

Modeling Steel Corrosion in Concrete Structures - Part 1: A New Inverse Relation between Current Density and Potential for the Cathodic Reaction

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Corrosion of steel reinforcement can seriously compromise the service life of reinforced concrete structures. Hence, service life prediction and enhancement of concrete structures under corrosion attack are of significant importance. As a result, numerical methods that can reliably predict the service life of concrete structures have attracted increasing attention. In this, the first of two companion papers, a simple and significantly improved inverse relation relating the current density with potential for the cathodic reaction is proposed. This enables the current densities to be determined accurately from the measured potentials. Equally importantly, the proposed inverse relation also enables the efficient and straight-forward nonlinear algorithm for modeling of steel corrosion in concrete structures to be developed. Such an algorithm is presented in the companion paper of this.

Keywords: Corrosion, Concrete, Numerical modeling, Inverse relation, Cathodic reaction

1. INTRODUCTION

Corrosion of steel reinforcement is a well-known and well-documented phenomenon, and is considered the most prevalent form of deterioration of reinforced concrete structures [1, 2]. Initially, due to the highly alkaline nature of the concrete, a passive protective oxide film is formed on the surface of the steel reinforcement, effectively preventing the steel surface from being corroded. The passive protection layer, however, may be seriously compromised when the chemical composition of the pore solution is altered by carbonation or chloride contamination of the concrete cover. As a consequence, corrosion begins, resulting in a reduction in steel cross-sectional area, cracking, and spalling as well as loss in bond between steel and concrete.

In recent years, numerical methods that simulate the corrosion processes of reinforcing steel in concrete and allow parametric studies in addition to laborious experimental investigations have gained increasing attention [3-6]. This is mainly due to the considerably improved understanding of the basic processes underlying reinforcement corrosion and the significantly increased possibilities for modelling complex electrochemical processes involved in corrosion. However, much remains to be investigated further to fully realise the potentials of current numerical models. Specifically, because of the concentration polarization, the polarized potential of the cathodic reaction expressed as a function of the current density is nonlinear and cannot be solved for explicit inverse relations, which have to be approximated instead. Current approximate inverse relations, however, do not represent well the exact solution. This paper thus aims to propose a new inverse relation between the current density and potential for the cathodic reaction.

2. KINETICS OF CORROSION

2.1. Potential-current density relations for anodic and cathodic reactions

The potential-current density relations for the anodic and cathodic reactions of steel corrosion are well-established [7, 8].

The corrosion of steel in concrete is caused by the dissolution of iron into the pore water at the anode [9], which can be represented by the following half-cell reaction



In order for electrical neutrality to be preserved, the electrons produced in this anodic reaction must be consumed at the cathodic sites on the steel surface [9]. The cathodic reaction is given by



At equilibrium, the rate of the forward reaction in Eqs. 1 and 2 is equal to the reverse one. The potentials and current densities at these states are called equilibrium potentials and exchange current densities, respectively. When the equilibrium is disturbed, there is a net current between the anodic and cathodic areas on the steel, and the equilibrium potentials are changed to new potentials at the electrodes. The extent of potential change caused by the net current at the electrodes, measured in volts, is termed polarization. There are three causes of polarization, namely activation, concentration and Ohmic potential drop. For steel corrosion in concrete structures, activation is considered as the only cause of the anodic polarization while activation and concentration are the causes of cathodic polarization [8].

2.1.1. Polarization of anodic reaction

The activation polarization of the anodes can be determined by

$$\eta_a = \beta_a \log \frac{i_a}{i_{a0}} \quad (3)$$

where β_a is the Tafel slope of the anodic reaction (V/dec), i_a is the anodic current density (A/mm²) and i_{a0} is the exchange current density of the anodic reaction (A/mm²).

Hence the polarized potential ϕ_a (V) of the anodic reaction can be written as [10]

$$\phi_a = \phi_{a0} + \eta_a = \phi_{a0} + \beta_a \log \frac{i_a}{i_{a0}} \quad (4)$$

where ϕ_{a0} is the equilibrium potential of the anodes (V).

2.1.2. Polarization of cathodic reaction

If the amount of oxygen at cathode is not sufficient, the concentration polarization controls the polarization of cathodes. Concentration polarization at the cathodes can be calculated as

$$\eta_{cc} = -\frac{2.303RT}{zF} \log \frac{i_L}{i_L - i_c} \quad (5)$$

where R is the universal gas constant (8.314 J/K.mol), T is the absolute temperature (K), F is Faraday's constant (9.65.10⁴ C/mol), z is the number of electrons exchanged in the cathodic reaction, i_c is the cathodic current density (A/mm²) and i_L is the limiting current density of the cathodic reaction (A/mm²).

The limiting current density i_L of the oxygen reduction at the cathodic sites can be calculated as follows [7]

$$i_L = \frac{D_{O_2} z F}{\delta t_n} C_{O_2} 10^{-3} \quad (6)$$

where D_{O_2} (m²/s) is the effective oxygen diffusion coefficient in concrete, δ (= 0.005 mm) is the thickness of the stagnant layer of electrolyte around the steel surface, t_n (=1) is the transference number of all ions in the solution except for the reduced species, and C_{O_2} (mol/l of pore solution) is the concentration of oxygen around the steel.

The activation polarization of the cathodes can be determined as

$$\eta_{ca} = -\beta_c \log \frac{i_c}{i_{c0}} \quad (7)$$

where β_c is the Tafel slope of the cathodic reaction (V/dec) and i_{c0} is the exchange current density of the cathodic reaction (A/mm^2).

Thus the polarized potential of the cathodic reaction can be written as [10]

$$\phi_c = \phi_{c0} + \eta_{cc} + \eta_{ca} = \phi_{c0} - \frac{2.303RT}{zF} \log \frac{i_L}{i_L - i_c} - \beta_c \log \frac{i_c}{i_{c0}} \quad (8)$$

where ϕ_c is the potential (V), and ϕ_{c0} is the equilibrium cathodic potential (V) under a certain environment. Fig. 1 illustrates the relation between potentials and the current densities for anodic and cathodic reactions given in Eqs. 4 and 8.

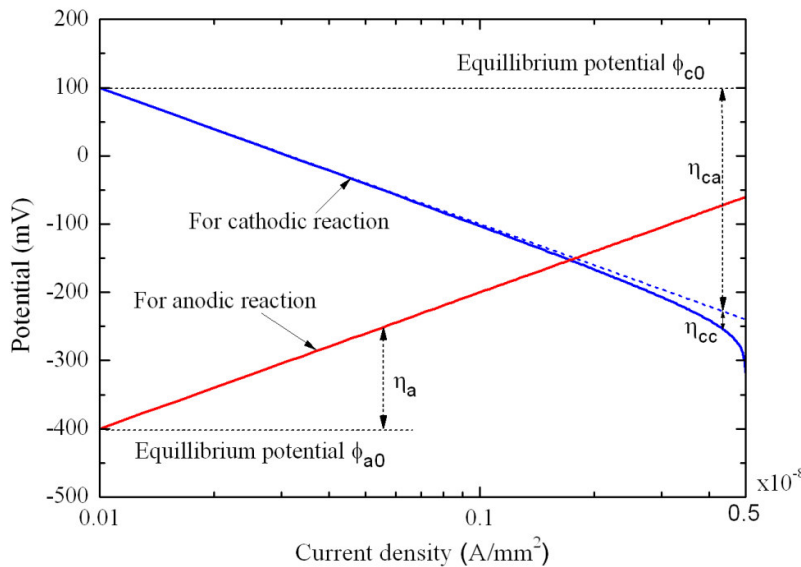


Figure 1. Potential-current density relations for anodic and cathodic reactions.

2.2. Inverse relations for anodic and cathodic reactions

In Eqs. 4 and 8, the polarized potentials ϕ_a and ϕ_c of the anodic and cathodic reactions are expressed as functions of the current densities. However, in reality, the potentials are usually measured and inverse relations are therefore required to enable the current densities to be determined from the obtained potentials.

Equally importantly, suitable inverse relations are also needed to allow the efficient and straight-forward nonlinear algorithm for modeling of steel corrosion in concrete structures to be developed. The modeling of steel corrosion in concrete structures involves solving the governing equation in Laplace form that satisfies the two boundary conditions of potential and current density at the steel-concrete interfaces [11, 12]. Currently available models often use only one of the above two boundary conditions, with the other satisfied by iteration to convergence. In contrast, with a suitable inverse relation, the two boundary conditions can be combined and satisfied simultaneously, resulting

in a straight-forward algorithm for modeling of steel corrosion in concrete structures. In addition, the incorporation of a suitable inverse relation also enables a unified algorithm for different types of corrosion modeling, e.g. to solve macro-cell modeling [12-14] and macro-and-micro-cell modeling [11] in one single algorithm. This is presented in detail in the companion paper [15].

2.2.1. For the anodic reaction

The inverse relation of Eq. 4 is the same as the Butler-Volmer relation for the anodic reaction

$$i_a = i_{a0} e^{\frac{2.303(\phi_a - \phi_{a0})}{\beta_a}} \quad (9)$$

2.2.2. For the cathodic reaction

Without the concentration polarization term η_{cc} , the inverse relation of Eq. 8 is similar to the Butler-Volmer relation for the cathodic reaction

$$i_c = i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}} \quad (10)$$

However, the effect of concentration polarization on the cathodic reaction often cannot be ignored due to the low oxygen concentration around the cathodic sites on the steel surface. As a result, Eq. 8 becomes nonlinear and cannot be solved for explicit inverse relations, which have to be approximated instead.

Kranc and Sagues [16] attempted to incorporate the concentration polarization into Butler-Volmer equation as follows

$$i_c = \left[\frac{C_{O_2}}{C_{O_2}^S} \right] i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}} \quad (11)$$

where C_{O_2} , $C_{O_2}^S$ are the concentrations of oxygen in the concrete pore solution and at the steel surface, respectively. This relation, however, is overly simplistic. Among various shortcomings, the relation fails to reflect the asymptotic nature of the curve at limiting current density i_L , an important characteristic of the current density-potential curve for cathodic reaction.

An improved approximation was proposed by Gulikers [3], which was also based on the Butler-Volmer relation

$$i_c = \frac{i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}}}{1 + \frac{i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}}}{i_L}} \quad (12)$$

A comparison of Gulikers' proposed relation and the exact solution for i_L between 0.2×10^{-8} and 60×10^{-8} (A/mm^2) is given in Fig. 2. The exact solution for the current density is obtained by solving Eq. 8 numerically with known values of i_{c0} , ϕ_{c0} , β_c , i_L , ϕ_c using Brent method [17]. It is clear from Fig. 2 that Gulikers' relation overcomes the non-asymptotic shortcoming of that proposed in [16]. However, Gulikers' relation still does not completely represent the inverse relation of Eq. 8, especially in the regions of significant change of slope in the current density-potential curve for cathodic reaction. A better relation that represents more fully the inverse relation of Eq. 8 is therefore needed.

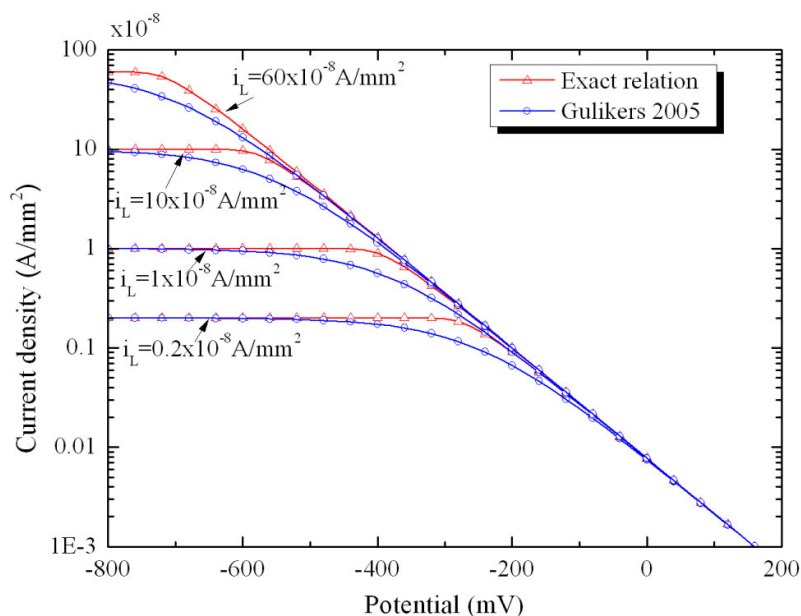


Figure 2. Gulikers' relation with exact inverse relation.

3. NEW INVERSE RELATION BETWEEN CURRENT DENSITY AND POTENTIAL FOR THE CATHODIC REACTION

Upon close examination of the potential-current density relation for cathodic reaction in Eq. 8 and Fig. 2, the following features can be observed

- i. When the limiting current density i_L of the cathodic reaction is significantly larger than the cathodic current density i_c , i.e. $i_L/(i_L - i_c) \cong 1$, the concentration polarization is negligible, resulting in the familiar Butler-Volmer relation for cathodic reaction as in Eq. 10.
- ii. When the polarized potential of the cathodic reaction ϕ_c approaches the equilibrium cathodic potential ϕ_{c0} , the cathodic current density i_c approaches the exchange current density of the cathodic reaction i_{c0} .
- iii. When the polarized potential of the cathodic reaction ϕ_c approaches negative infinity, the cathodic current density i_c reaches the limiting current density i_L (asymptotic nature of the curve).

Based on the above observations, a number of modified current density-potential relations for cathodic reaction have been investigated, among which the following relation provides the desired shape of the cathodic curves

$$i_c = \left(\frac{\left(i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}} \right)^\gamma}{1 + \left(\frac{i_{c0} e^{\frac{2.303(\phi_{c0} - \phi_c)}{\beta_c}}}{i_L} \right)^\gamma} \right)^{\frac{1}{\gamma}} \tag{13}$$

where γ is a curvature-defining constant. Fig. 3 illustrates the change of curvatures of the cathodic curves with different values of γ .

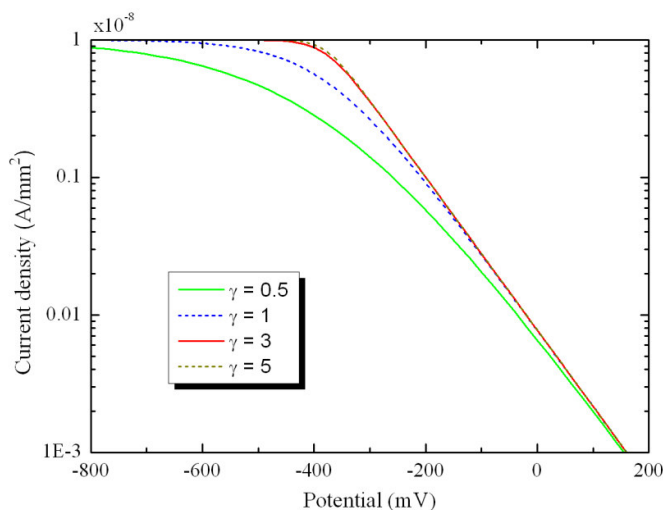


Figure 3. Effect of γ constant on the curvature of cathodic curves.

In order to determine the appropriate value for the constant γ , a sensitivity analysis is carried out by comparing the current densities determined by the exact relation and the proposed relation for a typical input data set and for a range of γ . Again, the exact solution for the current density is obtained by solving Eq. 8 numerically with known values of i_{c0} , ϕ_{c0} , β_c , i_L , ϕ_c using Brent method.

Based on the common values of parameters i_{c0} , ϕ_{c0} , β_c , i_L and ϕ_c for steel corrosion in concrete structures (Table 1), the input parameters for the sensitivity analysis are selected and given in Table 2. The resulting current densities determined by the exact and proposed relations for different values of γ are presented in Fig. 4. By observation, the current densities determined by the two relations correlate very well for γ of about 3, but differ considerably for γ of less than 1.

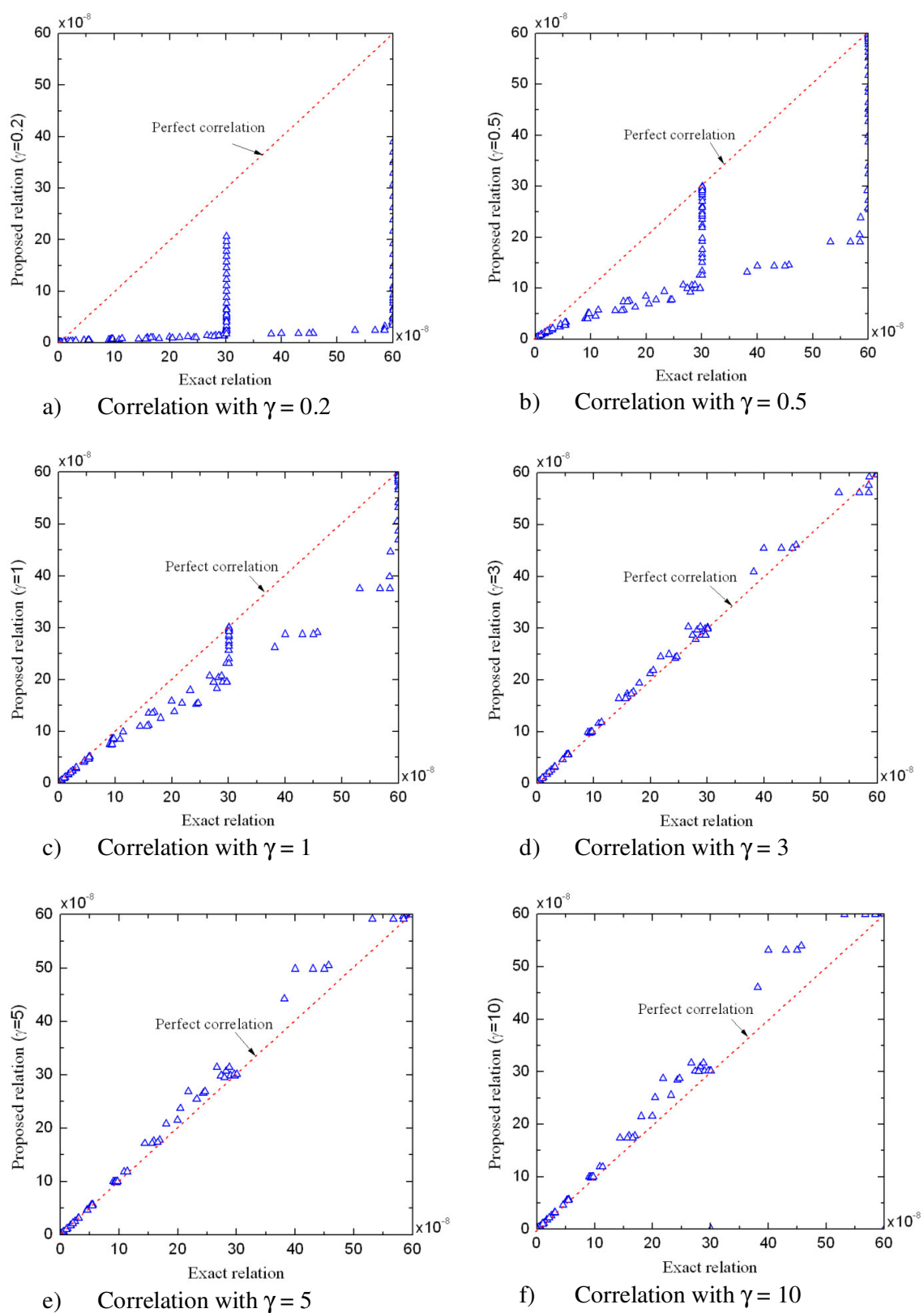


Figure 4. Current density determined by exact and proposed relation for different values of γ .

Table 1. Review of parameters for cathodic curve.

	$i_{c0}(A/mm^2)$	$\phi_{c0}(mV)$	$\beta_c(mV/dec)$
Kim and Kim [11]	0.0006×10^{-8}	160	176.3
Isgor and Razaqpur [12]	0.0006×10^{-8}	160	160
Ghods, Isgor and Pour-Ghaz [18]	0.001×10^{-8}	160	160
Kranc and Sagues [16]	0.000625×10^{-8}	160	160
Pour-Ghaz, Isgor and Ghods [13]	0.001×10^{-8}	160	180
Warkus, Raupach and Gulikers [19]	-	-	200

Table 2. Selected input parameters for sensitivity analysis.

(Note: the combination of different values of i_{c0} , ϕ_{c0} , β_c , i_L , ϕ_c provided in following table gives 891 data points)

Input parameters	Values
ϕ_c (mV)	-800,-700,-600,-500,-400,-300,-200,-100,0,100,200
$i_{c0}(A/mm^2)$	0.0001×10^{-8} , 0.00055×10^{-8} , 0.001×10^{-8}
$\phi_{c0}(mV)$	100,150,200
$\beta_c(mV/dec)$	100,150,200
$i_L(A/mm^2)$	0.2×10^{-8} , 30×10^{-8} , 60×10^{-8}

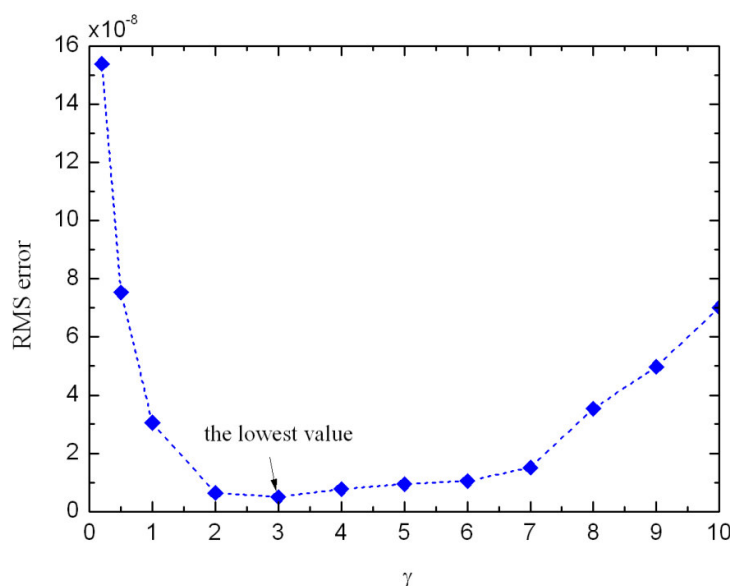


Figure 5. Variation of Root-Mean-Square error with γ .

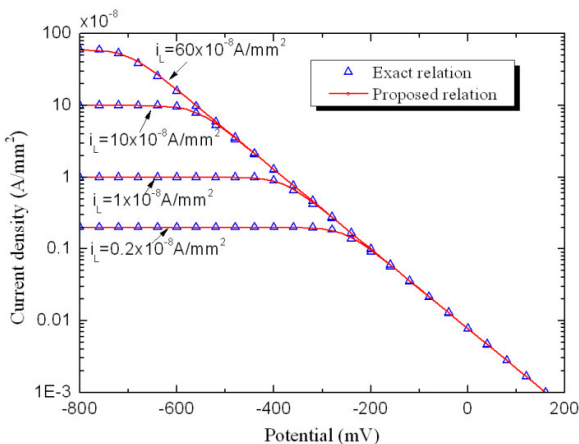
In order to find the optimal value of γ , the variation of Root-Mean-Square error, defined in Eq. 14, with γ is plotted in Fig. 5.

$$RMS\ error = \sqrt{\frac{\sum_{i=1}^n (i_c^{exact} - i_c^{proposed})^2}{n}} \tag{14}$$

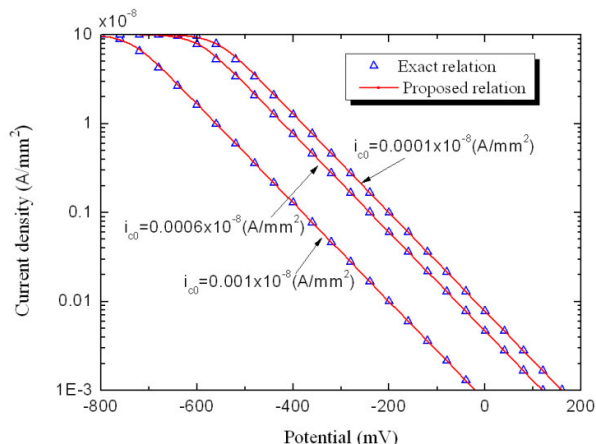
where i_c^{exact} and $i_c^{proposed}$ are current densities determined by the exact and proposed relations, respectively, and n is the number of data points ($n=891$).

It is clearly evident from Fig. 5 that the optimal value of γ is 3, and hence the proposed relation becomes

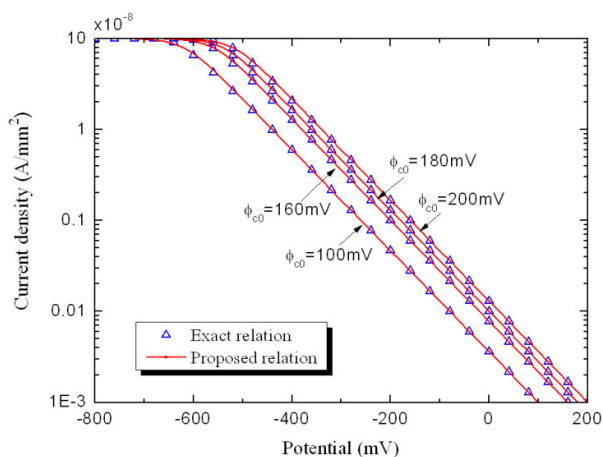
$$i_c = \left(\frac{\left(i_{c0} e^{\frac{2.303(\phi_{c0}-\phi_c)}{\beta_c}} \right)^3}{1 + \left(\frac{i_{c0} e^{\frac{2.303(\phi_{c0}-\phi_c)}{\beta_c}}}{i_L} \right)^3} \right)^{\frac{1}{3}} \tag{15}$$



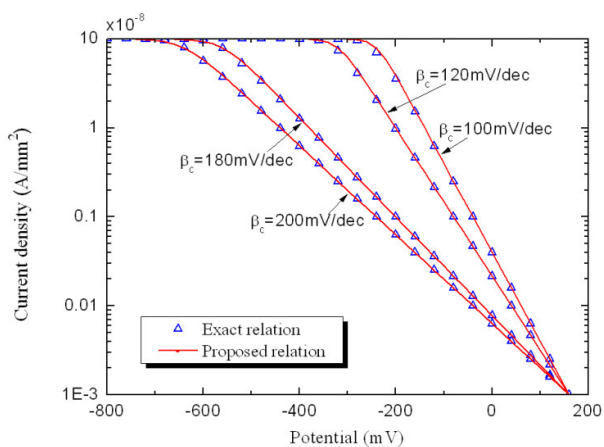
a) Changing i_L



b) Changing i_{c0}



c) Changing ϕ_{c0}



d) Changing β_c

Figure 6. The current density-potential curves for cathodic reaction.

The validity of this proposed relation is further demonstrated by the following illustration. Let's consider a typical base case (Table 1) of i_{c0} of 0.001×10^{-8} (A/mm²), ϕ_{c0} of 160 (mV), β_c of 180 (mV/dec), and i_L of 10×10^{-8} (A/mm²). Each of these parameters is varied in turn within its common range (Table 1), while the others remain unchanged. The resulting potential-current density curves are presented in Fig. 6. In all cases, the prediction by the proposed relation correlates very well with the exact solution, confirming the capability of the new relation between current densities and potentials for cathodic reaction.

4. CONCLUSIONS

In this paper, a new inverse relation that relates the current density with potential for the cathodic reaction has been proposed. Besides its desirable simple nature, the proposed inverse relation has been clearly shown to correlate very well with the exact solution.

The significantly improved inverse relation proposed enables the current densities to be determined accurately from the measured potentials. Equally importantly, the proposed inverse relation also enables the efficient and straight-forward nonlinear algorithm for modeling of steel corrosion in concrete structures to be developed. Such an algorithm is presented in the companion paper of this.

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