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An experimental study of the cathodic polarization of the reinforcement in chloride contaminated concrete

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Abstract
This paper reports an experimental study on the influence of chloride contamination on the polarization resistance, concrete resistivity, and the potential shift of concrete reinforcement under different cathodic protection (CP) current densities. Reinforced and non-reinforced concrete specimens of varied chloride contents and exposed to ventilated condition at 50±5% relative humidity and room temperature of 20±3°C were investigated. Five levels of cathodic current densities of 5, 10, 15, 20 and 25 mA/m² were applied during the cathodic polarization. A new correlation between the concrete resistivity and reinforcement corrosion rate was obtained and compared with previous work. The effect of concrete resistivity and polarization resistance on the reinforcement potential shift were also discussed. In the last, based on the findings of the research, some useful conclusions can be drawn.

Keywords: “Cathodic protection; concrete resistivity; polarization; reinforced concrete”
**Introduction**

Corrosion of steel reinforcement is the major cause of premature deterioration of reinforced concrete structures [1]. Previous research studies on the fundamental deterioration mechanism have concluded that chloride plays the most important role in the corrosion of the reinforcement [2, 3] when concrete structures are subjected to seawater or de-icing salts used in winter and also when chloride contaminated raw materials are used for preparing concrete [4]. Although chloride ions have only a little influence on the pH of the concrete pore solution, they have the ability to depassivate the steel in concrete even in highly alkaline conditions [5]. Corrosion products usually increase volume several times greater than basic metal and cause cracking and spalling of concrete cover, and the reduction of the cross-sectional area of rebars, which weaken the bond between reinforcing steel bars and surrounding concrete and threaten the safety of reinforced concrete structures [6-8]

Hence, monitoring of the corrosion activity of reinforcing steel is essential for a safe performance in concrete structures. It is widely accepted that corrosion potential technique is a main method to indicate the severity of corrosion as defined in ASTM C876 [9]. Potential more negative than -350 mV with respect to copper sulphate electrode (CSE), indicative of a high risk of corrosion and there is probability of 90% to corrode. A study by Huang and Chang [10] concluded that corrosion tendency is strongly related to the corrosion potential and polarization resistance, and the corrosion resistance of rebar in concrete can be predicted reliably from the corrosion potential. However, for structures with the same corrosion potentials, reinforcement corrosion rate is inversely proportional to the electrical resistivity of concrete has been reported [5].

Concrete resistivity can easily and frequently be measured, especially in the field, compared to other parameters in corrosion science such as the polarization resistance which reflects corrosion rate [11]. A number of researchers [12-16] have investigated the relationship between concrete resistivity and corrosion rate. The overall conclusion was that the corrosion rate decreases with increasing concrete resistivity with the exception of water saturated structures. However, considerable and not fully clarified deviations were found under conditions investigated [17]. The experimental design used have a major influence on the result as no standardized test method available to investigate the relationship between the reinforcement corrosion rate and the resistivity of concrete [17].

Concrete resistivity is not only important in determining the rate of corrosion but is also a significant factor in the determination of the degree of water saturation, the resistance to chloride penetration and it is essential in the design of cathodic protection systems for arresting and preventing corrosion [5, 12].

Different technologies using chemical, mechanical and electrochemical methods have been adopted to protect or maintain concrete structures against reinforcement corrosion [18, 19], but most of the techniques showed little or no success in reducing the corrosion rate [20]. CP so far has been recognised as the most effective technique in controlling the corrosion of steel reinforcement embedded in concrete [21, 22]. However, the specific information in national or international standards for the CP design were still limited even until recently [23].

Traditionally, titanium mesh sheet coated with noble metal oxides, such as iridium, ruthenium, cobalt, etc., is the most common material used for the CP anode [24] in practice. Meanwhile, new
anode materials have also been developed and used for the convenience of installation, reliability and low cost [25]. For example, recently, carbon fibre reinforced polymer (CFRP) has been reported to be successfully used as CP anode applied on reinforced concrete structures [26, 27].

This paper presents an experimental work to study the chloride effect on the concrete resistivity, polarization resistance, and the potential shift of reinforcement in concrete with various chloride concentration under different CP current densities. In the study, internal woven carbon fibre (CF) fabric sheet was used for the electrodes in the concrete resistivity test, and the anode in the cathodic polarization test. The experimental results provide new information for the relationship between concrete electrical resistivity and corrosion rate (calculated based on polarization resistance) together with cathodic polarization at different power supply.

**Experimental Programme**

**Specimen Concrete**
The specimen concrete used the Portland limestone cement, CEM II/A-LL, conforming to the British standard BS EN 197-1: 2011. The cement content in the concrete was 390 kg/m$^3$. The fine aggregate were uncrushed sands of the maximum size of 4.75mm and a relative density of 2.47. The fine aggregate content in the concrete was 580 kg/m$^3$. The coarse aggregates were limestone of the maximum size of 10mm and 2.49 specific gravity. The coarse aggregate content in the concrete was 1125 kg/m$^3$. The concrete was mixed according to the British standard BS 1881-125:2013, with a water to cement ratio of 0.4, which had the designed 28 days compressive strength of 35 MPa.

**Experimental Plan**
Reinforced concrete specimens with the size of 150mm x 90mm x 93mm, as illustrated in Figure 1 were used to investigate the polarization of rebars under CP operation. Each of the specimen has three reinforcing bars of a diameter of 10mm. The two ends of the rebars were coated using epoxy resin to prevent direct exposure to environment. The middle uncoated region of an effective length of 73 mm was embedded in concrete giving a total exposed surface area of 6880 mm$^2$ for the three rebars. The three bars in each individual concrete specimen were connected together using an external copper wire. A layer of woven carbon fibre (CF) fabric sheet was embedded near the front surface of the specimen to be the anode. The effective area of the embedded CF anode was 144mm x 93mm.

Different concentrations of chloride as pure NaCl salt of 0, 1, 2, 3.5 and 5% of the cement mass, respectively, were added into the mixing water at the time doing concrete mix. The casted concrete specimens were wet cured in the water of the same NaCl content for 28 days. Thereafter, they were exposed to the atmosphere of a relative humidity of 50±5% and room temperature of 20±3°C until their weight became stable. After then, these specimens were used to evaluate the degree of the deterioration of reinforced concrete under chloride contamination, and the effect of applied CP current density on the polarization of reinforcement when CP is operated.
In addition, a set of non-reinforced specimens of the size of 100mm x 100mm x 70mm were also made using the same concrete mixtures and cured following the same procedure as that used for the reinforced specimens. These specimens were used for electrical resistivity measurement. Each of the non-reinforced specimens, as illustrated in Figure 2, had two embedded electrodes of CF sheets. The distance between the two electrodes was 55 mm.

Figure 1: Details of the reinforced concrete specimens used for the cathodic polarization, all dimensions are in mm

Figure 2: Details of concrete specimen used for electrical resistivity measurement
Measurements
Polarization Resistance
Linear polarization resistance (RP) described by Stern and Geary [28] was measured on the reinforced specimens. A potential shift of ±20mV [29, 30] was applied to the open circuit potential of rebars at a scan rate of 0.125 mV/s, using a computer controlled Gamry potentiostat. The ohmic drop between the working and the reference electrode was auto compensated using the potentiostat. The current response during the scan was recorded. The polarization resistance, Rp, was then obtained from the slope of the potential against current at corrosion potential value.

Concrete Resistivity Measurements
The electrical resistivity is measured using the two-electrode technique on the non-reinforced specimens. An AC power of the amplitude voltage of 3000 mV and a sine wave of a frequency of 10 kHz was applied across the two electrodes [31]. The electrical resistivity of the concrete was then calculated using equation (1).

\[
\rho = \frac{V}{I \cdot \frac{A}{L}}
\]  

(1)

Where \( \rho \) is electrical resistivity, \( V \) is the applied voltage, \( I \) is the measured current, \( A \) is the effective surface area of the measured specimen perpendicular to the current flow, and \( L \) is the distance between the two electrodes.

Cathodic Polarization Test
Galvanostatic polarization technique was adopted by applying small CP currents on the specimens using potentiostat. 10 reinforced concrete specimens (2 specimens for each chloride concentration) were connected in series as shown in Figure 3 and applied with different cathodic current densities.

The applied cathodic current densities were 5, 10, 15, 20 and 25 mA/m² on the rebars surface. The period of operation of cathodic polarization for each current density was 24 hours when a steady state had achieved. The potential of the rebars was recorded using silver/silver chloride (Ag/AgCl/0.5KCl) reference electrode and data logger during the operation. Time intervals of 1 to 4 days were given between two consecutive tests to ensure the sufficient depolarization of the rebars after a specific CP operation.
**Results and Discussion**

**Concrete Resistivity and Polarization Resistance of reinforcement**

The influence of chloride content on the polarization resistance of rebars and resistivity of concrete are plotted in Figures 4 and 5 respectively, which show that both of the polarization resistance and concrete resistivity are strongly affected by chloride content. Presence of chlorides increases the conductivity of pore solution and thus decreases the concrete resistivity which reflect the electrical path between anodic and cathodic areas on the reinforcement, and then decrease the resistance of rebars to polarization.

*Figure 3: Electrical schematic of wiring arrangement for applying cathodic polarization*
In order to provide a quantitative non-destructive approach for rapid and reliable information on the activity of the reinforcement corrosion, an empirical correlation between the concrete resistivity and the corrosion rate of rebars is presented in Figure 6. The values of the corrosion current density ($i_{corr}$) in this Figure were calculated using the Stern-Geary relationship [28] ($i_{corr} = I_{corr}/A$, where $I_{corr}$ (corrosion rate)=$B/R_p$, assuming that $B=26$ mV for active corrosion, $A$ is the surface area of the rebars). It should be noted that the result of the specimens that are free of chloride (0% NaCl) was not presented in Figures 4 and 6 as it gives very high polarization resistance and then very low corrosion current density affecting the shape of the plot.
Figure 6 shows that severity of corrosion increases with decreasing concrete resistivity. The obtained data can be fitted well using power relationship with regression accuracy \( R^2 \) of 0.9797. Based on this correlation, the following equation can be obtained:

\[
\text{icorr} = 1413.2 \cdot \rho^{-1.917} 
\]

(2)

Where \( \rho \) is the electrical resistivity of concrete (kΩ.cm) and icorr is the corrosion current density in mA/m².

Different equations were reported earlier, for instance by Ahmed [16] and Gulikers [32] based on experimental and theoretical investigation respectively. A comparison between the equation generated by the present study and findings from previous research is presented in Figure 7 for the evaluation. Although that all the suggested equations follow the same trend, it is evident that there are noticeable differences among the results. These differences can be attributed to the experimental design and to the techniques used for the measurement of the resistivity and the assumptions used to simplify theoretical analysis. According to previous recommended interpretation [33], high corrosion rate is considered when icorr is greater than 10 mA/m². Based on this interpretation, it can be conclude from Figure 7 that concrete resistivity of less than 10, 14 and 30 kΩ.cm in the case of Ahmed [16], present and Gulikers [32] studies respectively, can describe high corrosion in the reinforcement exposed to the atmosphere and subjected to chlorides. It is worth noting that Gulikers [32] equation used in this comparison in a simplified form according to Ahmed [16]. The results of this study and Ahmed [16] finding are very close and more reservation that the obtained results by Gulikers [32].

\[\text{Corrosion rate, mA/m}^2\]

\[\text{Concrete resistivity, kΩ.cm}\]

\(\text{Present study}\)

\(\text{Guliker's study, 2005}\)

\(\text{Ahmed study, 2014}\)

*Figure 7: Comparison of the corrosion current densities with concrete resistivity obtained using different studies*
Cathodic Polarization of Reinforcement

Figure 8 shows the variation of cathodic polarization (potential shift) of the reinforcement in the concrete specimens of different chloride contents and under different applied cathodic current densities. The potential shift is defined as the difference between the open-circuit potential and the on potential during cathodic polarization when steady state has been achieved. In this study the measurements were taken at 24 hrs after the application of CP currents [34]. It can be seen that the potential shift is strongly dependent on the environment around the reinforcement and the applied current density. The amount of potential shift decreases as chloride content increases, and it is directly proportional to the applied current at any chloride content, but it is less influential at high amounts of chloride. A steep increase particularly happened at the initial chloride content increase starting from 0%. Potential of specimens with low chloride is always shifted more than those with high amount of chloride. This reflects that a small amount of current will effectively provide the required potential for the cathodic polarization.

![Figure 8: Variation of rebar polarization with chloride concentration and applied current](image)

Figures 9 and 10 show the influence of the concrete resistivity and the polarization resistance on the potential shift under a certain applied CP current density. It can be seen that potential shift increases with the increase of concrete resistivity and polarization resistance. The correlation is highly pronounced at high resistivity, polarization resistance and applied CP current density.

However, it should be pointed out that the observation here is opposite to a previous finding [35], which suggested that reinforcement in low resistivity concrete had a high polarization. A reasonable explanation for this is because the current study only considered the chloride effect.
Conclusion
From the experimental results, the following conclusions can be drawn:
1. Reinforcement polarization resistance and concrete resistivity present an approximately reversed linear relation against the chloride content.
2. A very well empirical correlation between concrete resistivity and corrosion rate is obtained with accuracy of regression ($R^2$) of 0.9797.
3. A small amount of chloride contamination on chloride free concrete will produce a significant decrease of reinforcement potential shift and reduce the effect of CP operation. With the
concrete chloride content increase, the degree of the influence on the decrease of reinforcement potential shift become less and less.

4. The influence of chloride content on CP potential shift is highly pronounced at high CP current density applied.

5. The potential shift of reinforcement presents an approximately linear relation against reinforcement polarization resistance. The rate of the increase of potential shift with the increase of polarization resistance will increase under a high CP current density.

Acknowledgement
This work is a part of an ongoing Ph.D. project funded by the Iraqi Ministry of Higher Education and Scientific Research Scholarship Program.

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