion and exposure in a splash zone in Japan—for over six years, monitoring and investigating the mutual effects of ASR-induced expansion development, chloride ion penetration, change in the electrochemical characteristics of the reinforcements and their corrosion status. Then, the reactive crushed andesite stone was used for concrete specimens.

2 OUTLINE OF EXPOSURE TEST

2.1 Types of specimens and concrete mixture

Table 1 and 2 give the specimen types, materials used and mix proportions of concrete. Specimen types were determined based on the reactivity of coarse aggregates, cement types (ordinary Portland cement (OPC) or Blast furnace cement type B (BB)) and equivalent alkali content of concrete adjusted by the amount of NaCl added. The concrete water/cement ratio was 50% for all specimens. These concrete mixes had slight difference of workability caused by NaCl content. However, as far as the result obtained in this experiment is concerned, the qualities (such as strength and bleeding) of concretes were almost equal. The reactive coarse aggregate used was crushed andesite. In actual concrete structures using this reactive aggregate, significant ASR-induced damage had been confirmed [8].

2.2 Specimen preparation and exposure conditions

As shown in Figure 1, each concrete specimen used in the experiment incorporated two round steel bars (10mm in diameter) located 20mm from the surface, with stainless steel terminals connected to the ends of the bars and six gauge plugs for expansion measurement on the exposed surface. Except for the exposed surface (bottom surface), each specimen was coated with vinyl chloride boards or elastic epoxy resin.

Two specimens were made for each specimen types (1) to (9) and cured from wet pack state at 20°C after removal of forms. Except for the exposed surface; coating was applied at the age of ten days. Exposures were initiated at the age of 14days (in late June) in seawater and splash zone under the superstructure of a jetty in Tokyo Bay. The exposure was continued for about 6.1years (2,230days). The specimens were set 1.0m below L.W.L. (low water level) in seawater and 0.1m above H.W.L. (high water level) in the splash zone, with the exposed surface oriented toward the bottom.

2.3 Measured parameters and measurement methods

The authors assessed the expansion of the concrete, half-cell potential and polarization resistance (by A.C. impedance method using a double-counter electrode sensor) before exposure (initial values) and at periodic intervals after the start of exposure. After 2.2years (800days) exposure and at the end of the exposure period, the authors measured chloride ion and water soluble alkali content in the concrete (according to JIS A 1154 and alkali extraction method with 40°C hot water) as well as corrosion status, corrosion area ratios and corrosion losses for the embedded reinforcements.

3 RESULTS AND DISCUSSION

3.1 Concrete expansion and cracking

Due to physical constraints, the expansion of the concrete in each specimen in the direction of the reinforcements was generally equal to or less than that along the perpendicular axis. Figure 2 gives measurements of the extent of expansion along the axis perpendicular to the reinforcements.

Specimens with equivalent alkali content of 10kg/m^3 showed rapid expansion from the start of exposure to seawater. The authors observed cracks along the axial direction of the reinforcements by 120 to 160days of exposure. The widths of the cracks were about 0.05 to 0.1mm, and were supposed to have occurred at an expansion rate of about 0.15% in the direction perpendicular to the reinforcements. Since such cracks were not observed in specimens of the same mix proportion of concrete exposed in the splash zone, they were presumed to be attributable to ASR expansion, not corrosion of the reinforcements. In the splash zone, specimens with equivalent alkali content of 10kg/m^3 started to expand after two years exposure. On the other hand, the authors observed no clear trends that alkali content affected expansion in specimens with equivalent alkali content not exceeding 5kg/m^3, either in seawater or in the splash zone. This appears to be attributable to the modest scale of the expansion in these specimens; additionally, to the measured values included the effects of expansion attributable to alkali from the volcanic glass and feldspar found in the crushed andesite, in spite of differences from specimen to specimen [8]. Additionally, the authors observed expansion on a lesser scale with BB than with OPC, suggesting that BB suppressed ASR expansion.

3.2 Half-cell potential and corrosion rate of reinforcements

Measurements of half-cell potential and corrosion rate of reinforcement are shown in Figures 3 and 4.

Specimens with higher alkali content (initial chloride ion content) exhibited low half-cell potential values much sooner after the start of expansion. And, the half-cell potential values of the specimens in seawater gradually became lower, reaching approximately -600 to -800mV vs.CSE, with small fluctuations. These changes were less pronounced in the specimens placed in the splash zone, reaching only around -200 to -600mV vs.CSE. In short, a lower half-cell potential value was observed with specimens immersed in seawater than those exposed in the splash zone.

Concerning the corrosion rate of reinforcement, as the half-cell potential shifts to low, the corrosion rate grows large. For specimens with alkali content of 10kg/m^3, the corrosion rate rose significantly from just after the start of exposure. It was considered that these trends in half-cell potential and corrosion rates of reinforcement were influenced by the lack of oxygen in seawater and the difference of chloride ion content in the concrete (quantity of initially mixed chloride ion content and/or external chloride ion content).

Although the half-cell potential of specimens (3) and (7) having equivalent alkali content of 5kg/m^3 (initial chloride ion content of 3.5 to 4.4kg/m^3) were equal to or lower than that of specimens (1), (2), (5) and (6) with equivalent alkali content of 1.2 to 2.5kg/m^3 (initial chloride ion content of 0 to 1.5kg/m^3), corrosion rates for the former tended to be equal to or less than for the latter. The half-cell potential of specimen (3) continued to be 0 to 200mV higher than that of specimen (9) using non-reactive aggregate with identical alkali content, although we observed fluctuation that appeared attributable to length of exposure. The corrosion rate of specimen (3) was a fraction or equal value of that of specimen (9). It is supposed that actively reacted ASR in specimens having equivalent alkali content of 5kg/m^3 generated highly alkaline ASR gel, which in turn passivated reinforcements [1,6,7]. The generation of ASR gel was confirmed both visually and using SEM-EDXA after 2.2years exposure and at the end of the exposure test.

3.3 Distribution of total chloride ion and water soluble alkali content in concrete

Figure 5 illustrates the distribution of total chloride ion and water-soluble alkali content in concrete at various depths, measured after 2.2years and 6.1years exposure.

In all specimens, significant amounts of chloride ions rapidly penetrated to approximately 10 to 16kg/m^3 near the surface of concrete after 2.2years exposure. Chloride ion content increased from initial values even around the reinforcements. The chloride ions clearly originated from the marine environment. We observed a heavier influx in seawater than in the splash zone. The chloride ion content in internal areas was lower with BB than with OPC, indicating BB's superior resistance to chloride penetration.

The distribution of water-soluble alkali content varied significantly with exposure conditions. In specimens immersed directly in seawater, water-soluble alkali content declined from the internal areas toward the surface, with a content of about 2kg/m^3 regardless of initial alkali content, while in specimens exposed in the splash zone, this content tended to be higher near the surface than in internal areas. The initially mixed alkali of specimens placed in seawater may have been leached out by seawater, or ASR gel formation may have consumed the initially mixed alkali and supplied alkali from the environment, subsequently leaching out in the continued time of exposure. In the splash zone, the alkali content appears to have increased somewhat from initial values at surface areas, since alkali is less likely to be leached out under this condition. In this case, then, the generation of ASR gel would consume the alkali and reduce the alkali content from initial values in the internal areas.

The authors attempted to estimate the chloride ion penetration process of specimen (1), which was initially free of chloride ions. Here we assumed that chloride ions penetrate according to Fick's diffusion law, and that surface chloride ion content in the early stages of exposure increases at a rate proportional to the square root of time, while the diffusion coefficient of the chloride ions remains constant. Figure 6 shows the results for estimating time-dependent changes in chloride ion content around the reinforcements, based on the chloride ion content distribution measured after 2.2years exposure shown in Figure 5 (a).

As shown in the figure, the chloride ion content 20mm from the surface reached 1.2kg/m^3 after approximately 120days of direct exposure to seawater and after approximately 700days of exposure in the splash zone. The chloride ion content 1.2 kg/m^3 is shown as the threshold value for initiation of corrosion in Standard Specification for Concrete Structures in Japan [9]. A past study has shown that the threshold alkali content required to initiate ASR ranges from 3 to 5kg/m^3 [10]. When the alkali content of concrete is presumed to be supplemented by NaCl from the environment, the chloride ion content required for the alkali content to reach the threshold value would be 1 to 3.5kg/m^3. According to Figure 6, the chloride ion content around the reinforcements had reached this value after 100 to 300days in seawater and after more than 600days in the splash zone.

For specimen (1) in seawater, it is assumed that the rising chloride ion content broke the passive film and activated corrosion, and the rising alkali content activated ASR gel formation at roughly the same time—around 100 to 300days after the start of exposure. Comparisons of this result against the result for specimen (1) in seawater (Figures 3 and 4) show that the half-cell potential rose, then declined once again and that the corrosion rate increased, then declined, then finally rose to a large value. The changes in the half-cell potential value and the corrosion rate did not coincide in terms of time, and it was not clear which exactly represented the condition of corrosion at each time. The reinforcements are assumed to have reached a complex state tending toward corrosion at this time, and to have gradually shifted to a stable corrosion condition as chloride ion content increased. Measurements of specimen (1) placed in the splash zone after the 600days exposure appeared to show a gradual shift (although with fluctuations) toward corrosion in the same manner as the specimen placed in seawater.

These test results suggest that the chloride ions around the reinforcements have an effect on the destruction of passive films and that the ASR gel around the reinforcements have an effect on the regeneration of passive films by the buffer effect of ASR gel [1]. Therefore, the possibility of regeneration of passive films is much influenced by the chloride ion content and the activity of ASR at the depth of reinforcement. The effect of ASR is influenced by the composition of the ASR gel and its generation rate, and these items appeared to be determined by the alkali content and characteristics of the reactive aggregates. As far as the conditions of reactive aggregates used and the alkali supply from the environment in this experiment is concerned, chloride ion content of about 1.2 to 3.5kg/m^3 appears to render reinforcements more susceptible to corrosion, but the corrosion of the reinforcements does not appear to have been significantly accelerated by active ASR gel formation at alkali content of about 3 to 5kg/m^3. Multiple cycles of passive film destruction and regeneration appear to have occurred during this period.

3.4 Corrosion area ratio and corrosion loss of reinforcement

Figure 7 gives the relationship between the initial alkali content, corrosion area ratio and corrosion loss measured after 2.2years exposure and at the end of the exposure period.

After 2.2 and 6.1years exposure, the authors confirmed cross-sectional defects along the entire length of the reinforcement of specimens (4) and (8) directly exposed to seawater, in which cracks occurred along the reinforcements in the relatively early stages, and along part of the length of the exposed sides of the reinforcement in specimens (1) and (2), which exhibited relatively high corrosion rates due to chloride penetration occurring approximately 400days after the start of exposure. In other specimens, the corrosion of the reinforcements was limited to the surface.

In specimens using reactive aggregates, we confirmed minimal corrosion area ratios and corrosion losses when the initial equivalent alkali content was 5kg/m^3. In the case of seawater immersion, corrosion appeared to have occurred in cases involving relatively modest ASR gel with equivalent alkali content of 2.5kg/m^3 or less, since corrosion began upon penetration of chloride ion. In the specimens with alkali content of up to 10kg/m^3, the expansion cracks caused by ASR facilitated chloride ion penetration, causing significant corrosion. In the specimens with alkali content of around 5kg/m^3, the buffer effect of the ASR gel appears to have suppressed corrosion. This is supported by the clear presence of corrosion in specimens incorporating non-reactive aggregate, even when the equivalent alkali content was 5kg/m^3. With certain differences in extent, this trend was also observed in the cases of specimens exposed to the splash zone.

There is a discussion that ASR increases the Cl^-/OH^- in the pore solution and promotes the progress of corrosion [1]. When paying the attention to the surface of reinforcements, the ASR gel may move through visible and/or micro cracks due to ASR, and may accumulate in the mortar-steel interfacial zone [5]. In such a case, it can be considered that regeneration of passive films and buffer effect of ASR gel suppresses the progress of corrosion.

4 CONCLUSIONS

The primary conclusions of this study are as follows.

(1) ASR expansion develops more readily in seawater than in the splash zone. In specimens in which cracks emerged along the axial direction in the early stages of exposure, the presence of corrosion accompanied by cross-sectional defects along the entire length of the reinforcements was confirmed.

(2) In the reinforced concrete using reactive aggregate constructed in marine environment, corrosion of reinforcement was sufficiently influenced by the chloride ion content and the presence of ASR gel around the reinforcement.

(3) The effects of chloride ion content around the reinforcements and ASR generation (generation of ASR gel) on reinforcement corrosion are generally as indicated in Table 2. Active formation of ASR gel around reinforcement due to alkali content of approximately 3 to 5kg/m^3 tended to suppress corrosion on a significant scale by the buffer effect of ASR gel, although reinforcements tended to exhibit corrosion state at chloride ion content in the range of approximately 1.2 to 3.5kg/m^3.

5 REFERENCES

[1] Japan Concrete Institute (2001): Report of Technical committee on Evaluation of Complex Deterioration on Concrete Structures and Maintenance Planning: pp.41-47. (in Japanese)

[2] Takashi Habuchi, Naoki Miyasaka, Hirokazu Tsuji and Kazuyuki Torii (2004): Evaluation of Combined Deterioration of Concrete Structures in Marine Environment due to Alkali-silica Reaction and Seawater Attack. Proceedings of the Fourth International Conference on Concrete under Severe Conditions, Vol.2: pp.2026-2033.

[3] Vassie P.R. (1993): A Secondary of ASR on Bridges-corrosion of Reinforcement Steel. Proceedings of the Second International Conference on Bridge Management, University of Surrey, Guilford: pp.18-21.

[4] Sanjuan, M.A. and Andrade, C. (1994): Effect of Alkali-silica Reaction on the Corrosion of Reinforcement. Supplementary Papers, Third CANET/ACI International Conference on Durability of Concrete, Nice: pp.613-622.

[5] Mitsunori Kawamura, Dhirendra Shinghal and Yasunobu Tsuji (1997): Effects of ASR on corrosion of reinforcement in concrete under saline environments. Proceedings of East Asia Alkali-aggregate Reaction Seminar, Tottori: pp.179-190.

[6] Takashi Habuchi and Kazuyuki Torii (2004): Deterioration of Concrete Caused by Combined Action of Alkali-silica Reaction and Sea Water Attack and its Evaluation Method. Journal of Materials, Concrete Structures and Pavements, Japan Society of Civil Engineers, No.774/V-65: pp.149-161. (in Japanese)

[7] Takashi Habuchi, Hirokazu Tsuji and Kazuyuki Torii (2004): Steel Corrosion Mechanisms caused by Combined Action of ASR and Chloride Penetration. Proceedings of the Japan Concrete Institute, Vol.26, No.1: pp.1017-1022. (in Japanese)

[8] Kazuyuki Torii and Hiroichi Tomotake (2003): Influence of Combination of Cement and Reactive Aggregate on the Expansion Behaviour of Mortars due to Alkali-silica Reaction. Journal of Materials, Concrete Structures and Pavements, Japan Society of Civil Engineers, No.739/V-60: pp.251-263. (in Japanese)

[9] Japan Society of Civil Engineers (2002): Standard Specifications for Concrete Structures-2002. Materials and Construction (in Japanese)

[10] Public Works Research Center (1989): Development of Durability Improving Technology for Concrete (Report of Research on Public Structures). General Technology Development Project on Ministry of Construction (in Japanese)

TABLE 1: Specimen types and mix proportions of concrete

Specimen type	Aggregate reactivity	Cement type	Na_2Oeq (kg/m^3)	Chloride content (kg/m^3)	Unit weight (kg/m^3)					
					W	C	S	GR	GNR	NaCl
(1) R-OPC-2	1:1 Mixture of reactive (GR) and non-reactive (GNR) aggregates (pessimum conditions)	Ordinary Portland cement (OPC)	2.0	0.00	175	350	721	583	583	0.00
(2) R-OPC-2.5			2.5	0.62						1.02
(3) R-OPC-5			5.0	3.48						5.73
(4) R-OPC-10			10.0	9.21						15.16
(5) R-BB-1.2		Blast furnace cement type B (BB)	1.2	0.00			716	580	580	0.00
(6) R-BB-2.5			2.5	1.50						2.47
(7) R-BB-5			5.0	4.36						7.18
(8) R-BB-10			10.0	10.09						16.61
(9) NR-OPC-5	GNR	OPC	5.0	3.48			721	---	1166	5.73

TABLE 2: Materials used to concrete

OPC	Ordinary Portland cement : specific gravity 3.16g/cm^3, specific surface area 3,300cm^2/g
BB	Blast furnace cement type B : specific gravity 3.04g/cm^3, specific surface area 3,800cm^2/g
S	Fine aggregate : Mountain sand from Kimitsu in Chiba, specific gravity 2.60g/cm^3, Water absorption 1.53%, Harmless by Chemical method (JIS A 1145)
GR	Reactive coarse aggregate : Crushed pyroxene andesite from Noto near Kanazawa, Containing reactive minerals such as volcanic glass, christbarite, feldspar and montmorillonite, Gmax=15mm, specific gravity 2.63g/cm^3, Water absorption 2.42%, Not-harmless by Chemical method (JIS A 1145, Rc=233mmol/L, Sc=609mmol/L)
GNR	Non-reactive coarse aggregate : Crushed peridotite from Toba, Gmax=15mm, specific gravity 2.98g/cm3, Water absorption 0.74%, Harmless by Chemical method (JIS A 1145)

TABLE 3: Effects of chloride ion content and ASR generation around the reinforcements on reinforcement corrosion

		Equivalent alkali content (kg/m^3)		
		About 0 to 3	About 3 to 5	About 5 or above
		ASR not generated	ASR generated	ASR generated
Chloride ion content (kg/m^3)	About 0 to 1.2*	No corrosion	No corrosion	No corrosion
	About 1.2* to 3.5	Corrosion	No corrosion	No corrosion
	About 3.5 or above	Corrosion	Corrosion	Corrosion

* Threshold chloride ion content for initiation of corrosion (Chloride-corrosion threshold value) presumed to be 1.2kg/m^3

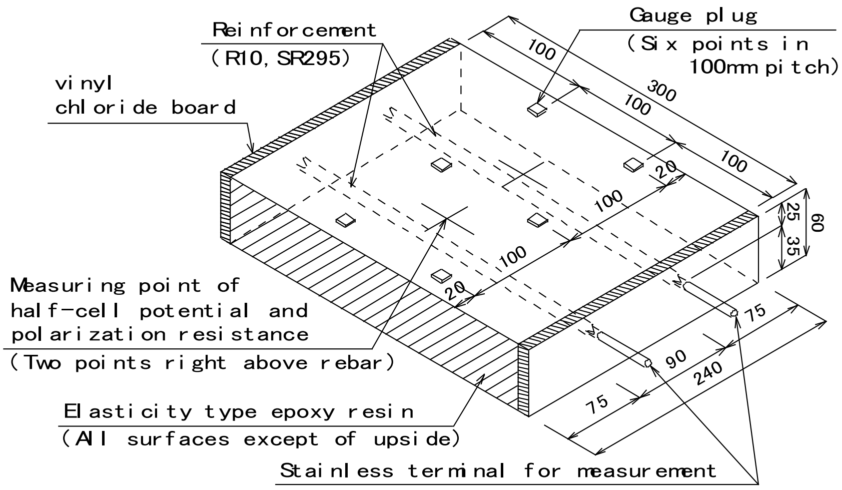


FIGURE 1: Outline of specimen. One reinforcement bar in each specimen was taken out for detailed observation of corrosion after 2.2years exposure, and the other was taken out at the end of the exposure period.

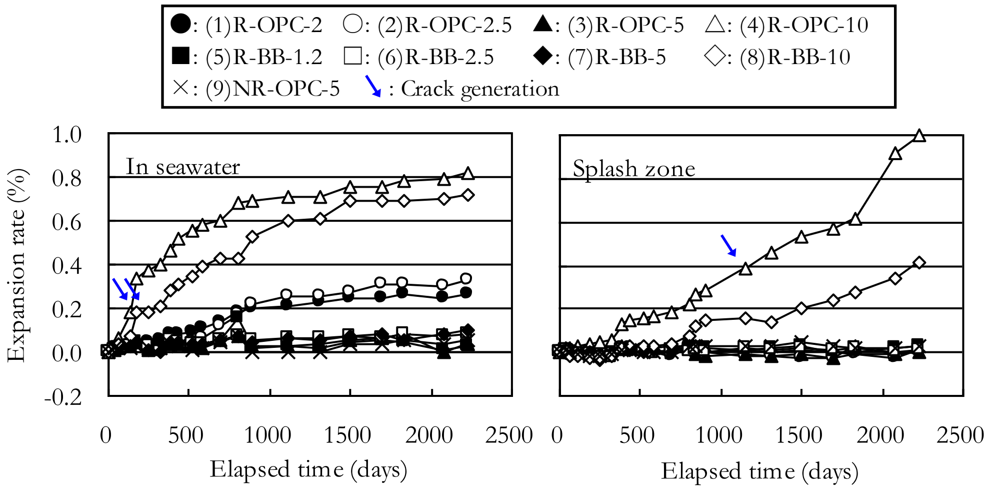


FIGURE 2: Time-dependent changes in expansion rate (direction perpendicular to reinforcement)

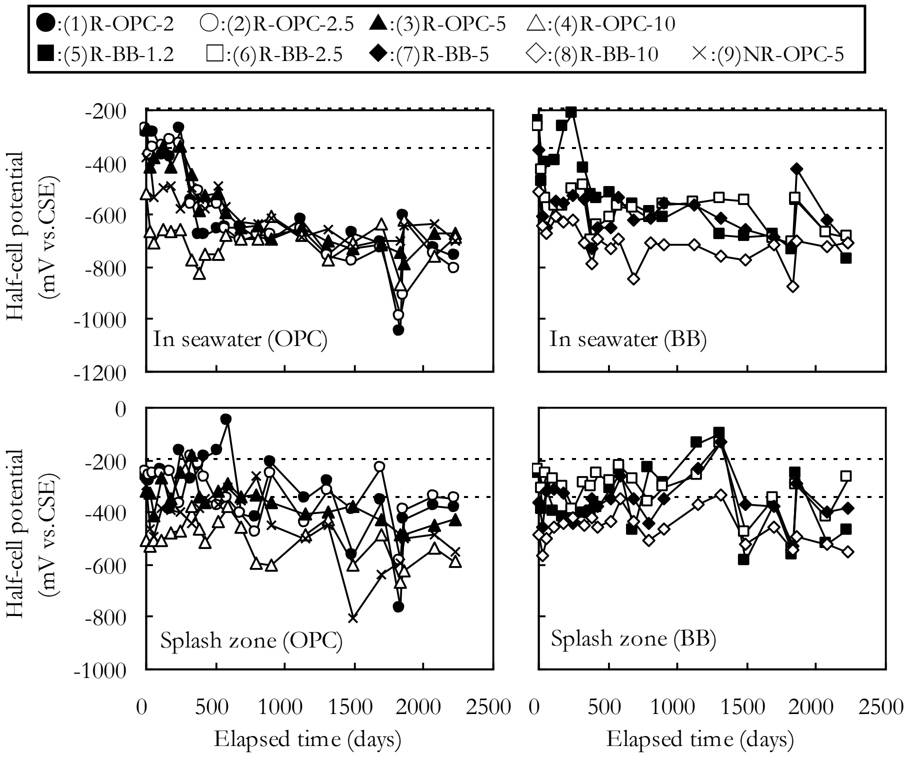


FIGURE 3: Time-dependent changes in half-cell potential of reinforcement

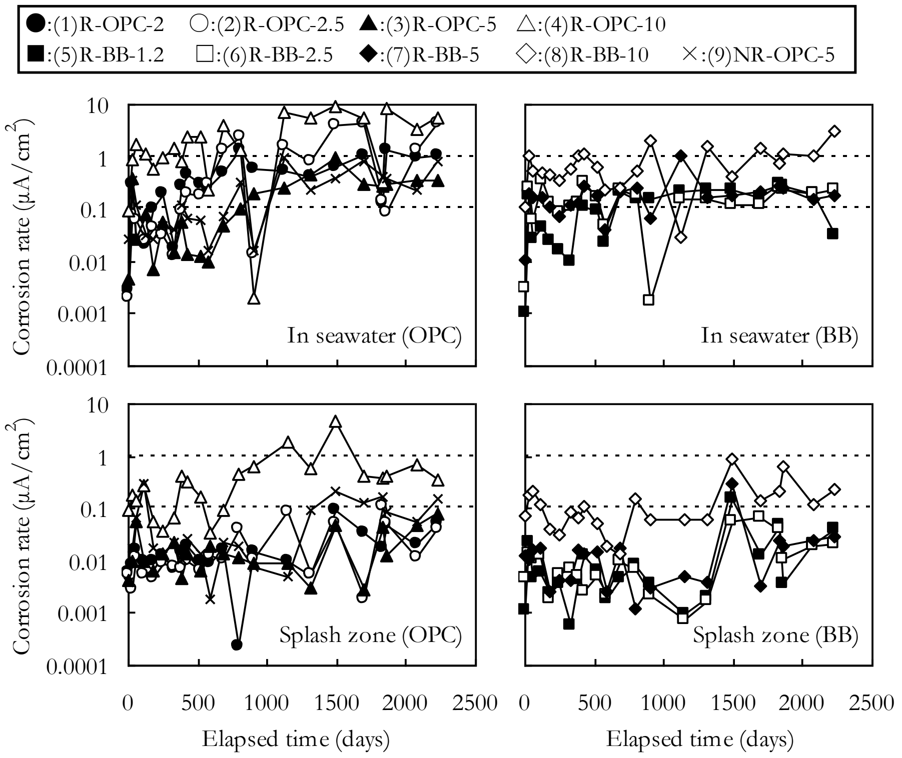
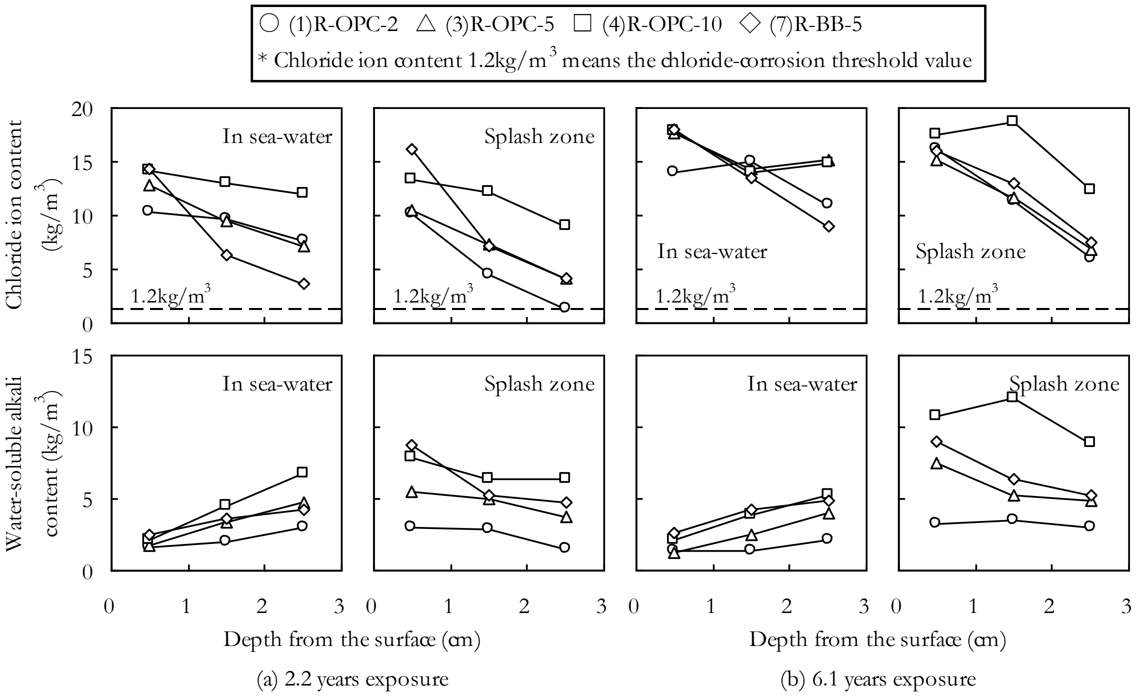


FIGURE 4: Time-dependent changes in corrosion rate of reinforcement



(a) 2.2 years exposure

(b) 6.1 years exposure

FIGURE 5: Distribution of chloride ion and water-soluble alkali content after 2.2 and 6.1 years exposure

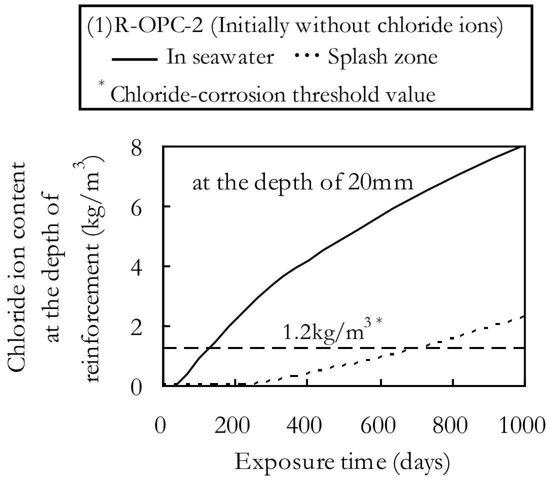
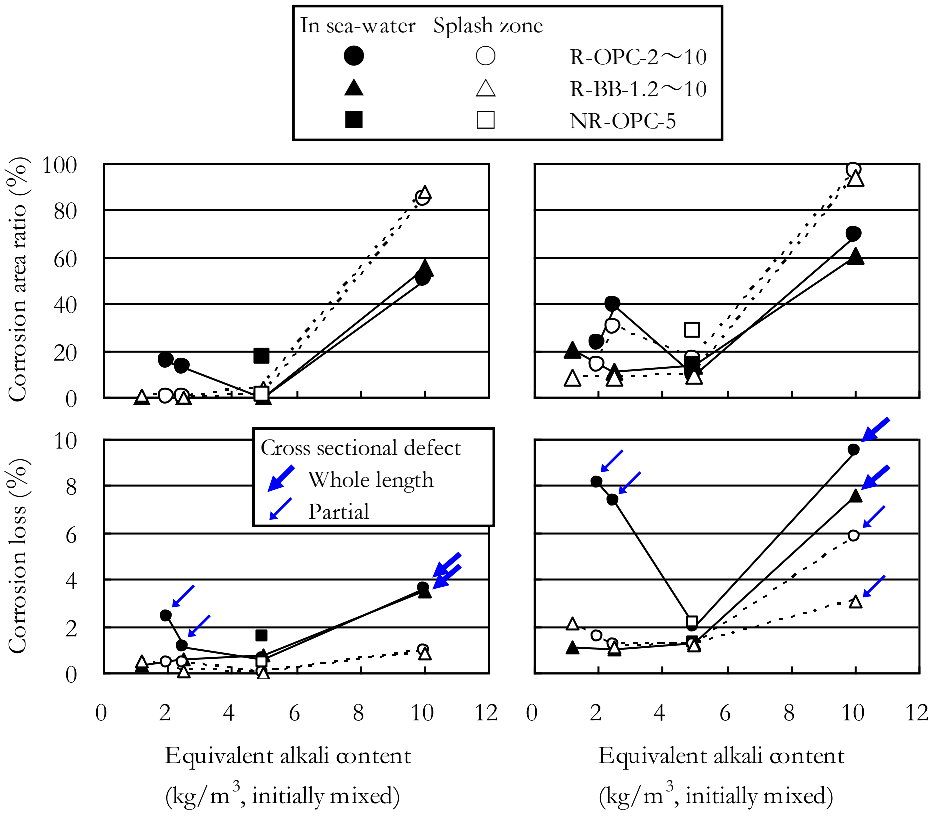


FIGURE 6: Estimation of time-dependent change in chloride ion content at the depth of reinforcement (specimen (1))



(a) 2.2 years exposure

(b) 6.1 years exposure

FIGURE 7: Relationship among initial alkali content, corrosion area ratio and corrosion loss of reinforcement