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Modelling Concrete Electrical Resistivity at Varied Water and Chloride Contents

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Abstract
Concrete electrical resistivity is an important property in the assessment of reinforcement corrosion in concrete, and an essential parameter in the design and operation of cathodic protection for reinforced concrete structures. Water and chloride contents in concrete are highly variable for reinforced concrete structures in real world hostile environments. It leads to the interest to the characterization of their coupling effects on the concrete electrical resistivity. This paper at first investigates the current available models. Seeing that all the current models are purely empirical, this paper proposes an improvement with a semi-empirical model. The improvement highlights that the correlation between concrete electrical resistivity and the water content intrinsically establishes on the pore-size-distribution of the pore structure of concrete. At the end, the proposed model has been tested on two sets of experimental data and been compared with other two empirical models.

Keywords: Durability-related properties, Electrical properties, Moisture-related properties, Plain concrete

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Notation

$\rho_c$: concrete electrical resistivity, $\Omega$-m

$\rho_p$: electrical resistivity of cement paste, $\Omega$-m

$\rho_w$: electrical resistivity of concrete pore water solution, $\Omega$-m

$\rho_{wf}$: electrical resistivity of the water film on pore surface, $\Omega$-m

$S, S_w$: water saturation in concrete, pore water volume/pore volume

$\phi$: porosity

$\varphi$: cement paste fractional volume in concrete

$\theta$: concrete pore water volumetric fraction, pore water volume/concrete volume

$C_l$: total chloride content in terms of cement or concrete weight, %

$Cl/W$: ratio of chloride mass to water mass

$w/c$: water to cement ratio

$T$: absolute temperature, K

$A, a, b, c, m, n, P_0, \alpha, \beta, f_0, \rho_0$: model parameters
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1. Introduction

Reinforced concrete (RC) used as structural material has outstanding advantages on cheap cost, convenient construction and high strength (Gao et al., 2011). However, for a long time, the corrosion of the steel reinforcement in concrete has become a major reason for the premature deterioration of RC structures, and posed serious problems in economy and safety (Sun et al., 2010). In the efforts to arrest the conditions for steel corrosion, cathodic protection (CP) so far has proved the most effective and reliable technique and has been increasingly used in civil engineering for structural repair and maintenance (Wilson et al., 2013).

Numerical modelling and simulation today has been popular employed for RC structure CP design and operation analysis (Qiao et al., 2015; Liu and Shi, 2012; Qiao et al., 2016). The mathematical model describing the CP process running in RC is generally based on the Nernst-Planck equation describing the principles of ionic transportation in concrete pore solution and the Ohm’s law describing the implemented DC current flow in concrete (Wang 2011). To solve the two equation model, concrete electrical resistivity as a material property is required at the first hand. At the second hand, concrete resistivity also plays an important role in the reinforcement corrosion process to influence the rebar surface potential and the corrosion current (Hornbostel et al., 2013). For the reason, accurate estimation of the electrical resistivity at varied concrete conditions is important to help assess the state of the reinforcement for CP design or under CP operation.

Fundamentally, concrete electrical resistivity depends upon the formation of concrete pore structure, pore water content, as well as the chemical composition of the pore water solution (Azarsa and Gupta, 2017; Layssi et al., 2015; Banea 2015). These factors are consequently decided by the nature of the component materials, mixture proportion, water to cement ratio (w/c), curing methods, and the exposure and environment (Whiting and Nagi, 2003; Elkey and Sellevold, 1995). For mature concrete, pore water saturation degree has been identified to have the most influence on concrete resistivity. It has been found that, for example, when water saturation changed from 20% to 100%, concrete electrical resistivity decreases in three orders from 6×10^6 to 7×10^3 Ohm-cm (Elkey and Sellevold, 1995; Gjorv et al., 1977). However, it has also been noticed that when the water saturation degree is over 70% or below 35%, the electrical resistivity is either too small or too large to have further big concern of the
effect of water content change (Lopez 1993). It was also found that when concrete exposed to a relativity humidity below 40% electrical resistivity was too large to be stable (Chen et al., 2014). The large resistivity at low water saturation may be explained by the fact that the water in the gel pore is much less electrically conductive due to the strong chemical bond to the inner surfaces of gel pores (Zaccardi and Maio, 2014) and their disconnected distribution. It was suggested that the electrical resistivity of concrete presents an exponentially decreasing trend along with the increase of the pore water content (Saleem et al., 1996; Zaccardi et al., 2009; Zaccardi and Maio, 2014). Second to water, chloride ions in concrete has been identified the other important factor influencing concrete electrical resistivity due to its wide presence in the exposed environments and high mobility in concrete. Once reaching the surface of the steel reinforcements in concrete, chloride will play an important role in the corrosion process. Although, in general, an inverse correlation exists between the chloride content and concrete electrical resistivity (Henry, 1964; Zaccardi and Maio, 2014), so far, there hasn’t had a widely recognised quantitative model to characterize their relationship.

In spite of the important role of electrical resistivity, most of previous work on numerical modelling and simulation of the CP process on concrete structures neglected the variation of concrete resistivity with the change of water content and the ionic redistribution in concrete under varied environmental situations. In these work, by assuming the resistivity as a constant, the electrical current and potential distribution in concrete was in general simply described using the Laplace equation. However, in order to accurately evaluate the electrical potential of the reinforcement under CP conditions, it needs to consider the variation of concrete electrical resistivity. A few researches so far have reported the combined influence of water and chloride contents on concrete electrical resistivity. However, the characterisation and modelling of the electrical resistivity under the coupling influence of the two important factors are still open for discussion for accuracy, reliability and fundamental underlying mechanisms. To provide an efficient tool for CP process modelling, this paper, at first, investigates two existing empirical models of concrete electrical resistivity. Thereafter it proposes a new semi-empirical model based on the understanding that the relationship between electrical resistivity and water content has an intrinsic linkage to the pore size distribution of concrete pore structures. At last, the three models are tested and compared on two sets of reported experimental data.

2. Two Empirical Models
Jiang and Yuan (2012) suggested a concrete electrical resistivity model as expressed in Eq. (1), which considers the effects of water-cement ratio, chloride-ion content, pore water saturation and temperature.

\[
\rho_c = \left[ 750,605 \left( \frac{w}{c} \right) - 106,228 \right] \exp \left[ -0.4417 Cl - 7.7212 S + 2889 \left( \frac{1}{T} - \frac{1}{303} \right) \right] \tag{1},
\]

where \( \rho_c \) is concrete electrical resistivity; \( w/c \) is the water-cement ratio; \( Cl \) is the total chloride-ion content (%) in terms of cement in concrete; \( S \) is the pore water saturation of concrete near the surface of the reinforcing bar, and \( T \) is the absolute temperature (K) of concrete. For a specific concrete under a certain temperature condition, the Eq. (1) may be rewritten into a general form as:

\[
\rho_c = A \exp [a Cl + b S + c] \tag{2},
\]

where \( A, a, b \) and \( c \) are four constants depending on the formation and the temperature of concrete. However, it has been found that using either Eq. (1) or (2) gave a low accuracy in many cases under the variation of pore water and chloride contents.

Another attempt was to use the Archie’s law (Zaccardi et al., 2009; Atkins and Smith, 1961; Whittington, 1981). A formula, shown in the form of the Eq. (3) below, was firstly proposed to describe the electrical resistivity of rocks for the effects of the porosity and the degree of brine saturation (Artchie, 1942).

\[
R_r = a \phi^{-m} S^{-n} R_b \tag{3},
\]

where \( R_r \) is the electrical resistivity; \( R_b \) is the brine electrical resistivity; \( S \) is the degree of brine saturation in rocks; \( \phi \) is the rock porosity; \( a \) is a factor for tortuosity; \( m \) and \( n \) are two constants. Assuming that concrete electrical resistivity is primarily decided by the cement past, Atkins and Smith (1961) revised the Archie’s law into the form below and applied it on concrete:

\[
\rho_c = A \phi^{-m} \rho_p \tag{4},
\]
where \( \rho_c \) is concrete electrical resistivity; \( \rho_p \) is the electrical resistivity of the cement paste in concrete; \( \varphi \) is the fractional volume of cement paste; \( A \) and \( m \) are two constants. Later, having recognised that the electrical conductivity of the pore solution is several orders higher than that of all the other phases in concrete, Archie's law was further revised into the form of the Eq. (5) to explicitly consider the effect of water content variation in concrete (Zaccardi et al., 2009; Whittington et al., 1981).

\[
\rho_c = A\theta^{-m}\rho_w
\]  

(5),

where \( \rho_w \) is the electrical resistivity of pore water solution, which depends upon the composition of the pore water solution; \( \theta \) is the pore water volumetric fraction of concrete; \( A \) and \( m \) are two redefined constants. To explicitly describe the effect of the variation of the chloride content in concrete pore solution, in this paper, we rewrite the Eq. (5) into the following form:

\[
\rho_c = A S_w^{-n} \rho_w(\text{Cl})
\]  

(6),

where \( S_w \) is the degree of pore water saturation, \( \rho_w(\text{Cl}) \) is the electrical resistivity of pore water solution, which is simply assumed to depend on the chloride content; \( A \) and \( n \) are two constants related to the pore structure, such as porosity and tortuosity. Referring to the work by Jiang and Yuan (2012), we use a general exponential function to describe the influence of chloride content, i.e.:

\[
\rho_w = ae^{bCl} + c
\]  

(7),

where \( a, b \) and \( c \) are three constants depending on the other condition of the concrete pore water solution such as temperature, pH and etc. Substituting Eq. (7) into (6) generates a new revision of the Archie’s law, i.e.:

\[
\rho_c = S_w^{-n}(ae^{bCl} + c)
\]  

(8),

where \( a \) and \( c \) are two redefined constants merged with \( A \) in the Eq. (6).
3. A Semi-Empirical Model

Although both Eqs. (2) and (8) provide the expected explicit form to describe the coupling influence of the water and chloride content variation on concrete electrical resistivity, they have little fundamental explanation for the underlying mechanism. Fundamentally, the pore water solution in concrete acts as the solely media for electrical conductivity. The more the water the higher the conductivity or the lower the electrical resistivity. In addition to absolute water quantity, the water distribution in concrete pore network plays an important role in deciding the electrical conductivity as well. Under unsaturated state, the bulk water phase presents two configurations in pores. The major part of water predominantly occupies the pore space of small sizes while a water film covers on all the empty pore surfaces. Such water occupying configuration state is due to the physicochemical absorption of pore surfaces and capillary condensation (Wang et al., 2008; Wang and Wu, 2008). Consequently, the water distribution or configuration at varied pore water saturation degree depends upon the pore size distribution. As a result, the influence of water content on electrical conductivity or resistivity is intrinsically related to concrete pore size distribution. Such intrinsic relationship is similar as that between the thermal conductivity of unsaturated soils and soil water saturation (Jin et al., 2017). To reflect the underlying mechanism, we revise the work by Jin et al. (2017) to characterise and model concrete electrical resistivity at varied water content.

Based on the physical chemistry theory of interfacial phenomena, for unsaturated porous media in general, the total pore volume average pressure of the bulk water phase in filled pores and the total pore volume average pressure of the bulk vapour phase in empty pores can be expressed respectively using two functions of water saturation (Wang 2010; Wang et al., 2012; Jin et al., 2017), i.e.:

\[
P_w = \frac{P_0}{\alpha} [exp(\alpha S_w) - 1] \tag{9a}
\]

\[
P_v = \frac{P_0}{\beta} [exp(\beta(1 - S_w)) - 1] \tag{9b}
\]

where \(P_w\) and \(P_v\) are the total pore volume average pressures of the water phase and the vapour phase pressure in porous media; \(S_w\) is the pore water saturation degree; \(P_0, \alpha, \beta\) are three constants related to the nature of the interfacial phenomenon at pore surfaces. Under thermodynamic equilibrium, the pressure difference of the two phases will be balanced by the interfacial meniscuses between the bulk water phase and the bulk vapour phase, and is related to the pore size distribution (Wang 2010; Wang et al., 2012).
Water pressure and water electrical conductivity has an intrinsic thermodynamic relationship. Both of them relate to the water molecular and ionic dynamics. On the ground, we adopt the same form of the Eq. (9) here to describe the electrical conductivity or resistivity of the bulk water in filled pores and the water film on the empty pore surfaces (the water film thickness relates to the vapour pressure in the empty pores), respectively. It gives that the concrete electrical resistivity at varied water saturation degree may be expressed as:

$$\rho_c = \rho_w + \rho_{wf} = \frac{\rho_0}{\alpha} [\exp(\alpha S_w) - 1] + \frac{\rho_0}{\beta} [\exp(\beta (1 - S_w)) - 1] \quad (10),$$

where $\rho_c$ is the concrete electrical resistivity; $\rho_w$ and $\rho_{wf}$ indicate the resistivity of the bulk water phase and the water film phase in concrete, respectively. By explicitly distinguishing the two water configuration phases, Eq. (10) has naturally taken account of the effect of pore size distribution. Rearranging Eq. (10) generates:

$$\rho_c = \rho_0 \left[ - \frac{1}{\beta} - \frac{1}{\alpha} + \frac{\exp(\alpha S_w)}{\alpha} + \frac{\exp(\beta (1 - S_w))}{\beta} \right] \quad (11).$$

A similar form as the Eq. (11) has been successfully used to model the water vapour adsorption isotherm of concrete materials for pore size distribution analysis (Wang et al., 2012). Based on the Eq. (11), for easy implementation and memorising, a simplified form was suggested as:

$$\rho_c = f_0 + \rho_0 [\exp(\alpha S_w) + \exp(\beta (1 - S_w))] \quad (12),$$

where $f_0$, $\rho_0$, $\alpha$ and $\beta$ are four redefined constants. The form of Eq. (12) has proved to generate a close result on water vapour adsorption isotherm compared with that of the similar form of Eq. (11) (Wang et al., 2012). For the reason, this paper uses the simplified form, Eq. (12), to describe effect of water saturation on concrete electrical resistivity.

To characterise the coupling effect of water and chloride contents on concrete electrical resistivity, this paper uses an exponential form function for the chloride effect to weigh the Eq. (12) and derives a model below:
\[ \rho_c = \exp(aCl^b)(f_0 + \rho_0[\exp(aS_w) + \exp(\beta(1 - S_w))] ) \] (13),

where \( Cl \) is the chloride content in concrete; \( a \) and \( b \) are two constants. In the next section, we use the Eqs. (2), (8) and (13) to model the experimental data of concrete electrical resistivity measurement to compare their performance.

### 4. Model Test

Two sets of experimental data were selected. One is from a reference published (Saleem et al., 1996). The other one is from an experimental study together with this work (Oleiwi, 2018). The MATLAB curve fitting tool was employed to perform the modelling. The model performance (goodness-of-fit) was evaluated in terms of two statistical measures, they are the root-mean-square error (RMSE) and the R-squared, which are defined as:

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n}(y_i - f_i)^2}{n}} \quad (14),
\]
\[
R\text{-squared} = 1 - \frac{\sum_{i=1}^{n}(y_i - f_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \quad (15),
\]

where \( \bar{y}_i \) is the average of all the experimental data \( y_i \), \( n \) is the total number of the experimental data, \( f_i \) is the modelling value from data fitting. The lower the RMSE value the better the modelling. Meanwhile, a value of R-squared closer to 1 indicates that the model has almost all the variability of the response data around its mean.

Saleem et al. (1996) conducted a series of study on the effects of both chloride and moisture (water) contents on the electrical resistivity of concrete made with w/c 0.45. The water content was accounted in terms of the mass percentage to the oven dry specimens, while the chloride content was accounted in terms of the weight in 1 m³ volume of the specimens. In the current study, with an estimation that the dry concrete specimens have a density of 2000kg/m³ and a porosity of 0.13, these data are converted to pore water saturation and chloride to water mass ratio. Fig. 1 compares the Eqs. (2), (8) and (12) to model the variation of the electrical resistivity at different water contents under certain chloride contents. It shows that Eqs. (12) and (8) outperformed Eq. (2). Both of them have produced a very closely good result fitting to the experimental data.
Fig. 2 compares the modelling results using Eqs. (2), (8) and (13) to fit all the reported experimental data in the linear-scaled 3D space of electrical resistivity against the pore water saturation ($S_w$) and the chloride to water mass ratio (Cl/W), respectively. Although all the three models present a surface fitting to the measurement points, it can be seen that Eqs. (8) and (13) have produced much better, stable and reliable results than Eq. (2) which fails to represents all the experimental data involved. Fig. 3 compares the modelling statistics of the three models. It shows that the RMSEs of the Eqs. (8) and (13) are about half of that of the Eq. (2) and quite small compared to the value range of all the experimental data. The R-squared values of the Eqs. (8) and (13) are very close to unity, which indicate that deviation around the mean value is small as well. Overall the model Eq. (13) presents the best performance.
Figure 2. Modelling the coupling effect of water and chloride contents on concrete resistivity for the data by Saleem et al. (1996)
Eqs. (2), (8) and (13) have been compared on another set of the data from an experimental study together with this work. The concrete specimens were made using locally produced Portland limestone cement, CEM II/A-LL conforming to the British standard BS EN 197-1: 2011, for the concrete mixes at 390 kg/m³. Natural sand of the maximum size of 4.75mm and a relative density of 2.47 was used for the fine aggregate at 580 kg/m³. The coarse aggregate was the limestone of 10mm maximum size and 2.49 specific gravity and used at 1125 kg/m³. The mix of concrete followed the British standard, BS 1881-125:2013. Four different chloride contents were prepared by adding NaCl in the mix water. The added chloride contents are 0, 1.5, 3 and 4.5% of the cement mass, respectively. Three water to cement ratios (w/c = 0.4, 0.5 and 0.6) were used for each chloride content. All the casted concrete samples were cured by submerged in the water of the same chloride content as that used for their mixes. This fully saturated curing method aims for an even distribution of chloride in the concrete and therefore makes the test results more reliable. The actual total chloride content in the cured samples for each mixture were measured specifically. For each mix, three specimens were prepared for each property measuring, and the final result took the average of the triplicate measurements. The electrical resistivity was measured using internal electrode methods. The detail of the experiments has been reported in the reference (Oleiwi. 2018). Fig. 4 compares the Eqs. (2), (8) and (12) to model the variation of the electrical resistivity at different water contents under certain chloride contents, where the electrical resistivity is presented in log scale to show difference more clearly. Fig. 5 shows the residuals of the modelling, the difference between the fitting results to the experimental data (i.e. f_i - y_i). It can be seen that except at an extremely low water saturation (<0.1) Eq. (12) produced the best fitting (close to the neutral line, 0) to all other data. The underperformance at very low water
contents may be due to the unstable measurement of the electrical resistivity under the situation.

(a) w/c = 0.4
(b) w/c = 0.5

Figure 4. Comparison of the three models on Oleiwi’s data at certain chloride contents

(c) w/c = 0.6

Figure 5. The residues of the three models on cases in Fig. 4

Fig. 6 shows that using the exponential weighting term in Eq. (13) to model the chloride effect on electrical resistivity of fully saturated samples, which proves a good performance.
Figure 6. Modelling chloride effect using the exponential weighting term in Eq. (13)

Fig. 7 shows the results using the Eq. (2) to fit all the experimental data in the linear-scaled 3D space of electrical resistivity against the pore water saturation and total chloride content in terms of pore water content. Visually, the fitting surfaces for the three concretes of different w/c have showed a good agreement with the experimental data in this case.
Figure 7. Modelling the coupling effect of water and chloride contents on concrete resistivity using Eq. (2) for the data by Oleiwi (2018)

Fig. 8 shows the results using the Eq. (8) to fit these experimental data in the same way. A visual inspection shows that the fitting surfaces for the three concretes of different w/c are close to that represented by the Eq. (2) in the Fig. 6.
Figure 8. Modelling the coupling effect of water and chloride contents on concrete resistivity using Eq. (8) for the data by Oleiwi (2018)

Fig. 9 shows the results using the Eq. (13) to fit all the experimental data again in the same way. A visual inspection shows that Eq. (13) has produced a better performance than Eqs (2) and (8) in representing the experimental measurements over all.
Figure 9. Modelling the coupling effect of water and chloride contents on concrete resistivity using Eq. (13) for the data by Oleiwi (2018)

Fig. 10 compares the modelling statistics of the three models for this set of data. It shows that in all the cases the R-squared values of the three models are very close to unity. However, the model Eq. (13) presents the best performance with a quite small the RMSE. It produces the smallest RMSE and the highest R-squared value in all the cases.

Figure 10. Modelling statistics for the data by Oleiwi et al. (2018)
5. Conclusions
This paper has investigated the characterization models for the coupled effect of water and chloride contents on the electrical resistivity of concrete of different pore structures (related to different w/c). It proposed a semi-empirical model based on the understanding that concrete electrical resistivity at varied water content is related to the pore size distribution of the pore structure. Comparison of the three different models have been conducted on two sets of experimental data. From the investigation, we can draw the following conclusions:
1. Archie’s law demonstrates a good representation for the effect of degree of pore water saturation on the concrete electrical resistivity, while an exponential function well represents the effect of chloride.
2. The proposed semi-empirical model established on the water phase configurations in pore network highlights the important role of the pore size distribution of pore structure in the electrical resistivity of unsaturated concrete.
3. The semi-empirical model has demonstrated a more accurate and reliable performance compared to the other two empirical models to characterize the coupling effect of the variation of water and chloride contents on concrete electrical resistivity.
4. The proposed semi-empirical model provides a useful tool for the modelling of the cathodic protection process in concrete to describe the coupling effects of the water and chloride variation when reinforced concrete structures expose to varying severe environments.

References