

Development of a galvanic sensor system for detecting the corrosion damage of the steel embedded in concrete structure

Part 2. Laboratory electrochemical testing of sensors in concrete

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Abstract

The correlation between sensor output and the corrosion rate of steel bar was confirmed in concrete environment. Open-circuit potential, linear polarization resistance (LPR) measurement and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion behavior of steel bar embedded in concrete. Also, galvanic current measurements of designed sensors were conducted to obtain the charge of sensor embedded in concrete.

In this study, the results of corrosion behavior of reinforcing steel showed a consistence among the data obtained by open-circuit potential monitoring, LPR and EIS measurements. Steel/copper sensor showed a good correlation in concrete environment between sensor output and corrosion rate of steel bar. However, there was no relationship between steel/stainless steel sensor output and corrosion rate of steel bar due to the low galvanic current output. Through the relationship between the steel/copper sensor output and the corrosion rate of reinforcing steel, the real corrosion damage of the reinforcing steel can be detected. Consequently, this confirms that the galvanic sensor system is a good method for detection of corrosion in reinforced concrete.

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1. Introduction

It has been stated that the combination of concrete and reinforcing steel is an optimal one not only because of the mechanical performance but also from the point of view of long-term performance. Because steels embedded in concrete are protected from corrosion by a thin oxide layer that is formed and maintained on their surfaces because of the highly alkaline environment ($\text{pH}>13$) of the surrounding concrete. In spite of the theory and favorable performance record in many structures, corrosion of steel in concrete has become a considerable durability problem in mild as well as in severe climatic conditions. This problem has reached alarming proportions in the past three decades, leading to

very high repair costs, sometimes above the initial construction cost, or in extreme situations, to the final collapse of the structure [1–4].

The most important causes of corrosion initiation of reinforcing steel are the ingress of chloride ions and carbon dioxide to the steel surface. After initiation of the corrosion process, the corrosion products (iron oxides and hydroxides) are usually deposited in the restricted space in the concrete around the steel. Its formation within this restricted space sets up expansive stresses which crack and spall the concrete cover. This in turn results in progressive deterioration of the concrete. As a result, the repair costs nowadays constitute a major part of the current spending on infrastructure. Moreover, the repair operation themselves are quite complex and require special treatments of the cracked zone, and in most instances the life expectancy of the repair is limited. Accordingly, sensor systems are needed to enable

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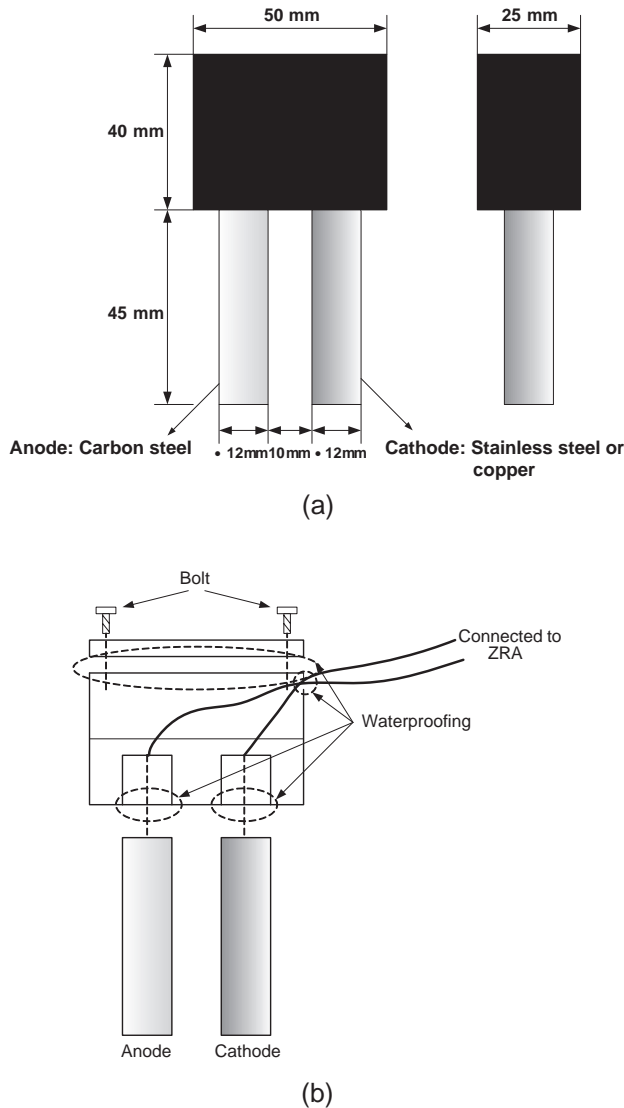


Fig. 1. Galvanic sensor consisting of a black steel and noble metal cathode: (a) geometry of the galvanic sensor, (b) electrical connection of sensor elements.

owners of the structures to monitor the corrosion risk and to take protective measures before severe damage was caused. Corrosion monitoring can give more complete information of changing condition of a structure in time [1,5–7].

In the previous part of this study (part 1) [8], galvanic sensor system was examined in saturated $\text{Ca}(\text{OH})_2$ solution with and without 3.5 wt.% NaCl addition. An ingress point in time of chlorides can be detected by measuring the

galvanic current between the two metals. Furthermore, through the relationship between the sensor output and the weight loss of steel, real corrosion damage of steel embedded in concrete can be detected. In part 2 (this paper), the galvanic sensor system was evaluated in a concrete environment with 0.5 water-to-cement ratio. The purpose of the present study was to present the performance of corrosion sensors in concrete and to establish the reliability of the system. The sensor uses well-known principles of galvanic corrosion and consists of two dissimilar metals, which generate a current by a natural potential difference.

2. Experimental procedures

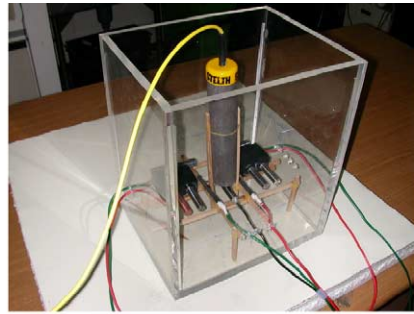
2.1. Sensor system

Two types of corrosion detection sensors were designed, one galvanic cell consisting of black steel (anode) and copper (cathode) electrodes, and the other galvanic cell consisting of black steel (anode) and stainless steel (cathode) electrodes. These electrodes were mounted in an epoxy resin, which insulated them from each other. The geometry of corrosion detection sensor is schematically shown in Fig. 1. The anode material used in this investigation was a steel bar for concrete reinforcement. Type 304 austenitic stainless steel (UNS S30400) and 99.99% pure copper were used as the cathode materials. The chemical composition of sensor materials is given in Table 1. All specimens were fabricated in the shape of a bar with a diameter of 12 mm and polished using 600-grit silicon carbide (SiC) paper for the final step. After polishing, specimens were rinsed in distilled water ultrasonically and dried with methanol before placement in the test fixture.

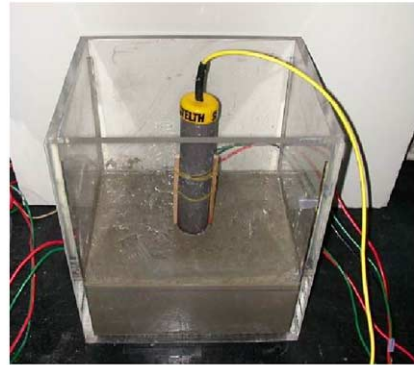
To evaluate the correlation between sensor output and corrosion rate of reinforcing steel in a concrete environment, sensor system was designed (Fig. 2). In the middle of the acrylic cell, a steel bar with a diameter of 12 mm, a length of 50 mm served as working electrode (WE) and there are high-purity graphite rods with a diameter of 8 mm, a length of 50 mm on both sides of the steel bar as counter electrode. The depth between the top of the steel and the surface of the concrete was 50 mm. All potential values were reported with respect to a copper/copper sulfate (Cu/CuSO_4) electrode (CSE) positioned in the center, right above the

Table 1
Chemical composition of sensor elements

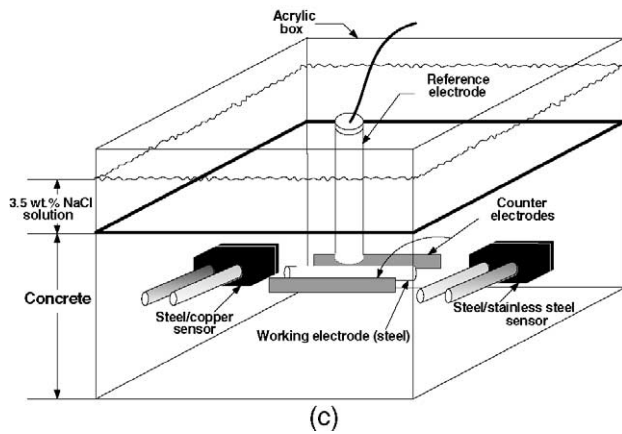
Designation	Composition (wt.%)								
	C	Si	Mn	P	S	Cr	Ni	Cu	Fe
KS D3504	0.22	0.14	0.59	0.02	0.025	–	–	–	bal
Stainless steel	0.08	1.0	2.0	0.045	0.03	18.2	8.2	–	bal
Copper	–	–	–	–	–	–	–	99.99	–



(a)



(b)



(c)

Fig. 2. Experimental setup of galvanic sensor system for electrochemical measurements.

steel bar. Two types of galvanic sensors, steel/copper and steel/stainless steel sensors, were placed in same height with steel bar (Fig. 2).

2.2. Electrochemical testing

All electrochemical tests were conducted at designed sensor system under complete immersion in 3.5 wt.% NaCl solution. Open-circuit potential monitoring test, linear polarization resistance measurement and electrochemical impedance spectroscopy (EIS) were made using an EG and G Model 273A potentiostat and Model 1025 frequency response detector controlled by Model 398 electrochemical impedance software. Linear polarization resistance measure-

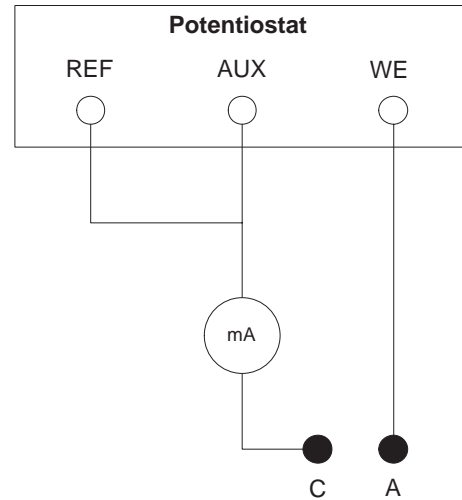


Fig. 3. Zero-resistance ammeter for measurement of galvanic current at shot circuit.

ments were carried out within ± 20 mV with respect to the corrosion potential (E_{corr}). EIS measurements were performed in the frequency range between 100 kHz and 10 mHz. Sinusoidal voltage of ± 10 mV was supplied, and direct current (DC) potential was set to the corrosion potential.

Galvanic current measurements were performed using a zero resistance ammeter (ZRA) in a Gamry potentiostat Model PC3-750. The carbon steel was connected to the working electrode terminal (anode), the stainless steel and copper to the reference electrode terminal (cathode), which was connected to the counter electrode terminal (Fig. 3). The sensor elements are electrically coupled together whether the galvanic current was measured or not. The galvanic current was measured for 30 min every 10 days. The averages of the measured values were taken after their stabilization within the range of stabilized current.

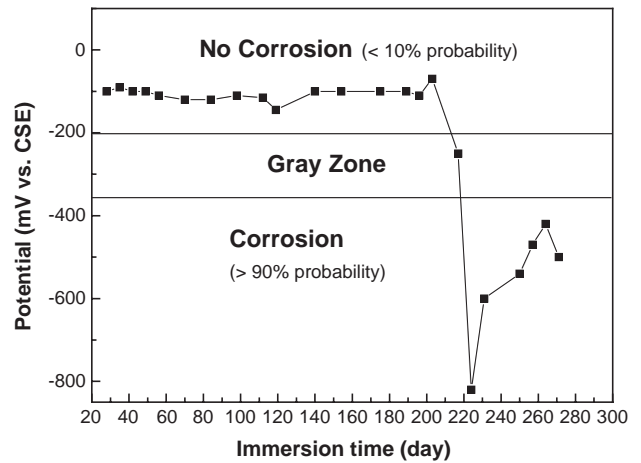


Fig. 4. Open-circuit potential evolution of reinforcing steel compare with ASTM C876 criteria.

3. Results and discussion

3.1. Electrochemical behavior of steel bar

The time-to-corrosion is the time required for chlorides to penetrate the concrete cover in sufficient quantities to initiate corrosion and was determined with corrosion potential. Fig. 4 shows the corrosion potential of the steel bar in concrete. The readings were in the range -250 to -150 mV vs. CSE until 210 days after immersion, corresponding to a state of passivity based on the Pourbaix diagram [9]. After 210 days of exposure, a sharp drop in the corrosion potential was observed, which indicated the initiation of the corrosion process. According to ASTM C 876, if the potential becomes more negative than -350 mV vs. CSE, there is a greater than 90% probability that corrosion of reinforcing steel is occurring [10].

Corrosion rates of steel bar were measured by LPR. Using the polarization resistance (R_p) obtained from LPR measurement, the corrosion rate can be determined through the following equation [11,12]:

$$i_{\text{corr}} = \frac{\beta_{\text{ox,M}} \times \beta_{\text{red,C}}}{2.3 \times R_p \times (\beta_{\text{ox,M}} + \beta_{\text{red,C}})} \quad (1)$$

Corrosion rate (mm/y)

$$= \frac{0.00327 \times i_{\text{corr}} (\mu\text{A}/\text{cm}^2) \times \text{E.W.}}{\text{Density (g}/\text{cm}^3)} \quad (2)$$

where $\beta_{\text{ox,M}}$ is the anodic Tafel constant, $\beta_{\text{red,C}}$ is the cathodic Tafel constant, 0.00327 is the metric and time conversion factor, and E.W. is the equivalent weight in grams.

Fig. 5 shows the variation of corrosion rate measured by LPR measurements with immersion time. After 210 days of immersion, corrosion rate increased significantly, which indicates the onset of the corrosion of steel bar.

For better information on the mechanism of the corrosion reaction, impedance measurement was performed. Fig. 6

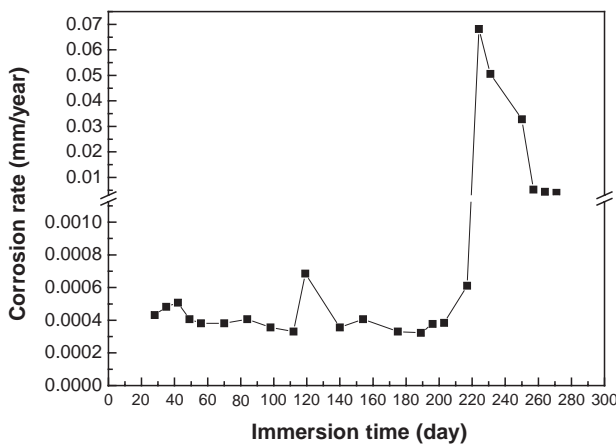


Fig. 5. Corrosion rate of reinforcing steel calculated from linear polarization measurement.

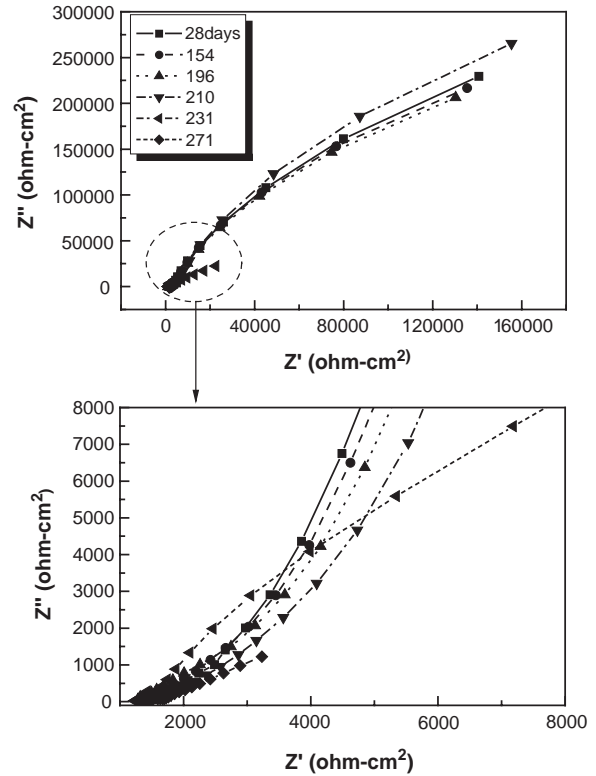


Fig. 6. Impedance spectra in Nyquist plot of reinforcing steel.

shows the typical Nyquist plots for the steel bar after EIS tests. These spectra are constituted by a capacitive arc at experimental frequency region. The shape of spectra with respect to time was similar, but, after 210 days, this was a significant reduction in the diameter of the semicircle corresponding to the charge transfer resistance. The electrical equivalent circuit represented in Fig. 7 was applied to model the EIS data for steel bar. The equivalent circuit consists of the following element: an ionic resistance R_s in the electrolyte filling the pores; a capacitance C_{film} and a resistance R_{film} for surface layer of steel bar; and a capacitance C_{dl} and a charge transfer resistance R_{ct} for steel bar. The presence of depressed semi-circles suggests a non-ideal behavior of the capacitors, leading to the introduction of the constant phase element (CPE) in the equivalent circuits. CPE is widely used in data fitting to allow for depressed semicircles [13]. The capacitance is replaced with a CPE for a better fit quality. The fitting

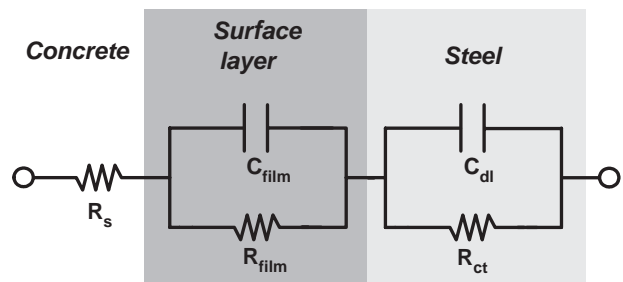


Fig. 7. Equivalent circuit for the corrosion behavior of reinforcing steel.

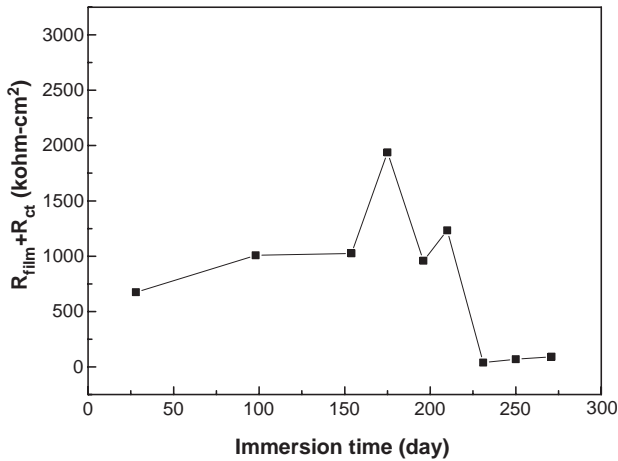


Fig. 8. The sum of R_{film} and R_{ct} vs. immersion time.

procedure was performed using a ZsimpWin program. The simulated sum of R_{film} and R_{ct} are presented in Fig. 8. Until 175 days of immersion, the sum of R_{film} and R_{ct} had increased with increasing time, which induced the stable layer on the steel bar surface. After 196 days of exposure, however, the sum of R_{film} and R_{ct} tend to decrease due to onset of breakdown in the passive film. A drop in the sum of R_{film} and R_{ct} was observed after 210 days. Accordingly, it is considered that corrosion process of steel bar started after 210 days of immersion. This result corresponds to the results of open-circuit potential monitoring and linear polarization resistance measurement.

3.2. Galvanic corrosion test of sensor

Fig. 9 shows the galvanic current density obtained from galvanic sensor versus time. The galvanic current density maintains a steady state with time close to zero. After 80 days, the galvanic current densities started to be measured in negative values for both steel/copper and steel/stainless steel sensors. This indicated that the steel acted as a cathode, whereas the copper and the stainless steel acted as anodes,

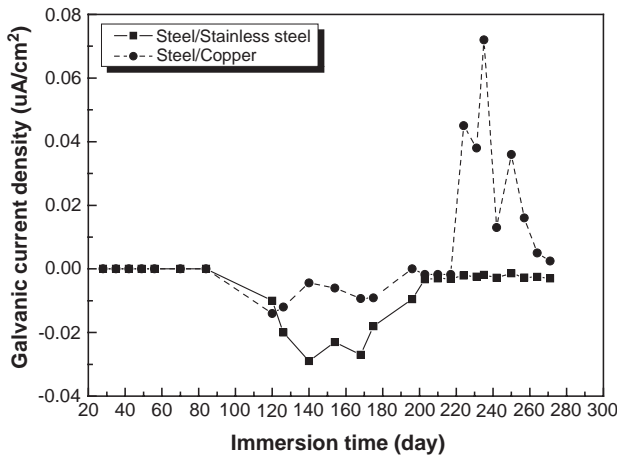


Fig. 9. Galvanic current density as a function of time for sensors in concrete.

due to the passivation of steel. From results in Part 1, it was found that the potential of steel was higher than that of copper and stainless steel in chloride free $Ca(OH)_2$ solution. However, the potential of steel decreased rapidly in the initial stage of immersion in saturated $Ca(OH)_2$ solution with 3.5 wt.% NaCl addition. The reason for this is that chloride ions destroyed the passive films of steel. Thus, after 217 days, it was observed that galvanic current density of steel/copper sensor increased significantly. The trend of galvanic current density of steel/copper sensor has a strong resemblance to that of electrochemical behavior of steel bar. However, steel/stainless steel sensor maintains a galvanic current density value of nearly zero at the time of corrosion.

Electrochemical reactions either produce or consume electrons. Faraday’s law is the connecting relationship between the current density, $i=I/area$, and other expressions of corrosion rate. The rate of electron flow to or from a reacting interface is a measure of reaction rate. Electron

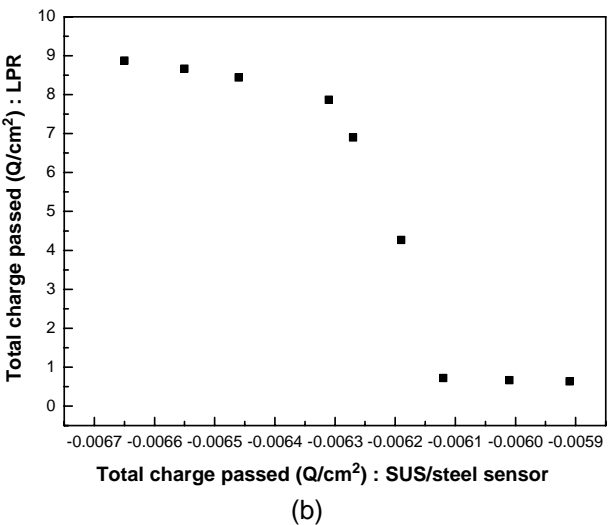
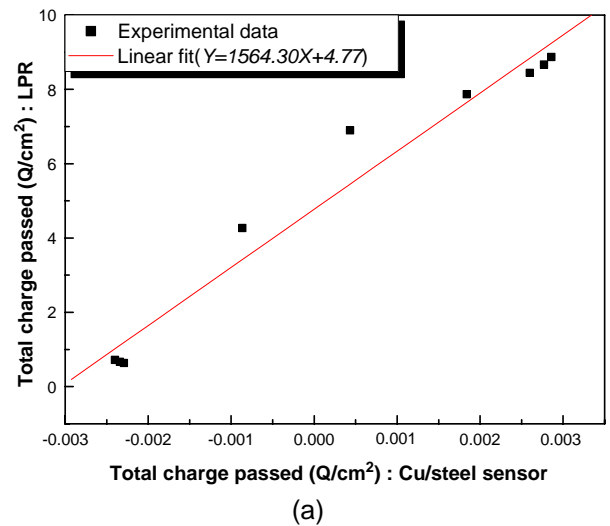


Fig. 10. The relationship between the charges of reinforcing steel obtained from linear polarization resistance measurement (LPR) and sensor system: (a) steel/copper sensor system, (b) steel/stainless sensor system.

flow, that is current (I), is expressed in amperes (A) or coulombs (C) per second (s), where 1 A is equal to 1 C of charge (6.2×10^{18} electrons) per second. The galvanic current and time were integrated to the coulomb value based on Faraday's law [11,14,15].

$$Q = \int I(t)dt = \frac{nFw}{a} \quad (3)$$

where F is Faraday's constant (96,500 C/equivalent), n is the number of equivalents exchanged, w is the weight loss, a is the atomic weight and Q is the total charge.

Fig. 10 presents the correlation between the coulomb values of the galvanic sensor and the steel bar obtained from linear polarization resistance (LPR) measurement. A good correlation was observed between steel/copper sensor and steel bar. Accordingly, galvanic current of steel/copper sensor makes a detection of corrosion initiation time and corrosion rate possible. In previous part of this study, the output of steel/stainless sensor indicated the better linear relationship than that of steel/copper sensor in simulated concrete pore solution. In this part of the study, however, there is no correlation between steel/stainless steel sensor and steel bar because the resistance of the concrete is too high to support the galvanic current [8]. Therefore, the steel/stainless steel sensor is not suitable for detecting corrosion damage of reinforcing steel.

4. Conclusions

From this investigation, the following conclusions could be drawn:

1. The steel/copper sensor could provide a useful non-destructive method of determining actual corrosion rate. This was confirmed by electrochemical measurements in concrete.
2. The onset of corrosion could be detected by measuring the galvanic current of steel/copper sensor.
3. The steel/copper sensor is a reliable corrosion detection system in concrete environment. However, steel/stainless steel sensor is not suitable for detecting corrosion damage of reinforcing steel due to the low current output. Through the relationship between the steel/copper sensor output and the corrosion rate of reinforcing steel, onset of corrosion and corrosion rate of the reinforcing steel could reliably be detected.
4. However, several issues remain to be solved in the practical application of this galvanic sensor system to structures in field, including reliable sensor design,

effects of concrete chemistry and cathodic protection. If these problems are solved, the system could be a valuable tool for continuous evaluation of the effectiveness of corrosion control methods at difficult accessible areas.

Acknowledgments

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