Scientific paper

Influence of Degree of Deterioration and Electrolyte Solution on Repair Effect of Realkalization for Reinforced Concrete

Takao Ueda1*, Hiroshi Takahashi2, Akira Nanasawa3, Kazuhide Nakayama4 and Masayuki Tsukagoshi5

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Abstract

Electrochemical realkalization has been applied to many concrete structures deteriorated by carbonation of concrete. As the repair effect of this method, it has been reported that the pH value of the carbonated concrete recovered by the electrolysis reaction at the steel in concrete and the electro-osmosis of the electrolyte solution in the anode system set on the concrete surface. However, the protection effect of the realkalization against the steel corrosion in concrete has not been clarified enough. Therefore, this study investigated the steel corrosion behavior in concrete after the application of realkalization in the cases of different degree of deterioration and different kind of electrolyte solution by measuring content profiles of several sort of ions and electrochemical indicators for evaluating steel corrosion. As a result, the electrochemical removal of Cl− ions from carbonated concrete and the electrochemical penetration of K+ ions from the electrolyte solution into carbonated concrete were both promoted compared with the case of non-carbonated specimen. Moreover, the protection ratio calculated by the corroded area ratio of steel bars in the electrochemically treated specimens and non-treated specimens subjected to the cyclic drying and wetting storage for 400 days after the period of realkalization achieved around 80% regardless of the difference of the deterioration condition before applying realkalization.

1. Introduction

Realkalization method is an electrochemical repair method for reinforced concrete (RC) structures deteriorated by carbonation of concrete and application cases are increasing year by year with the publication of guidelines or standards for design and construction of this method (CEN/TS 2004; JSCE 2020). It was reported that the pH value in concrete maintained around 12.2 even for 17 years after the electrochemical treatment and that the protection condition against reinforcement corrosion had been confirmed (Nomura et al. 2012).

After finishing the electrochemical treatment of the realkalization, the pH recovery of the carbonated concrete is generally confirmed, but the content profiles of ions in concrete after the treatment and the protection condition of reinforcing steel against corrosion are not considered enough. In addition, the different carbonation depth or chloride content in concrete before the treatment will affect the repair effect and its duration. The authors reported the short-term evaluation of the realkalization effects by using some electrochemical indexes of the steel corrosion (Takahashi et al. 2020). However, the longer-term variation of such indexes and the actual corrosion situation in concrete must be investigated for improving the reliability of the realkalization.

In addition, the electrochemical repair methods have the risk of accelerating ASR of concrete due to the accumulation of the alkali metal ions around the reinforcement (Page and Yu 1995; JSCE 2020). For reducing such risk, electrochemical introduction of lithium ions by using lithium-based electrolyte solution has been investigated (Ashida et al. 1999; Whitemore and Abbott 2000) expecting the effect of suppressing ASR-induced expansion of concrete (MacCoy and Caldwell 1951; Diamond and Ong 1992; Lumley 1997). Past investigations (Souza et al. 2017; Ueda et al. 2005, 2006, 2011; Folliard et al. 2008) found that the ASR-induced expansion of concrete after the electrochemical treatment tended to be suppressed compared with the non-treated case mainly around the exposed surface.

Considering these, this study was conducted as an experimental investigation using RC specimens with...
different depths of carbonation for clarifying the repair effect of realkalization using two kinds of electrolyte solutions, which are a conventional potassium carbonate, and a lithium carbonate solution.

2. Experimental program

2.1 Preparation of specimens

The mix proportions of concrete used in this study are shown in Table 1. To promote carbonation, the water to cement ratio of concrete was set at 60% and NaCl was solved into mixing water adding 1% Cl⁻ by mass of cement, which is 3.0 kg/m³ for concrete volume, supposing the case using sea sand without enough washing. 30% of fly ash (FA) was mixed for concrete named FA as a substitute of cement. For extracting pore solution and measuring pore size distribution, mortar cylinders were made by removing coarse aggregate from the concrete mixtures. The data of compressive strength of concrete measured at 70 days of age when the accelerated carbonation started are shown in Table 1.

The specimens prepared in this study are shown in Fig. 1. The concrete part of a RC specimen was a prism in the size of 300×100×100 mm, and one deformed steel bar D13 was located at 25 mm from the exposed surface. The specimens were sealed for curing for 14 days in a constant temperature room at 20°C. Thereafter, the specimen was dried for 4 weeks, and epoxy resin was applied to the five surfaces except for one exposed surface followed by drying for 4 weeks before the accelerated carbonation test. As shown in Fig. 1, the size of mortar specimen was φ50×100 mm with φ2 mm stainless steel wire at the center part of the circular cross section, which were cured and dried under the same condition as RC specimens. The whole side surface of the cylinder mortar was exposed, while the top and the bottom surfaces were covered with epoxy resin. In addition, mortar cylinders without steel wire were prepared for measuring the pore diameter distribution.

The accelerated carbonation was carried out in the condition of 20°C, 60% RH and 5% CO₂ concentration in accordance with JIS A 1153, using RC and mortar specimens. The aimed carbonation depth of concrete was 15 mm or 30 mm, which were achieved within the error of ±2 mm. 15 mm was estimated as the initiation point of steel corrosion in concrete, judged by the drop of the half-cell potential referring to ASTM C 876-91 as the criterion for estimating state of the steel corrosion in concrete. Cylindrical mortar specimens finished accelerated carbonation at the same time as RC specimens using same kind of concrete. RC specimens and mortar specimens without accelerated carbonation were stored in a constant temperature room at 20°C during the accelerated carbonation period until applying realkalization.

2.2 Realkalization treatment

After completion of the predetermined accelerated carbonation, electrochemical treatment was carried out using RC and mortar specimens with 1.5 mol/L K₂CO₃ solution or 0.18 mol/L Li₂CO₃ solution as an electrolyte. As the solubility of Li₂CO₃ is quite low, 0.18 mol/L is a saturated solution. The concentration of the electrolyte was monitored during the treatment and adjusted if necessary. The realkalization using Li₂CO₃ solution was applied only for the “N” specimens after the carbonation to 30 mm. Titanium mesh was used as an anode material, and direct electric current was supplied between the anode and steel bar in a RC specimen or stainless wire in a mortar specimen as the cathode for 14 days. The current density was 1.0 A/m² to the exposed surface. The electrochemical treatment was conducted in a constant temperature room at 20°C. Non-treated specimens were also prepared and stored in a wet state (20°C, 95% RH)

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Table 1 Concrete mix proportion.

| Name | W/B (%) | s/a (%) | C (kg/m³) | W (kg/m³) | S (kg/m³) | G (kg/m³) | (C+FA)% | Slump (cm) | Air (%) | Compressive strength (N/mm²) |
|------|---------|---------|-----------|-----------|----------|-----------|---------|-----------|--------|-----------------------------|
| N    | 60      | 48      | 300       | 828       | 902      | –         | 0.5     | 15.5      | 6.6    | 33.1                        |
| FA   |         |         | 210       | 814       | 887      | 90        | 0.3     | 17.0      | 5.8    | 25.6                        |

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

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Fig. 1 Outline of the specimens.
during the realkalization period.

The list of specimens is shown in Table 2. The name of specimen indicates concrete name followed by the aimed carbonation depth (mm), and the end “K” or “Li” indicates the sort of the electrolyte solution, K₂CO₃ or Li₂CO₃ solution employed respectively for realkalization.

2.3 Tests
(1) Ion concentration in pore solution and pore size distribution of mortar
The pore solution in the mortar specimen before and after the electrochemical treatment was extracted (more than 5 ml) by compressive loading. The epoxy resin on the upper surface and the lower surface, and the stainless-steel wire were removed before the extraction of the pore solution. Cl⁻ concentration in the pore solution was measured by the potentiometric titration with 0.01 mol/L silver nitrate and OH⁻ concentration was measured by the direct titration with 0.01 mol/L hydrochloric acid.

The pore size distribution of mortar was measured by mercury porosimetry. After the measurement of the carbonation depth of mortar specimens by spraying phenolphthalein solution, the carbonated part was separated from the non-carbonated part and both parts were crushed into pieces around the size of 5 mm. The mortar pieces of carbonated and non-carbonated parts were immersed in acetone in a vacuum desiccator for stopping the hydration of cement.

(2) Ion content profiles in the RC specimen
Content profiles of Cl⁻, K⁺ and pH profiles in concrete before and after realalkalization were measured. As shown in Fig. 2, eight concrete slices with 10 mm thickness were cut out from the specimen for the chemical analysis. Total content and soluble content of Cl⁻ were measured by potentiometric titration according to JIS A 1154. The pH value was measured by using the solution sample of the concrete powder of 12.5 g with the mixing pure water of 25 ml. K⁺ and Li⁺ content was measured by using an atomic absorption photometer for samples extracted by nitric acid.

(3) Electrochemical indicators for steel bar corrosion
Half-cell potential and polarization resistance of RC specimens after the realalkalization period were measured periodically while they were stored in the condition of cyclic drying and wetting. One week consisted of three days of drying (20°C, 60% RH) and four days of wetting (40°C, 95% RH). As shown in Fig. 3, the half-cell potential of the steel bar in a specimen was measured by using a saturated silver-silver chloride electrode (Ag/AgCl) as the reference electrode attached to concrete surface with a wet absorbent cotton. Polarization resistance was measured by the rectangular wave current polarization method using a titanium mesh as a counter electrode as impedance values of applied current of 100 μA, frequency of 800 Hz and 0.1 Hz. The half-cell potential and polarization resistance were measured on the next day after the wetting period in the 20°C environment while maintaining the wet state of the specimen.

After measuring the half-cell potential and polarization resistance, anodic polarization curves were measured. As measurement conditions of linear sweep voltammetry, the sweep rate was 100 mV/min (JCT 2018), and the applied voltage was +300 mV from the natural potential. The Tafel extrapolation method was applied to the anodic polarization curve to estimate the corrosion

| Name of concrete | Carbonation depth (mm) | Current density (A/m²) | Electrolyte solution | Name of specimen |
|------------------|------------------------|------------------------|-----------------------|-----------------|
| N                | 0                      | 1.0                    | K₂CO₃                | N-0             |
|                  | 0                      | -                      | K₂CO₃                | N-15            |
|                  | 0                      | -                      | Li₂CO₃               | N-30            |
| FA               | 30                     | 0                      | -                     | FA-30           |
|                  | 30                     | 1.0                    | K₂CO₃                | FA-30           |

Fig. 2 Cutting of RC specimen for chemical analysis.

Fig. 3 Measuring situation of electrochemical indicators of steel corrosion.
current density and Tafel slope. Referring to the previous report (JCI 2018), the Tafel slope was determined using a straight line between two points polarized at +50 mV and +100 mV from the half-cell potential. The corrosion current density was determined as the current density at the intersection of the Tafel line and the half-cell potential.

(4) Corroded area ratio of steel bar
After the storage in the cyclic drying and wetting condition for 400 days, reinforcing steel bars were removed from the RC specimens for measuring the corrosion area rate. A removed steel bar was cleaned by a wire brush and wrapped by a transparent paper for tracing the corrosion area in the steel bar. The traced corroded area was measured by using image analysis software and the corroded area ratio was calculated by the following equation.

\[
\text{Corroded area ratio (\%)} = \left( \frac{\text{Corroded area}}{\text{Surface area of steel bar}} \right) \times 100 (1)
\]

3. Results and discussion

3.1 pH values and Cl\(^-\) concentrations in electrolyte solution during realkalization
The variation curves of pH values and Cl\(^-\) concentrations in the electrolyte solution during realkalization are shown in Figs. 4 and 5 respectively. Figure 4 shows that the pH values of N-30Li using Li\(_2\)CO\(_3\) solution are lower than the values of other cases using K\(_2\)CO\(_3\) solution due to the lower concentration of Li\(_2\)CO\(_3\) solution. In addition, the pH values of all cases are decreasing during the period of realkalization, which would be caused by the generation of H\(^+\) ions in the anodic reaction progressing around the titanium mesh in the electrolyte solution. However, since even in the case of N-30Li, the lowest pH value exceeds 10.0, a stable treatment without the generation of chlorine gas could be completed.

In Fig. 5, the Cl\(^-\) concentrations of the cases of carbonated specimens are higher than the values of non-carbonated N-0K. It means that the electrochemical migration rate of Cl\(^-\) ions in the carbonated concrete is larger than the rate in non-carbonated concrete. The mechanism of this phenomenon will be discussed in Section 3.2. Regarding the sort of the electrolyte solution, the Cl\(^-\) concentrations in the Li\(_2\)CO\(_3\) solution are higher than the values in the K\(_2\)CO\(_3\) solution. This would be caused by the larger transference number of Cl\(^-\) ions in the concrete treated with the Li\(_2\)CO\(_3\) solution due to the smaller transference number of OH\(^-\) than the cases of the K\(_2\)CO\(_3\) solution.

The potential difference between the anode and the cathode during the treatment was around 4 V in the cases with K\(_2\)CO\(_3\) solution as the electrolyte, while that was around 6 V in the cases with Li\(_2\)CO\(_3\) solution as the electrolyte. Such a difference in the potential difference would be also caused by the difference in the concentration of the electrolyte solution.

3.2 pH values and Cl\(^-\) concentrations in mortar pore solution before and after realkalization
The pH values and Cl\(^-\) concentrations in the pore solution of mortar before and after the treatment are shown in Fig. 6. Each shown value is an average of data from two specimens and the variation of these two data are relatively small. As shown in Fig. 6, the pH values in the pore solution of N-15, N-30 and FA-30, which were subjected to accelerated carbonation, indicate lower level around 7 to 8, while the pH values in the pore solution of
N-15K, N-30K and FA-30K, which were subjected to realalkalization, indicate higher level around 14. The pH value of N-0 increases from 12.9 to 14.1 by applying realalkalization. These rises in pH value should be caused by the concentrated OH⁻ generated by the cathodic reaction near the steel bar in concrete with the electro-osmosis of the electrolyte. Regarding the sort of the electrolyte solution, N-30Li using Li₂CO₃ solution shows the lower pH value of the pore solution than the case of N-30K using K₂CO₃ solution because of not only the lower pH value of the Li₂CO₃ electrolyte solution as shown in 3.1 but also the smaller transference number of Li⁺ than that of K⁺ considering the electro neutrality with OH⁻ ions in the pore solution.

From Fig. 6, in comparison with the case of N-0 without carbonation, Cl⁻ concentrations in the pore solution of N-15, N-30 and FA-30 increase with the progress of carbonation. It is considered that the concentration of concrete released fixed Cl⁻ ions from cement hydration products into the pore solution in mortar (Kobayashi 1991). The Cl⁻ concentration in the pore solution of FA-30 shows the largest value, which would be caused by the smaller Cl⁻-fixing ability of the mortar admixing fly ash than the case of normal mortar without fly ash. On the other hand, Cl⁻ concentrations in the pore solution of N-15K, N-30K and FA-30K show significantly lower values compared with the cases of non-treated specimens. This would be caused by the electrochemical migration of Cl⁻ ions in the pore solution toward the anode located over the exposed surface. It could mean that the corrosion environment of a steel bar in mortar was improved. However, the concentration of Cl⁻ in the pore solution of N-0K is higher than that of N-0, which may indicate that a part of the fixed Cl⁻ ions was released by applying realalkalization.

3.3 Pore size distribution of carbonated mortar
Pore size distributions of the carbonated or non-carbonated mortar are shown in Fig. 7. The names of the cases in this figure indicate concrete name followed by C or N that means carbonated or non-carbonated mortar respectively.

In Fig. 7, both of N and FA mortar show the decrease in the total volume due to the carbonation of mortar while the increase in the relatively large pore volume more than 100 nm in diameter. During the carbonation process of mortar, CO₂ gas supplied from the air changes to HCO₃⁻ in the pore solution and reacts with Ca(OH)₂ for producing CaCO₃ in the pore. The produced CaCO₃ will fill the pore and decrease the relatively small pore volume, while the dissolution of Ca(OH)₂ from the hydration into the pore solution will result in the increase in the relatively large pore volume. Such an increase in the pore volume over 100 nm in diameter could affect the migration of several kinds of ions in mortar or concrete. That will be discussed in Section 3.4.

3.4 Ion content profiles in RC specimen before and after realalkalization
(1) K⁺, Li⁺ content and pH value profiles in RC specimens
K⁺ and Li⁺ content profiles in RC specimens are shown in Figs. 8 and 9 respectively. In Fig. 8, a large amount of K⁺ ions penetrate from the concrete surface with the permeation of the electrolyte. The contents of penetrated K⁺ ions in N-15K, N-30K and FA-30K are higher than those in N-0K without carbonation. The reason of this is supposed that the carbonation of concrete increased the volume of the relatively large size pore in concrete as described in Section 3.3, which would accelerate the electrochemical migration of the electrolyte solution and K⁺ ions toward the steel in concrete. Moreover, the increase in the transference number of K⁺ ions in the carbonation area due to the decrease in that of OH⁻ could promote the electrochemical penetration of K⁺ ions. Figure 9 shows that Li⁺ ions penetrate concrete and...
reach almost all part of the cover concrete by using Li₂CO₃ solution as the electrolyte in realkalization. However, the content values of Li⁺ ions are smaller than the cases of specimens treated by using K₂CO₃ solution as shown in Fig. 8 due to the weaker concentration of Li₂CO₃ solution and the smaller transference number of Li⁺ ions. Such a difference in the contents of alkali metal ions in concrete would affect the repair effect of realkalization.

The pH value profiles in the RC specimens are shown in Fig. 10. The pH values of carbonated concrete show the lower level around 9, while the pH values of carbonated concrete were largely recovered to around 12 by applying realkalization. The pH values of the carbonated part of N-15K, N-30K and FA-30K, which were treated electrochemically after carbonation, were slightly lower than those of N-0K without carbonation. Since the pH values in concrete is electrochemically recovered by the penetration of the electrolyte and the supply of OH⁻ ions from the cathodic reaction at the steel into the liquid phase in concrete, in the cases of N-15K, N-30K and FA-30K, the solid phase of CaCO₃ formed by carbonation reaction remains after realkalization, which may result in the lower pH value in concrete than the case of non-carbonated concrete with the solid phase of Ca(OH)₂. FA-30K shows slightly lower pH values than the case of N-30K, which would be caused by the lower Ca(OH)₂ content due to the smaller amount of cement mass and the progress of the pozzolanic reaction of fly ash. Regarding the sort of electrolyte solution, the pH values of the carbonated part in N-30Li rise to the similar level as in case of N-30K. As shown in Section 3.1, the pH value of Li₂CO₃ solution is lower than that of K₂CO₃ but the OH⁻ ions produced by the cathodic reaction during the realkalization could compensate the difference in pH values of the electrolyte solution and the recovered pH values in N-30Li reached around 12 after the realkalization.

(2) Cl⁻ content profiles in RC specimens
The soluble Cl⁻/total Cl⁻ ratio profiles and the total Cl⁻ content profiles in RC specimens before and after realkalization are shown in Figs. 11 and 12 respectively. From Fig. 11, in the cases of N-15, N-30 and FA-30 without realkalization show higher values of soluble Cl⁻/total Cl⁻ in the carbonated part of concrete. It is considered that Cl⁻ ions fixed as Friedel's salt were released by the carbonation reaction of concrete as described in 3.2. As shown in Fig. 12, in the cases of N-15K, N-30K and FA-30K, Cl⁻ content values in the carbonated part of concrete decrease remarkably by applying realkalization. This can be explained by the electrochemical extraction of Cl⁻ ions in pore solution released from the hydration products due to the carbonation of concrete as shown in Figs. 6 and 11. Especially, N-30K and FA-30K show the highest effect of the chloride removal because of the larger carbonation depth reaching to around steel bar position. On the other hand, as shown in Fig. 11, the ratios of soluble Cl⁻/total Cl⁻ in the carbonation part are similar regardless of applying realkalization or not. Therefore, it is considered that a part of the fixed Cl⁻ ions remaining after realkalization could be released rapidly to form a new Cl⁻ equilibrium in the pore solution.
Regarding the sort of the electrolyte solution, N-30Li shows smaller values of soluble Cl-/total Cl- compared with the case of N-30K as shown in Fig. 11, which may be caused by the lower pH value of the Li2CO3 solution or a chemical reaction with Li2CO3 for promoting the fixing of Cl- ions in the pore solution. The detailed mechanism should be clarified by the further investigation.

3.5 Variations in electrochemical indexes of steel corrosion with time

(1) Variation curves of half-cell potential of steel bar in RC specimen with time

The variation curves of half-cell potential of steel bars in RC specimens during the cyclic drying and wetting period after the period of realkalization are shown in Fig. 13. According to this figure, non-treated and carbonated specimens show the values in the 90% probability of corrosion range defined by ASTM C876-91 due to the combined deterioration of premixed chlorides and carbonation of concrete, which results in the increased Cl- layer in concrete around the steel bar as shown in Fig. 12.

In Fig. 13, the electrochemically treated specimens show the negative potential around -1.0 V immediately after the cathodic polarization, although it recovered to the nobler potential than the cases of non-treated specimens within two weeks after completing realkalization, which may suggest the formation of the steel passive film after the treatment, likely because of the pH recovery of the carbonated concrete as shown in Fig. 10 and the removal effect of the Cl- ions as shown in Fig. 12. In addition, from Figs. 10 and 13, the higher the pH values of the concrete at the steel bar position after realkalization, the more positive the half-cell potential after realkalization recovers, which suggests that the pH value after realkalization affects the degree of corrosion protection for the steel in concrete. For example, the potential values of FA-30K are more negative than those of N-30K.

Regarding the influence of the sort of the electrolyte, the potential values of the case of N-30Li are nobler than those of N-30K. As shown in Figs. 6 and 11, the concentration of free Cl- ions in the pore solution of N-30Li would be lower than the case of N-30K after completing realalkalization, which may contribute to form a more protective condition against corrosion. However, since the lower pH value of the Li2CO3 may affect the long-term stability of the passive condition of the steel, long-term investigation should be continued.

(2) Variation curves of corrosion current density of steel bar in RC specimen with time

The variation curves of the corrosion current density of steel bars in RC specimens evaluated by the measured polarization resistance during the cyclic drying and wetting period after the period of realkalization are shown in Fig. 14. Final values of polarization resistance measured after cyclic dry-wet for 400 days and those of corrosion current density evaluated by the polarization resistance are shown in Table 3. The corrosion current density was calculated by the following equation.

\[ I_{corr} = \frac{K}{R_p} \]  

where \( I_{corr} \): corrosion current density (A/cm²), \( R_p \): polarization resistance (Ω·cm²), and \( K \): a constant (V) determined by metal type and environmental conditions. A proportional constant \( K \) of 0.026 V was used in this

![Fig. 13 Variation curves of half-cell potential of steel bars in RC specimens.](image)

![Fig. 14 Variation curves of corrosion current density of steel bars in RC specimens evaluated by polarization resistance.](image)

| Name     | N-0 | N-0K | N-15 | N-15K | N-30 | N-30K | N-30Li | FA-30 | FA-30K |
|----------|-----|------|------|-------|------|-------|--------|-------|--------|
| \( R_p \) (kΩ·cm²) | 26.33 | 11.01 | 4.26 | 6.22 | 6.42 | 3.59 | 6.13 | 12.88 | 2.15 |
| \( I_{corr} \) (μA/cm²) | 0.99 | 2.36 | 6.10 | 4.18 | 4.05 | 7.24 | 4.24 | 2.02 | 12.07 |

Table 3 Final values of polarization resistance and those of corrosion current density evaluated by the polarization resistance.
study, referring to previous studies (Stern and Geary 1957; Andrade and Alonso 1996).

The corrosion current density values of non-treated specimens tend to gradually increase during the cyclic drying and wetting period, which would be caused by the supply of moisture for accelerating the steel corrosion especially after the carbonation of concrete, while the corrosion current density values of FA-30 are relatively large from the beginning but decreasing with time likely because of the progress of the pozzolanic reaction of fly ash.

On the other hand, the corrosion current density values of the electrochemically treated specimens show larger than those of the non-treated specimens, although the corrosion current density values tend to decrease with time of the cyclic wet-dry period. Such larger corrosion current density would be obtained by the remarkably small cathode polarization resistance due to the large cathode polarization by applying realkalization. However, the corrosion current density values of the treated specimens are gradually decreasing with the progress of the cyclic wet-dry period, and the values of the treated specimens with the smaller carbonation depth, namely N-0K or N-15K become smaller than those of the non-treated specimens, which would mean that the actual protection effect against the steel corrosion is confirmed with the disappearance of the influence of the electric field formed by applying realkalization. Moreover, the corrosion current density values of N-30Li are smaller than those of N-30K, which agrees with the tendency of the results of the half-cell potentials shown in Fig. 13.

In Table 3, the estimated values of the corrosion current density of the treated specimens are generally larger than those in the non-treated specimens, because of the smaller polarization resistance after completing the treatment of realkalization. Considering the strong influence of the electric field on the polarization resistance values measured after realkalization, the data of estimated corrosion current density of the treated specimens could not be compared with those of the non-treated specimens directly. However, among the treated cases or non-treated cases, the obtained data could be compared with each other. In the cases of the non-treated specimens, the carbonated specimens show the larger estimated corrosion current density than the non-carbonated N-0, especially N-15 shows the largest value likely because of the condensed Cl- ions in front of the carbonated concrete part as shown in Fig. 12. In the cases of the treated specimens, the larger carbonation depth before applying realkalization results in the larger values of the estimated corrosion current density, which would mean that the corrosion protection effect obtained by realkalization is strongly affected by the carbonation condition of concrete before the treatment. Regarding the sort of the electrolyte solution, the specimen treated with the Li2CO3 solution shows the smaller estimated corrosion current density than the case of the specimen treated with the K2CO3 solution.

(3) Variations of polarization curves of steel bars in RC specimens with applying realkalization

The anodic polarization curves of steels in specimens at 4 weeks after completing realkalization are shown in Fig. 15. Although the potential values of steels in the treated specimens increase overall, the anodic polarization curves shift to the right direction in comparison with the cases of non-treated specimens, which means that the corrosion current density increases with the realkalization treatment apparently. On the other hand, the anodic polarization curves of the treated specimens show a steeper rise compared with the cases of the non-treated specimens. Therefore, the corrosion protection effect of steel bars after realkalization is evaluated by using Tafel slope.

The variation curves of the Tafel slope obtained from the anodic polarization curves during the cyclic drying and wetting are shown in Fig. 16. Previous studies have reported that the anode Tafel slope of corroding steel showed a value between 0.05 and 0.23 V/decade (Sugimoto 2009). In the cases of N-15, N-30 and FA-30, the Tafel slope values are around 0.2 V/decade, which suggests active steel corrosion taking the results of the half-cell potential into consideration. On the other hand,
the Tafel slope values of the treated specimens show relatively small level around 0.18 V/decade immediately after realkalization since the passivation film of steel bar disappeared temporarily because of the effect of cathodic polarization. However, the Tafel slope values of the treated specimens rapidly increase in the cyclic drying and wetting period of 2 to 4 weeks after completing realkalization. According to the past research (Ishibashi et al. 1997), it is reported that the steep rise of the polarization curve indicated the passivation of steel bar. Therefore, the passive condition would be formed by applying realkalization. The Tafel slope of FA-30K was the largest among the specimens. The reason of this would be that the pore structure of concrete was densified by the pozzolanic reaction of fly ash during the cyclic drying and wetting period after realkalization, which could suppress the supply of water and oxygen to the steel bar. However, since the Tafel slope values of the treated specimens are larger than the generally reported data (JCI 2018), the measured electrochemical reaction of the treated specimens may be different from that of the non-treated specimens.

For verifying the differences between the results shown in Figs. 14 and 16, it is necessary to confirm the actual corrosion state of steel bars in the specimens, which is discussed in the next part.

(4) Corroded area of steel bars taken from RC specimens
The data of corroded area ratio of steel bars taken from RC specimens subjected to the cyclic drying and wetting condition for 400 days after the period of realkalization and the calculated values of the protection ratio are shown in Fig. 17. The protection ratio “P” is calculated by using the following equation.

\[ P = \frac{(R_n - R_t)}{R_n} \times 100 \]  

where \( R_n \): corroded area ratio of a steel bar in a non-treated specimen (%), \( R_t \): corroded area ratio of a steel bar in a treated specimen (%)

According to this figure, the values of the corroded area ratio of the electrochemically treated specimens are greatly reduced compared to the cases of the non-treated specimens, which is different from the tendency of the steel corrosion estimated by the polarization resistance as shown in Table 3. From these results, it is confirmed that the protection effect against steel corrosion in concrete could be achieved by applying realkalization regardless of the difference of the deterioration condition before the treatment. Among the non-treated specimens, the values of corroded area ratio increase with the increasing of the carbonation depth of concrete before the treatment. Along with this, the values of corroded area ratio of the treated specimens also increase in proportion to the carbonation depth of concrete before the treatment. As a result, the protection ratio calculated by the corroded area ratio of steel bars in the electrochemically treated specimens and non-treated specimens subjected to the cyclic drying and wetting storage for 400 days after the period of realkalization achieved around 80% regardless of the difference of the deterioration condition before applying realkalization.

In Fig. 17, the corroded area ratio of FA-30K is almost same as the case of N-30K. Regarding the effect of fly ash mixing in carbonated concrete, the acceleration of the steel corrosion rate was estimated by the polarization resistance while the suppression of the corrosion rate was predicted by the Tafel gradient. These contrasting results indicate that the electrochemical evaluation of steel corrosion in fly ash mixed concrete should be investigated more as the future issue.

Regarding the sort of electrolyte solution, the realkalization using Li₂CO₃ solution could successfully suppress the steel corrosion after the treatment compared with the conventional case using K₂CO₃ solution within the condition of this study. As shown in Fig. 17, the protection rate of N-30Li achieves about 90%, while the protection ratio of N-30K is about 80%. However, the longer-term investigation is necessary because the lower pH value of Li₂CO₃ may affect the long-term durability after completing realkalization.

As a result of this study, the realkalization including the case of Li₂CO₃ electrolyte solution is a reliable repair method not only from the viewpoint of the pH recovery of the carbonated concrete but also from the viewpoint of the protection effect against steel corrosion in concrete even if the concrete contains Cl⁻ of 3.0 kg/m³. The duration of the repair effect should be clarified quantitatively by the future investigation using appropriate indexes for evaluating the re-passivation state of the steel affected by the electric field.

4. Conclusions
The results obtained in this study can be summarized as follows.
(1) The electrochemical removal of Cl\(^-\) ions from carbonated concrete and the electrochemical penetration of K\(^+\) ions from the electrolyte solution into carbonated concrete were both promoted compared with the case of non-carbonated specimen.

(2) Half-cell potentials of the electrochemically treated specimens reached more positive values than the cases of non-treated specimens regardless of the degree of carbonation before the treatment. The higher pH values around the steel bar after realkalization result in more positive half-cell potential with time after the treatment up to 400 days.

(3) The protection ratio calculated by the corroded area ratio of steel bars in the electrochemically treated specimens and non-treated specimens subjected to the cyclic drying and wetting storage for 400 days after the period of realkalization achieved around 80% regardless of the deterioration condition before applying realkalization.

(4) Applying realkalization using Li\(_2\)CO\(_3\) solution as the electrolyte could successfully suppress the steel corrosion after the treatment, comparable with the conventional case using K\(_2\)CO\(_3\) solution within the conditions of this study.

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