

Influence of Temperature on Electrochemical Remedial Measure and Complex Deterioration due to Chloride Attack and ASR

Takao Ueda¹, Junji Kushida¹, Masayuki Tsukagoshi¹ and Akira Nanasawa²

¹*Department of Civil and Environmental Engineering, The University of Tokushima, 2-1, Minami-jyosanjima cho, Tokushima City, Tokushima, Japan*
ueda@ce.tokushima-u.ac.jp, kushida@iji-lab.sakura.ne.jp,

mtsukagoshi@ce.tokushima-u.ac.jp
²*DENKI KAGAKU KOGYO KABUSHIKI KAISHA, Omi Plant, 2209 Omi, Itoigawa City, Niigata, Japan,*
akira-nanasawa@denka.co.jp

ABSTRACT

Complex deterioration mechanism due to both chloride attack and ASR would be greatly affected by the environmental temperature. In this study, the influence of the environmental temperature on the concrete expansion and the steel corrosion was experimentally investigated. As a result of this, some protection effect of steel corrosion was found in the cases of storage in 30 °C or 40 °C, although ASR expansion was promoted. This would be caused by the formation of alkali silica gel around the steel. As a remedial measure against such a complex deterioration, electrochemical penetration of lithium from the electrolyte solution was also investigated. It was clarified that electrolyte temperature greatly affected the extent of lithium penetration and the treatment in 40 °C remarkably accelerated lithium penetration into concrete compared with the case of 30 °C. Regarding the kind of lithium salt, LiNO₃ solution was most effective among some kinds of lithium salt.

Keywords. Complex deterioration, Chloride attack, ASR, Lithium salts, Electrochemical method

INTRODUCTION

Chloride attack and ASR are serious deterioration mechanisms of concrete structures respectively. Moreover, in the cases of marine environment and cold climate area, complex deterioration of these mechanisms can be observed because of the supply of sea water or de-icing salt. Complex deterioration mechanism due to both chloride attack and ASR has not been clarified yet but it would be greatly affected by the environmental temperature. In this study, the influence of the environmental temperature on the concrete expansion and the steel corrosion was experimentally investigated to make an adequate decision on the strategy of remedial measure considering environmental situations of structures. Using reinforced concrete specimens, concrete expansion and electrochemical steel corrosion indexes, namely,

half-cell potential, polarization resistance and electric resistivity of concrete were measured regularly during the saving period in each temperature condition.

As a remedial measure against such a complex deterioration, this study tried an electrochemical penetration of lithium from electrolyte solution. It has been confirmed by many researchers that lithium salts have the effect of suppressing ASR-induced expansion of concrete [MacCoy and Caldwell 1951]. Supposing the application of the lithium salts as a repair additive for concrete structures deteriorated by ASR, sufficient amounts of Li^+ must be driven into the ASR-affected concrete [Diamond and Ong 1992]. Then, an electrochemical technique to accelerate the penetration of the lithium ions (Li^+) in a lithium-based electrolyte solution into concrete has been employed for the purpose of suppressing ASR-induced expansion due to Li^+ . However, from the results of past research work, the penetration area of Li^+ is limited around the concrete surface and it is difficult to make Li^+ penetrate into the deeper part of concrete [Ueda et al. 2006]. In this study, experimental investigations were carried out aiming to grasp the influence of kinds of lithium salts and the temperature of the electrolyte solution on migration properties of ions in concrete and ASR-induced expansion of concrete.

EXPERIMENTAL PROGRAM

Materials

Mixture proportions 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 NCl is supposed to be deteriorated by chloride attack solely. This concrete contained only non-reactive aggregate and NaCl was dosed to adjust the amount of the alkali. Concrete named RCl is supposed to be damaged by the complex deterioration. This concrete contained reactive aggregate and NaCl was added as the source of alkali. Concrete named ROH is supposed to be damaged by ASR solely. This concrete contained reactive aggregate and NaOH was mixed to adjust the amount of alkali in concrete. In order to adjust the total alkali contents as $\text{R}_2\text{O} = 10.0 \text{ kg/m}^3$ for the acceleration of deterioration, a corresponding amount of NaCl or NaOH were dissolved in the mixing water. All specimen subjected to electrochemical treatment was made of concrete named RCl.

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: 2.60 g/cm^3) were mixed at the pessimum weight ratio of 3:7. 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 mixed at the pessimum weight ratio of 3:7.

Preparation of specimens and electrochemical treatment

Specimens prepared in this study were $100 \times 100 \times 300 \text{ mm}$ reinforced concrete prisms with a

Table 1. Mixture proportions of concrete

Name	W/C (%)	s/a (%)	Content (kg/m^3)							
			C	W	S1	S2	G1	G2	NaCl	NaOH
NCl	55	48	338	186	832	-	871	-	15.1	-
RCl	55	48	338	186	250	591	261	641	15.1	-
ROH	55	48	338	186	250	591	261	641	-	10.3

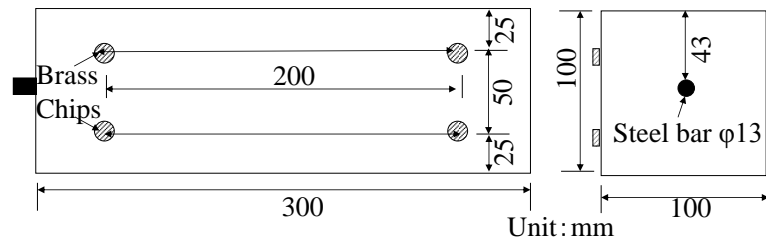


Figure 1. Outline of a RC specimen

steel bar $\phi 13$ SR235 (JIS number) at the center of the square section as shown in Fig. 1. All specimens were cured in the wet 20 °C condition.

In the case of specimens to investigate complex deterioration mechanism, brass chips were pasted to concrete surfaces for the measurement of concrete expansion after the curing for 14 days. These specimens were kept in the moist condition and the temperature levels were 20, 30 or 40 °C. In the case of specimens to be subjected to electrochemical treatment after curing for 28 days, five concrete faces of each specimen were insulated with epoxy resin coating, leaving one exposed surface.

After the epoxy coating, each specimen was immersed into electrolyte liquid in a plastic container, and direct electric current was supplied between rectangular shaped titanium mesh as the anode and the steel bar in concrete as the cathode. As the current density, 1.0 A/m² to the exposed concrete area was adopted. Treated period was 8 weeks. Kinds of electrolyte liquid and their temperature conditions are shown in Table 2. The standard temperature level of electrolyte liquid was 30 °C to accelerate the lithium penetration except the case of 40 °C of LiNO₃ solution.

Tests of specimens

Specimens for investigating complex deterioration mechanism were kept in the wet and constant temperature (20, 30 or 40 °C) environment and the expansion rate of concrete was measured regularly by means of a contact gauge. At the same time to measure the concrete expansion, half-cell potential, polarization resistance of steel in specimens and resistivity of concrete were measured regularly. As a reference electrode for these electrochemical monitoring, saturated silver chloride (Ag/AgCl) was used. Polarization resistance was

Table 2. List of electrolyte

Name of salt	Content of salt (%)	content of Li (%)	Temperature (°C)
LiOH	10	3.0	30
Li ₂ CO ₃	1.2	0.22	30
Li ₂ SiO ₄	23	2.9	30
LiNO ₃	30	3.0	30
			40
Ca(OH) ₂	0.2	0	30

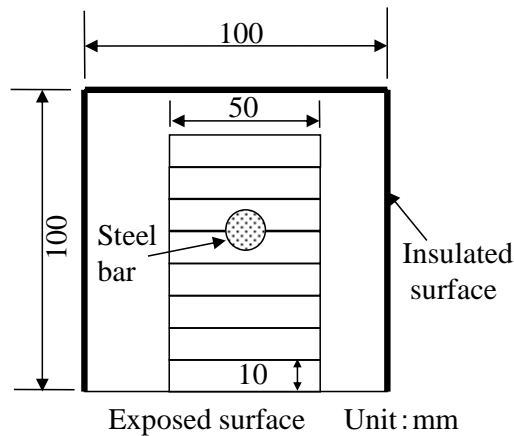


Figure 2. Cutting way of a specimen for chemical analysis

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.

After finishing the electrochemical treatment, the distribution profiles of ion content (Cl^- , Na^+ , K^+ , Li^+) in the concrete specimens were measured using powder samples grinded from the cut out seven concrete plates in a specimen, as shown in Fig. 2. The Na^+ , K^+ and Li^+ contents were measured by means of atomic absorption spectrometry using a crashed fine powder sample solved by HNO_3 solution. Cl^- content was measured according to JIS A 1154.

RESULTS AND DISCUSSIONS

Variation of expansion rate of concrete

Regarding the specimens kept in 20, 30 or 40 °C after curing, variation curves of the concrete expansion rate with time are shown in Figure 3. The horizontal axis of this figure expresses the period after the end of the curing. The legends used in this figure mean the name of concrete followed by the environmental temperature. From this figure, ROH40 shows the earliest initiation of concrete expansion because of the higher alkalinity by the dosage of NaOH and the higher temperature. The next initiation of concrete expansion occurs with the specimens of RC140 and ROH30. RC130 shows about 100 days delay of the initiation from the other early expansion specimens. However, when one year passed from the beginning of the storage, RC130 shows largest expansion rate with the widest concrete cracking along the steel bar as shown in Fig. 4. Including the cases of specimens kept in 20 °C, slow concrete expansion cases may result in long term progressing of expansion and larger expansion rate.

Monitoring of steel corrosion in concrete

Variation curves of half-cell potential and polarization resistance of steel in specimens during the storage period in each temperature condition are shown in Fig. 5 and Fig. 6 respectively. The standard lines to judge the steel corrosion probability specified in ASTM C876-91 are also indicated in Fig. 5. Moreover, the variation curves of electric resistivity of cover concrete in concrete specimens are shown in Fig. 7.

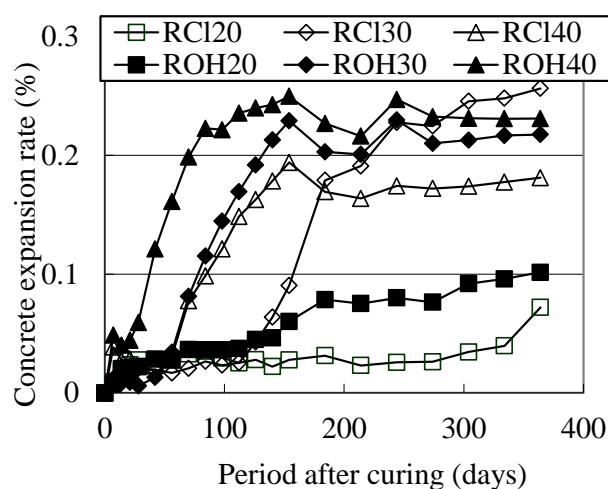


Figure 3. Variation of concrete expansion rate after curing



Figure 4. Concrete cracking observed in RC1 specimen stored in 30°C

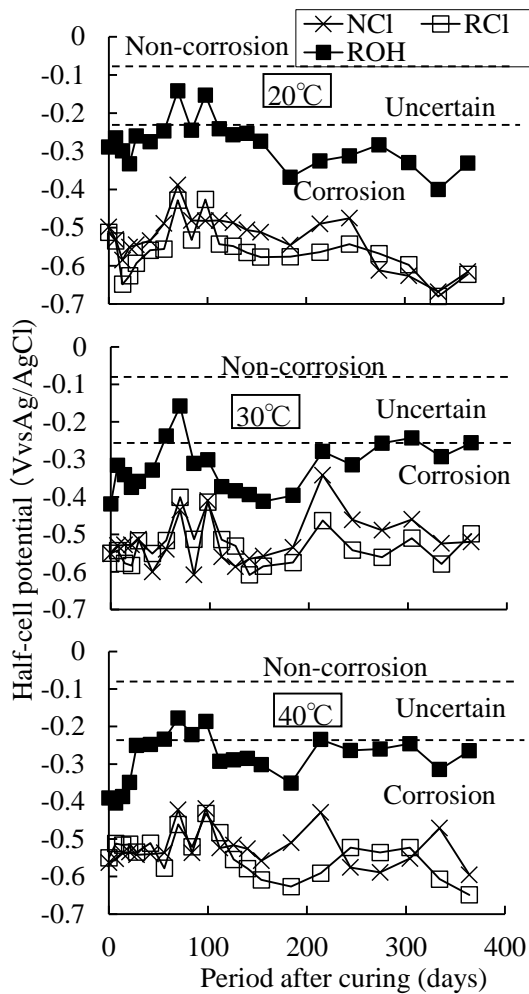


Figure 5. Variation of half-cell potential

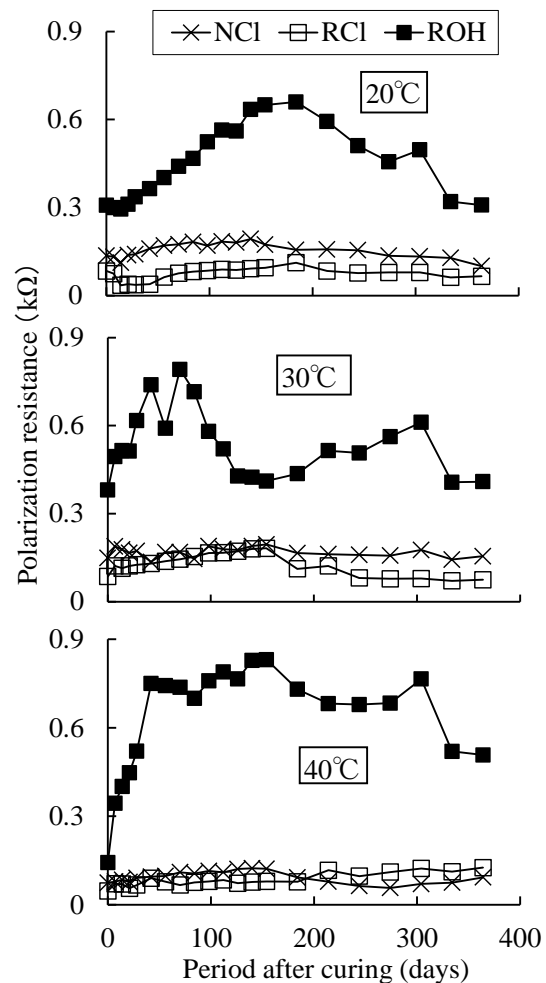


Figure 6. Variation of polarization resistance

According to Fig. 5, NCI and RCI specimens generally show the base values of half-cell potential with the dosage of high amount of NaCl into concrete. These specimens initially contained Cl^- of 9.1 kg/m^3 that is much higher than the threshold Cl^- content to initiate steel corrosion. On the other hand, ROH specimens keep relatively nobler potential values because these ones don't contain the pre-mixed NaCl. Especially, when the storage temperature is 30 or 40 °C, the half-cell potential values of ROH specimens are gradually increase with time regardless of the growing concrete expansion due to ASR as shown in Fig. 3. As the reason of this result, there is a possibility of the closing of concrete crack due to the self-mitigation mechanism [Shindo et al., 2010] or the steel protection by the formation of alkali silica gel around the steel bar [Habuchi et al. 2004]. In the cases of 20 °C storage, the half-cell potential values tend to decrease gradually with the progress of ASR.

As shown Fig. 6, in the cases of NCI and RCI specimens, the values of polarization resistance keep small during the whole period of the storage because of the high amount of the dosage of NaCl into concrete. Such a small polarization resistance means a high rate of steel corrosion. Although RCI specimens stored in 30 °C show larger values of polarization resistance compared with the cases in 20 or 40 °C until about 160 days from the beginning of

the storage, the drop of the polarization resistance is observed after this point. On the other hand, the value of RCI stored in 40 °C becomes larger than those of NCI specimens.

While in the cases of ROH specimens, the variation tendency of the polarization resistance depends on the storage temperature. The polarization resistance is increasing in accordance with the concrete expansion growing due to ASR. This tendency suggests that the formation of alkali silica gel due to ASR may suppress the corrosion rate of steel in concrete. In each temperature case, the drop of the polarization caused by the growing of concrete crack can be observed in Fig. 6. However, when the storage temperature is 40, the protection effect against steel corrosion may be maintained by the crack closing due to the self-mitigation of concrete.

According to Fig. 7, generally speaking, the concrete resistivity values become large with the concrete expansion growing due to ASR. These specimens don't show the reduction of concrete resistivity even when the drop of the polarization resistance is observed. This may show that the damage of cover concrete due to ASR is not so significant.

Migration of ions in concrete due to applying electrochemical treatment

The distributions of Cl^- content in the specimens just after completing treatment are shown in Fig. 8. The steel bar is located at the center (50 mm from the exposed surface) of each specimen. Although this technique is not for extracting Cl^- from concrete, Cl^- content around the steel bar is decreased by the electrochemical treatment compared with the non-treated case (N), because

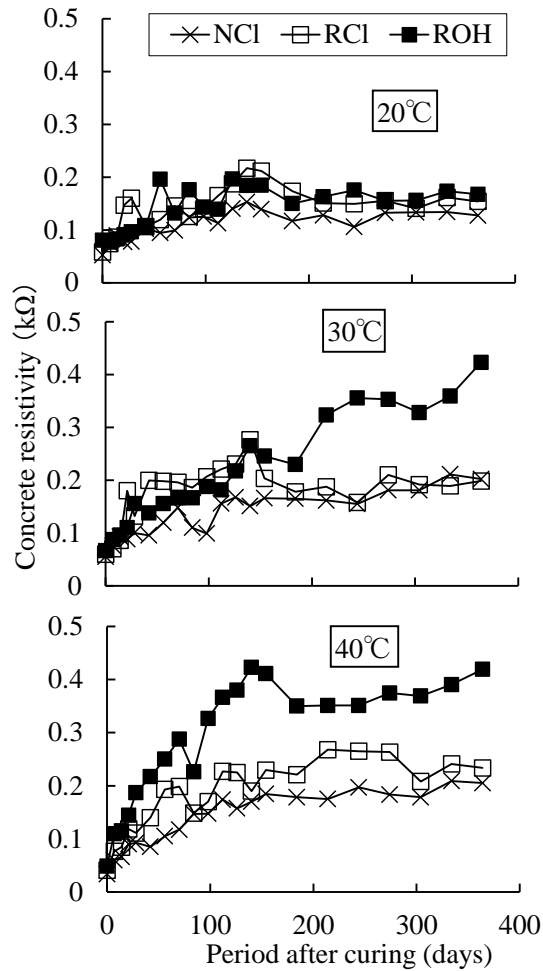


Figure 7. Variation of concrete resistance

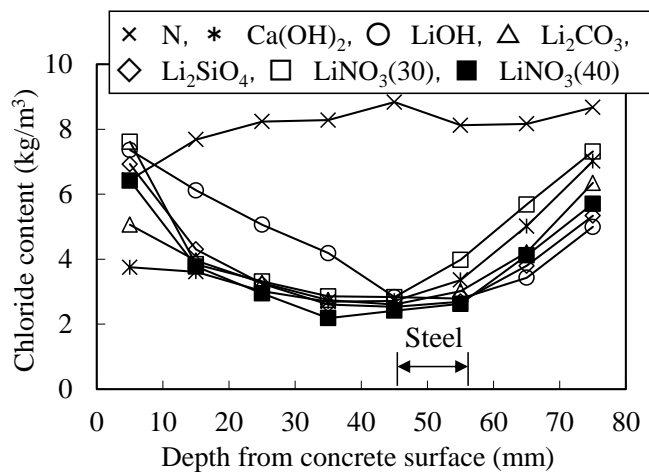


Figure 8. Distributions of chloride content in concrete after treatment

this technique is based on the same principle as that of desalination. Since such a side effect is expectable, this technique could be applied with good effect on concrete structures deteriorated by the complex mechanism of chloride attack and ASR. There isn't significant difference of the chloride removal effect among the some kinds of lithium salts but the rise in the electrolyte temperature from 30°C to 40°C improves the desalination effect in the case of LiNO₃.

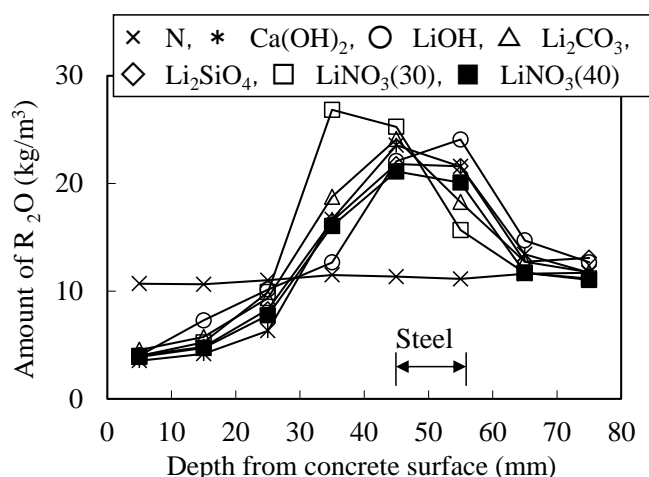


Figure 9. Distributions of R₂O content in concrete after treatment

The distributions of R₂O content in concrete specimens immediately after completing treatment are shown in Fig. 9. The amount of R₂O was calculated by the following formula.

$$R_2O = Na_2O + 0.658K_2O \text{ (kg/m}^3\text{)}$$

According to this figure, in the case of the specimens treated with the electrolyte of 20°C, a great amount of R₂O accumulates around the steel bar in concrete. It is considered that such an accumulation of alkali is caused by the electrophoresis of cations (Na⁺, K⁺) contained in the concrete toward the steel bar as the cathode.

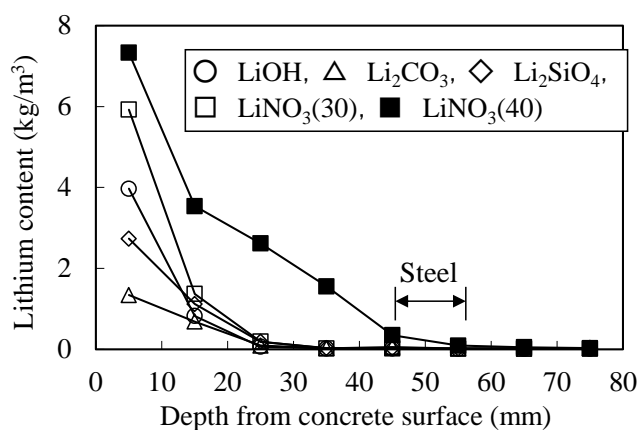


Figure 10. Distributions of lithium content in concrete after treatment

Like the case of Cl⁻ distribution, the rise in electrolyte temperature from 30°C to 40°C might accelerate the electrophoresis of Na⁺ and K⁺. Then, it can be expected that the rise in temperature would result in a larger amount of R₂O accumulation around the steel bar. However, in Fig. 9, the accumulated amount of R₂O is reduced with the rise in the electrolyte temperature from 30°C to 40°C. Such a moderation of the alkali accumulation at the steel bar may be caused by the decrease of the transference numbers of Na⁺ and K⁺ in concrete with the migration of lithium-based electrolyte solution. The authors reported similar results in the past paper [Ueda et al. 2011]. The reduction of the concentrated alkali at the steel bar would mean the reduction of the risk of ASR or ASR-induced expansion of the concrete around the steel bar.

Distributions of Li⁺ content in the concrete immediately after treatment are shown in Fig. 10. In this figure, Li⁺ content around the concrete surface increases with the electrochemical

treatment. However, when the temperature of electrolyte is 30 °C, the penetration depth of lithium is about 25 mm regardless of the kinds of lithium salt. The authors already reported that it was difficult to drive a sufficient amount of Li^+ into the concrete at the depth of the steel bar by the electrochemical treatment with the LiOH electrolyte solution at room temperature [Ueda et al. 2006]. On the other hand, Fig. 10 shows that 40 °C electrolyte of LiNO_3 increase the amount and the depth of lithium penetration compared with the case of 30 °C. The authors reported similar results from the experiment using Li_2CO_3 solution as the electrolyte. Further investigation is necessary to clarify the adequate conditions of the electrochemical treatment considering the concrete expansion behavior after the treatment.

CONCLUSIONS

This study conducted experimental investigations to grasp the complex deterioration mechanism due to chloride attack and ASR, and to confirm the effect of the electrochemical remedial measure against it. The results obtained from this study can be summarized as follows.

- (1) The storage of specimens in 30 °C or 40 °C promoted concrete expansion due to ASR, while the protection effect against steel corrosion was observed. The possible reasons are the closing of concrete crack or the formation of alkali silica gel around the steel.
- (2) The polarization resistance and concrete electric resistivity increased with the progress of ASR until the effect of concrete crack became dominant.
- (3) The rise in temperature of electrolyte solution from 30 °C to 40 °C remarkably accelerated the migration of Cl^- and Li^+ in concrete due to applying electrochemical treatment. Regarding the kind of lithium salt, LiNO_3 solution was most effective among some kinds of lithium salt contained in electrolyte solution from the viewpoint of lithium penetration.
- (4) The rise in temperature of electrolyte solution from 30 °C to 40 °C didn't promoted the accumulation of Na^+ and K^+ around the steel bar in concrete.

REFERENCES

- Diamond, S. and Ong S. (1992). "The Mechanism of Lithium Effects on ASR." *Proceedings of the 9th International Conference on Alkali-Aggregate Reaction*, pp. 269-278.
- Habuchi, T. Tsuji, H. and Torii, K. (2004). "Steel corrosion mechanisms caused by combined action of ASR and chloride penetration", *Annual Proceedings of Japan Concrete Institute*, Vol.26, No.1, pp. 1017-1022.
- MacCoy, W. J. and Caldwell, A. G. (1951). "New Approach to Inhibiting Alkali-Aggregate Expansion." *Journal of ACI*, 22, pp. 693-706,.
- Shindou, Y. Munekane, M. Ueda, T. and Watanabe, T. (2010). "Self-healing effect of fly ash concrete", *Annual Proceedings of Japan Concrete Institute*, Vol.32, No.1, pp. 137-142.
- Ueda, T. Yoshida, Y. Yamaguchi, K. and Ashida, M. (2006). "Electrochemical migration of lithium ions into hardened concrete and ASR expansion after treatment." *Proceedings of Structural Faults & Repair-2006*, CD-ROM.
- Ueda, T. Baba, Y. and Nanasawa, A. (2011). "Effect of electrochemical penetration of lithium ions on concrete expansion due to ASR", *Journal of Advanced Concrete Technology*, Vol.9, No.1, pp. 31-39.