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Application of electrochemical techniques for the control of cracks and steel corrosion in concrete

J-S. RYU[1]* and N. OTSUKI[2]
[1] *Department of Civil and Environmental Engineering, University of California, 721 Davis Hall, Berkeley, CA 94720, USA*
[2] *Department of International Development Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*
*(*author for correspondence)*

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Abstract

Electrochemical techniques are becoming increasingly popular as a means of rehabilitating deteriorated reinforced concrete. In this paper we explore the possibility of using an electrodeposition technique for repairs of land-based cracked concrete structures and investigate the effect of this technique on various concrete properties. Concrete specimens reinforced with steel rebars were used as test specimens in this study. The specimens were first precracked by exposing rebars to chloride-induced corrosion, and then immersed in a solution of zinc sulfate and subjected to a constant d.c. current. The current was applied between the reinforcing steel in the concrete and an external electrode immersed in the solution for eight weeks. The degree of crack closure, water permeability, condition of reinforcing steel, and chloride concentration were investigated in order to assess the effectiveness of this method as a potential rehabilitation technique. The results indicate that the formation of electrodeposits caused the closure of cracks and led to improvement of the concrete watertightness. In addition, the investigation shows that the application of the electrical current increases the passivity of steel in concrete.

1. Introduction

Precipitation of electrodeposits on a concrete surface has been recently proposed to repair cracks in corroded reinforced concrete [1]. Investigations showed that it was possible to close the crack in reinforced concrete by applying an electric current, especially under a marine environment where other traditional repair techniques are inefficient.

When an anode is set up in seawater and reinforcing steel in concrete acts as cathode, Ca^{2+} and Mg^{2+} migrate to the surface of the concrete. In this condition, when there is a crack in the concrete, electrical flow becomes remarkably large near the crack and Ca^{2+} and Mg^{2+} migrate through the cracks. Ca^{2+} and Mg^{2+} react with CO_3^{2-} or OH^-, which comes from the cathode (reinforcing bar), and $CaCO_3$ and $Mg(OH)_2$ are formed, respectively, as deposition products. The purpose of electrodeposition technique is to fill the crack in concrete and to coat the concrete surface by electrodeposits with chemical compounds such as $CaCO_3$ and $Mg(OH)_2$. These layers of inorganic compounds are known to provide a physical barrier, and reduce the penetration of gas or solution from outside to the inside of concrete. Moreover, the deposition products can improve the microstructure on the surface of the concrete. This can be accomplished by feeding a weak direct current between the reinforced steel in a concrete structure and an electrode located in seawater. As concrete itself is a conductor, a hard layer of electrodeposit is formed on the submerged surface of concrete.

The electrodeposition technique has been developed by several researchers in the last ten years and applied to marine structures. The amount of information available in the literature is limited, however, because previous researchers have considered the electrodeposition method almost exclusively as a technique for marine structures. Since the electrodeposition method can close concrete cracks and can improve the penetration resistance of concrete, with proper application methods it can also be used for the rehabilitation of concrete structures on land.

The present research builds on earlier efforts and examines further the materials likely to be used in the practical application of this method. Experiments were performed to examine the feasibility of the electrodeposition technique as a means of repair for cracked reinforced concrete, as well as to investigate the effects of this method on crack closure, permeability and reduction of steel condition.

Table 1. Percentage chemical composition of steel bar

C	Si	Mn	P	S	Fe	Σ
0.13	0.12	0.49	0.03	0.02	99.2	100

Table 2. Mixture proportion of concrete

W/C /%	Water /kg m^{-3}	Cement /kg m^{-3}	Coarse agg. /kg m^{-3}	Sand /kg m^{-3}	NaCl /kg m^{-3}	Ad* /m*l* m^{-3}
70	165	236	1032	837	10	9.4

* Air-entraining agent.

2. Experimental methods

2.1. *Materials and mix proportions*

A normal portland cement (Blaine fineness 3270 cm^2 g^{-1}, density 3.17, ignition loss 0.6%) was used as the binder in this investigation. The fine aggregate was river sand (density 2.62, water absorption 1.73%, fineness modulus 2.8) while coarse aggregate was crushed sandstone with $D_{\max}$ of 20 mm (density 2.63, water absorption 0.68%, fineness modulus 6.68) and Japanese Industrial Standard deformed steel bars were used. The diameters of the steel bars were 13 mm and 6 mm for main bars and stirrups, respectively. The chemical composition of the steel bar is given in Table 1.

The mixture proportion of concrete is shown in Table 2. The slump of fresh concrete was 12 ± 1 cm and air content was 4 ± 1%. The water-cement ratio was 0.7. To accelerate the corrosion process, 10 kg m^{-3} of solid NaCl was added during mixing of the concrete.

2.2. *Specimens and exposure condition*

Twelve reinforced concrete prism specimens, having a cover depth of 2 cm, with the dimensions of 15 cm × 15 cm × 125 cm were made for investigation. The specimens were cured for 28 days (temperature 20 ± 2 °C, and relative humidity (RH) 80 ± 5%). After curing, the specimens were transferred to the outside exposure site. During the 18 months exposure period (temperature −5 to 35 °C), saltwater solutions (3.5% by weight) were sprayed twice a week over the specimens to accelerate the corrosion process. The details of the beam shape and crack shapes in 18 months exposure beam are shown in Figure 1. The maximum recorded crack width in the prism was 0.5 mm. After the exposure cycle was completed, the specimens were sealed with epoxy resin except for the cracked side. They were placed in plastic containers crack side downward containing a zinc sulfate solution ($ZnSO_4$, 0.1 mol dm^{-3}). The environmental conditions (temperature 20 ± 2 °C, and relative humidity (RH) 80 ± 5%) were kept constant during eight weeks exposure to external solution ($ZnSO_4$).

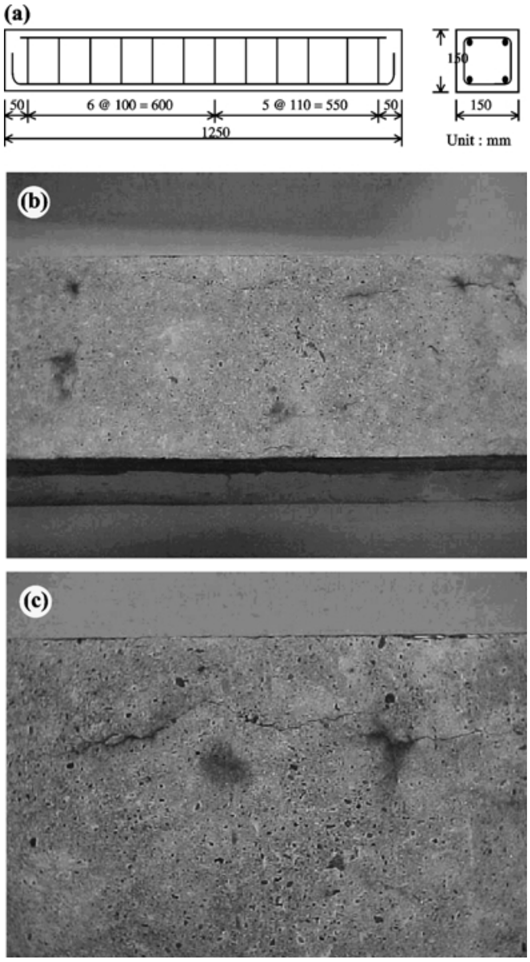

Fig. 1. Details and crack shapes of beam. (a) Details; (b) crack shapes of beam exposed outside for 18 months; (c) close-up of upper figure.

2.3. *Electric current and external solution*

A direct electric current (0.5 A m^{-2} at 1.5–4.0 V) was passed between the embedded reinforcing steel and a titanium mesh anode immersed in the external $ZnSO_4$ solution and positioned at the bottom of the container. The current was applied for eight weeks.

Using previous investigations conducted by the authors as a basis for this study [2, 3], a zinc sulfate solution ($ZnSO_4$) was chosen as the immersion solution electrolyte during current passage. This solution is slightly acidic and safe for the human body. It is not considered harmful to the surface of concrete, if the time of application is not excessive [4]. The depth of the solution was at the level of the embedded reinforcing steel. The cover depth of concrete was 2 cm. To maintain a constant concentration, the solution was replaced every week.

2.4. *Methods of testing*

2.4.1. *Measurement of precipitation*

The rate of crack closure was qualitatively measured every week from the beginning of the test. The rate of crack closure was defined as the percentage of the length of closed crack with respect to the total length of crack

[5–7]. Also, a visual observation and the photographing of the crack on the concrete surface were carried out in order to examine the precipitation of electrodeposits.

2.4.2. *Measurement of water permeability*

A modified method of the Japanese Industrial Standard Water Permeability Test B (JIS A 6909) was used to evaluate the coefficient of permeability every four weeks [8]. It was obtained by measuring the change of water level in the pipette after 24 h while the water percolated in the cracked surface of the beam specimen undergoing electrodeposition. To avoid an error due to the evaporation of water, liquid paraffin was placed on the water surface in the pipette.

2.4.3. *Measurement of steel corrosion*

The electrochemical measurements of the half-cell potential and the passivity grades of the reinforcing steel in concrete were performed in order to examine the degree of the corrosion of the reinforcing bars using a portable corrosion monitor. The passivity grades were evaluated by using the anodic polarization curves of the steel. The passivity grades are defined as follows [9].

(i) *Grade 0* indicates no passivity between +0.2 and +0.6 V; anodic current density is over 100 μA cm^{-2} at least at one point.
(ii) *Grade 1* indicates a certain degree of passivity, between +0.2 and +0.6 V; anodic current density is between 10 and 100 μA cm^{-2}.
(iii) *Grade 2* indicates a certain degree of passivity that is better than grade 1, between +0.2 and +0.6 V; anodic current density is over 10 μA cm^{-2} at least at one point.
(iv) *Grade 3* indicates a certain degree of passivity that is better than grade 2, between +0.2 and +0.6 V; anodic current density is between 1 and 10 μA cm^{-2}.
(v) *Grade 4* indicates a certain degree of passivity that is better than grade 3, between +0.2 and +0.6 V; anodic current density is over 1 μA cm^{-2} at least at one point.
(vi) *Grade 5* indicates excellent passivity, between +0.2 and +0.6 V; anodic current density is always less than 1 μA cm^{-2}.

2.4.4. *Measurement of chloride concentration*

After electrodeposition treatment, drilled concrete samples were taken from the crack locations at depths of 1.5 to 2.5 cm from the bottom that was exposed to the solution. The samples were used to determine the chloride concentrations at the level of the reinforcing steel. The chloride content was measured according to the Japan Concrete Institute method [10].

3. Results and discussion

3.1. *Closure of concrete cracks*

The concept of electromigration can be applied to the concrete, because concrete is a porous material having an electrolyte in the form of pore solution. The electrodeposition process has been shown to rehabilitate marine concrete structures by using seawater as the electrolyte. In this investigation, for the purpose of selecting the external solutions which can precipitate the electrodeposits on the surface of land-based concrete, one type of solution (zinc sulfate) was chosen and its characteristics was previously studied [3].

Table 3. Results of rate of crack closure (percentages)

Crack width	Time of charging			
	0 week	2 weeks	4 weeks	8 weeks
0.1 mm	0	61	77	92
0.5 mm	0	42	63	89

The development of crack closure is shown in Table 3. The rate of crack closure increases with the testing period and the rate of closing of the 0.1 mm crack is slightly faster than that of the 0.5 mm crack. It is also observed from Table 3 that the rate of crack closure increases quite rapidly during the first two weeks and that cracks are closed about 90% at the end of the testing period of eight weeks. The electrodeposits penetrate into the crack at a depth of 3–6 mm.

The deposition pattern on the concrete surface after electrodeposition is shown in Figure 2. It is observed that electrodeposition developed on the concrete surface and along the crack. The deposits were analysed using an X-ray diffraction technique, and the results indicate that the electrodeposit is ZnO of density 5.7 g cm^{-3}. The results of the X-ray diffraction test are shown in Table 4. The properties of the electrodeposits and the concrete are shown in Table 5. The chemical reactions in the solution are shown in Table 6.

3.2. *Water permeability*

A modified permeability test was conducted to examine the watertightness of the electrodeposited concrete. Table 7 shows the relationship between the length of electrodeposition and the coefficient of permeability. From this table, it is observed that the water permeability decreased with the increase in the length of electrodeposition time, and it reached about 3.7×10^{-8} cm s^{-1} (0.1 mm crack, after eight weeks of charging). Such a low permeability was close to that of a non-cracked specimen. This decrease of the permeability was attributed to the closure of the crack and the refinement of the concrete surface by the precipitation of electrodeposits. From the results of the permeability test, the electrodeposits on the concrete surface reduced the coefficient of water permeability and helped to improve the concrete quality.

3.3. *Condition of reinforcing steel*

Due to the electrical potential difference between the anode and the cathode, water reduces to hydroxide ions

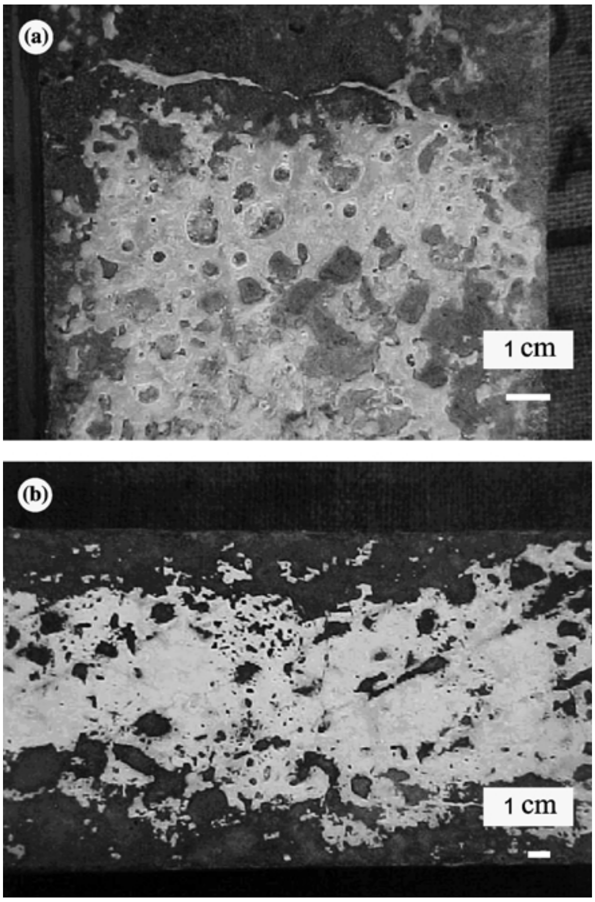

Fig. 2. Deposition pattern on concrete surface. (a) Cracked part; (b) noncracked part.

Table 4. Results of X-ray diffraction test

No.	2θ	D	I	I/I_0	ZnO	I/I_0
1	31.72	2.819	4329	61	2.82	70
2	34.38	2.606	4168	59	2.60	60
3	36.20	2.479	7042	100	2.48	100
4	47.48	1.913	1291	18	1.91	30
5	56.54	1.626	2462	35	1.63	40
6	62.80	1.478	1735	25	1.48	40
7	67.90	1.379	1586	23	1.38	30
8	69.90	1.360	823	12	1.36	10

Table 5. Properties of electrodeposits and concrete

Property	Electrodeposits	Concrete (28 days)
Density/g cm^{-3}	5.7	2.8
Bulk density/g cm^{-3}	4.8	2.4
Vickers hardness/HV0.01	100–200	–
Compressive strength/MPa	6–20	20–50
Bending strength/MPa	5–7	3–6
Thermal conductivity /kcal nh °C^{-1}	1.18	1.3
Young's modulus/GPa	0.02	0.03

Table 6. Chemical reactions in the solution

Aqueous reaction
$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$ $H_2O \rightarrow OH^- + H^+$
$Zn^{2+} + 2OH^- \rightarrow ZnO \downarrow + H_2O$

Electrode reaction
(anode) $2H_2O \rightarrow O_2 \uparrow 4H^+ + 4e^-$
(cathode) $2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$

Table 7. Results of water permeability test (cm s^{-1})

Crack width	Time of charging		
	0 week	4 weeks	8 weeks
0.1 mm	7.8×10^{-4}	6.4×10^{-7}	3.7×10^{-8}
0.5 mm	2.4×10^{-2}	7.6×10^{-6}	4.2×10^{-7}

at the reinforcement. At the external conductor, water or hydroxide is oxidized to oxygen and hydrogen ions. These reactions are referred to as electrolysis, which results in a pH increase around the reinforcement.

The passivity grades of the reinforcing steel were evaluated from the anodic polarization curve. The reinforcing steel in the non-charged concrete specimens (cracked but not exposed to electrical current) show 0–1 passivity grades, indicating almost complete loss of passivity. However, the passivity grade of reinforcing steel in the charged concrete specimens (cracked and exposed to electrical current) was 2–4 degrees of passivity. Comparing the passivity grades of the non-charged and the charged specimens, it can be inferred that the passivity grades of the charged specimen are comparatively superior to those of the noncharged specimen, indicating less corrosion activity in the charged specimen.

The results of the half-cell potential of the reinforcing steel measured before charging contrasted to three months after charging are shown in Table 8. A dramatic reduction in the half-cell potential is observed indicating that the steel passivated in most cases. This is probably due to an increase in the pH value near the reinforcing steel due to the fact that the pH increases at the location of the reinforcing steel due to electrolysis.

3.4. *Desalination*

As a result of the applied potential difference, negatively charged ions (chloride, hydroxide) will move towards the anode and positive ions (sodium, potassium) will move to the cathode. This process is called electromigration or electrophoresis. Electromigration is a very important process with regard to chloride removal, because it transports chloride ions away from the

Table 8. Results of half-cell potential test (mV)

Specimen	Case 1	Case 2	Case 3	Case 4
Before	−456	−372	−506	−320
After	−121	−174	−189	−216

Table 9. Results of decrease in chloride content (percentages)

Specimen	Time of charging		
	0 week	4 weeks	8 weeks
Case 1	0	64	72
Case 2	0	56	67

reinforcement towards the anode and into the external electrolyte.

The measurements of chloride ion concentrations in the concrete were carried out to examine the effectiveness of the electrodeposition technique as a means of removing chloride ions from chloride-containing concrete specimens. Table 9 indicates the chloride removal efficiency near the reinforcing steel in the specimen. It can be seen that the efficiency of chloride removal increases with the length of testing. After eight weeks of charging, about a 70% decrease in the chloride content was observed around the reinforcing steel. This seems to indicate that negative-charged chloride ions were removed from the concrete and migrated toward the anode placed in the external solution.

4. Conclusions

This paper shows the potential for an application of the electrodeposition technique in the rehabilitation of deteriorated concrete, laying the groundwork for research on the practical application of this method on real structures. The following conclusions can be drawn from the present study:

(i) The electrodeposition started from the fracture surface of the crack and gradually filled and closed the crack in the concrete. The electrodeposits penetrated to a depth of 3 to 6 mm into the crack.

(ii) The electrodeposits inside the crack and on the surface reduced the coefficient of water permeability and helped to improve the quality of the concrete.

(iii) The passivity and half-cell potential measurements showed that the reinforcing steel in the concrete was re-passivated by applying the electrodeposition technique.

(iv) The electrodeposition treatment effectively reduced the amount of chloride ions in the concrete. After eight weeks of continuous charging, a decrease of about 70% in the chloride ion concentration was observed around the reinforcing steel.

References

1. H. Sasaki and M. Yokoda, Proceedings of Annual Conference of JCI, The Japanese Concrete Institute, Kyoto (1992), p. 849.
2. N. Otsuki and M. Hisada, Proceedings of Annual Conference of JSCE, The Japanese Society of Civil Engineering, Tokyo (1997), p. 332.
3. N. Otsuki, M. Hisada and J.S. Ryu, *J. Japanese Soc. Civil Eng.* **42** (1999) 201.
4. A.J. Hondel and R.B. Polder, *Concrete Repair*, Sep to Oct. (1992) 19.
5. J.S. Ryu and N. Otsuki, Proceedings of ACI 4th International Conference on the 'Repair of Concrete Structure' Seoul (2000), p. 324.
6. N. Otsuki and J.S. Ryu, Proceedings of 5th International Conference of CANMET/ACI, SP-192-56, Barcelona (2000), p. 917.
7. J.S. Ryu and N. Otsuki, Proceedings of 15th International Conference of SMiRT, Vol. VI Seoul (1999), p. 65.
8. JIS Handbook 24-1, Architecture/Material Part, (1995) 764.
9. S. Nagataki, T. Fukute and N. Otsuki, *J. Japanese Soc. Civil Eng.* **20** (1993) 59.
10. JCI-SC 13, Standard Test Method for Corrosion and Passivation of Reinforcing Steel in Concrete Structure, The Japan Concrete Institute, 150 (1987).