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Influence of chloride ions and hot weather on isolated rusting steel bar in concrete based on NDT and electro-chemical model evaluation

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ABSTRACT

The most prominent durability concern for reinforced concrete (RC) structures is the corrosion of steel reinforcement in concrete. RC buildings exposed to chloride and high temperature environments like sea and deserts suffer from accelerated corrosion of rebars. The chloride attack and increase in the electro-chemical reaction rate of corrosion due to high temperature is a thermodynamic phenomenon influenced by several parameters and some of them are being neglected in the past research works. The purpose of this present paper is therefore, to model and verify by NDT the coupled effects of chloride and temperature on corrosion of reinforcement throughout the life of concrete buildings by incorporating realistic thermodynamic model evaluations and actual field condition NDT. The model evaluation has been accomplished by the use of concrete durability model as a computational platform on which the corrosion based reinforced concrete building performance and quality at early age and throughout the life of concrete structure is examined in both space and time domains under environmental actions of chloride and temperature. On this line, the thermodynamic modeling evaluation of concrete forms the fundamental core of the theoretical approach to achieve both the scientific knowledge and engineering simulations of altering materials. The NDT results for the effect of chloride and temperature on corrosion have been compared with the DuCOM electro-chemical thermodynamic corrosion model evaluation and are found to be in close agreement with each other.

1. Introduction

Steel reinforcement corrosion in concrete is of great concern in the view of safety and durability of reinforced concrete structures. The reinforced concrete structures exposed to sea environments suffer from corrosion of steel bars due to chloride ingress. The premature deterioration of reinforced concrete member has become a major concern in many countries throughout the world. Since steel corrosion is an electro-chemical process, its rate is influenced by temperature and corrosion of steel may vary from one place to another due to the differences in season and temperature conditions. Therefore, it is necessary to conduct in-depth investigations in order to further understand the mechanisms of corrosion in concrete influenced by hot weather and chloride for which the previous research data is limited [1–3].

2. Generalized thermo-hydro dynamic evaluation system

In this research, a three dimensional finite element program, DuCOM developed by our research group is implemented as a general framework for durability assessment and numerical analysis of arbitrary cementitious materials and structures subjected to various environmental conditions. A general framework of mass and ion equilibrium equations and a chemical reaction model of corrosion in reinforced concrete have been presented elsewhere in detail [4]. Thus the influential parameters on the theorem of corrosion process for the effect of chloride and temperature are determined experimentally and simulated in numerical terms for the enhancement of existing model in this paper. The reliability of this model is verified through comparison of simulation with well-documented experimental results.

The constituent material models employed in DuCOM are formulated based on micro-mechanical phenomena such as hydration, moisture, transport and cementitious microstructure formation. Their strong interrelationships are taken into account by real time sharing of material characteristic variables across each sub-system. The development of multi-scale micro pore structures at early age is obtained based on the average degree of cement hydration in the mixture. The non-linearity in corrosion process and coupling terms (chloride and temperature) are taken into account in the unified framework of the program as schematically shown in Fig. 1 [4,5].

3. Non destructive testing (NDT)

3.1. Materials and specimen preparation

Schematic diagram and original picture of the prismatic concrete specimen (100 × 100 × 400 mm^3 and 100 × 100 × 200 mm^3) with two

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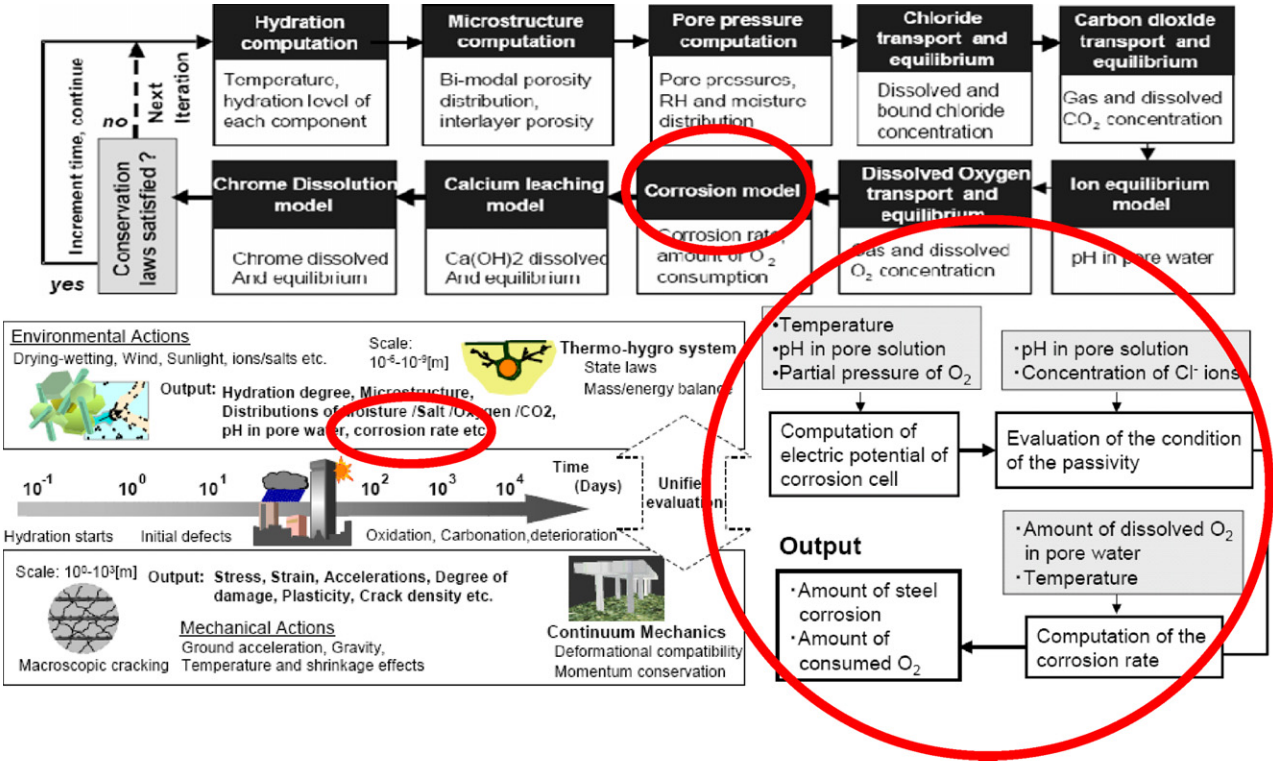

Fig. 1. Multi-scale scheme visualizing the corrosion simulation.

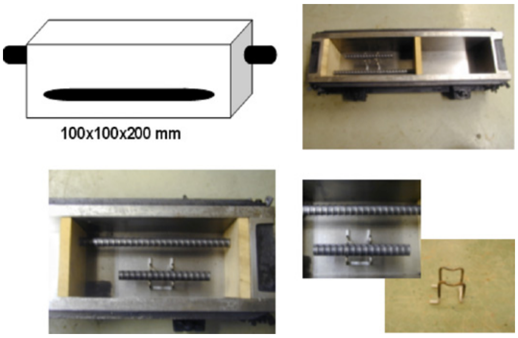

Fig. 2. Diagram of specimens.

Table 1
Mix proportions of concrete.

W/C	Binder (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m^3)
0.45	386	174	629	1122

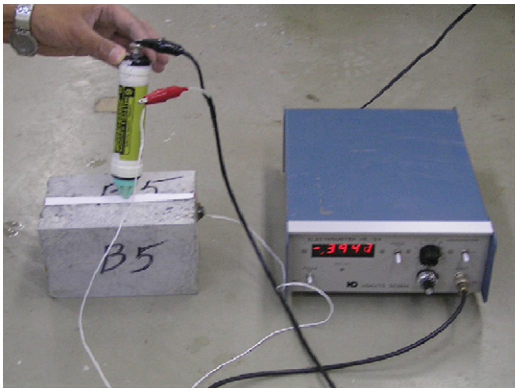

Fig. 3. Corrosion potential measurement.

13 mm steel bars (one bar completely embedded and other coming out from both faces, both having a clear cover of 15 mm) cast in steel molds are as shown in Fig. 2. The chloride was admixed into the concrete specimens as sodium chloride in the mixing water, of which concentrations vary from 0% to 10% by mass of binder for all the test series.

The W/C ratio was kept at 0.45 with mix proportions as shown in Table 1. The specimens were demoulded 24 h after casting and cured at 20 ± 2 °C, 95 ± 5% relative humidity for 28 days.

3.2. *NDT scheme and objective*

The test consists of 24 specimens having a total Cl concentration varying from 0% to 6% (NaCl: 0–10%) in mixing water consisting of three sets for 20, 40 and 60 °C temperature conditions and 60% relative humidity in environment control chambers.

4. NDT results and discussion

The test consists of 24 specimens having a total Cl concentration varying from 0% to 6% (NaCl: 0–10%) in mixing water consisting of three sets of 20, 40 and 60 °C temperature conditions and 60% relative humidity in environment control chambers. Half-cell potentials were measured with two days interval for all specimens using a copper–copper sulfate reference electrode (CSE), in accordance with ASTM C-876, which can be found elsewhere. For further illustration of the method consider Fig. 3. The details will be explained in the next sections. The objectives of the above assembly include enhancement of the existing corrosion model of DuCOM [4], corrosion potential vs. chloride profile with respect to time variable and determination of the relation between temperature and corrosion rate.

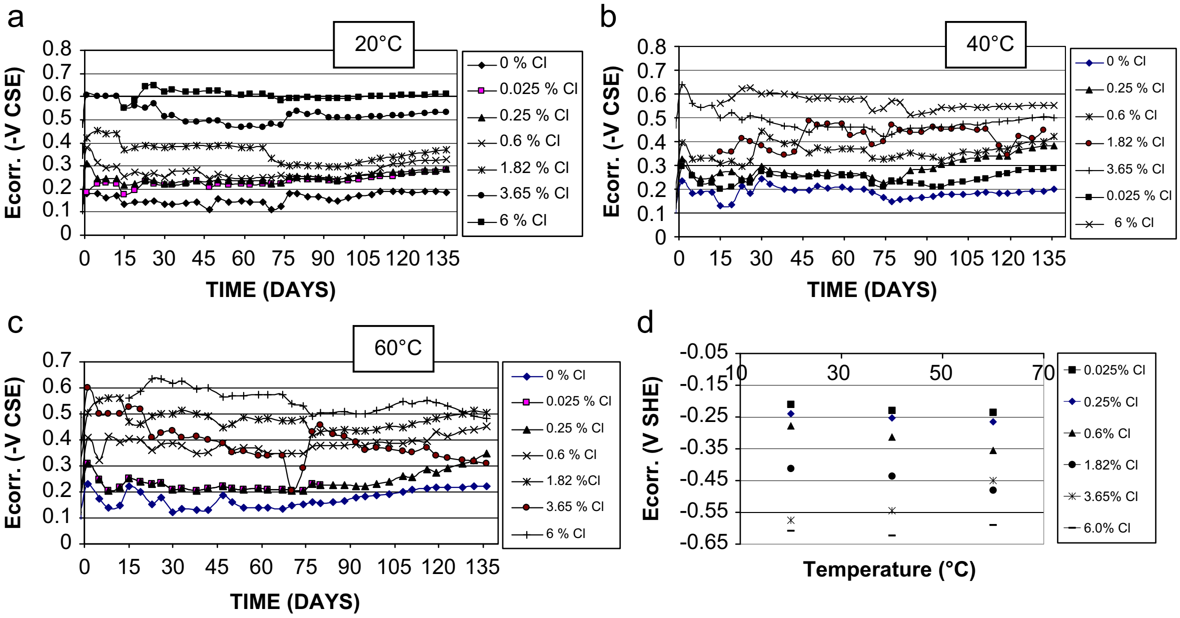

Fig. 4. Variation of half-cell potential with age, Cl and temperature. (OPC, W/C=0.45).

Fig. 4 shows the results of half-cell potential measurements for the ordinary cement concrete mixed with 0.0%, 0.04%, 0.4%, 1.0%, 3.0%, 6.0% and 10% sodium chloride by mass of binder and three temperature conditions of 20, 40 and 60 °C. The half-cell potential values for various cases have a tendency to increase in early age and then approach to certain uniform values but not strictly constant. Therefore, weighted average values of the corrosion potential were adopted. In general the corrosion potential shows a non-linear increase with the increase of chloride content and temperature as shown in Fig. 4. But, only in the case of the specimens having the highest concentration of NaCl, i.e., 6% and 10% by wt. of binder and 60 °C temperature show a falling trend and reduction in the corrosion potential values with the increase in temperature. The possible reason could be intensive corrosion cracking occurred in these two specimens. The crack width on the surface near the 15 mm cover became more than 5 mm. Thus causing the loss of moisture needed for corrosion process and discontinuity of the specimen material along the crack. Mortar specimens were also cast to find the effect of the volume of coarse aggregate on corrosion and it has been proven experimentally that the effect of the volume of coarse aggregate on corrosion potential is not more than 10%.

5. Electro-chemical computer aided evaluation of corrosion

The corrosion model was firstly adopted from DuCOM [4]. In the corrosion model a general scheme of a micro-cell corrosion model is introduced based on thermodynamic electro-chemistry [5]. First of all, electric potential of corrosion cell is obtained from the ambient temperature, pH in pore solution and partial pressure of oxide, which are calculated by other subroutine in the system. The half-cell potential can be expressed by the following Nernst equation.

$$\mathrm{Fe}(s)\rightarrow \mathrm{Fe}^{2+}(\mathrm{aq})+e(\mathrm{Pt}),\quad E_{\mathrm{Fe}}=E^{\Theta}_{\mathrm{Fe}}+(RT/z_{\mathrm{Fe}}F)\ln h^{2+}_{\mathrm{Fe}},$$
$$\mathrm{O}_2(\mathrm{g})+2\mathrm{H}_2O(l+4\mathrm{e}(\mathrm{Pt})=4\mathrm{OH}^-(\mathrm{aq}),$$
$$E_{02}=E^{\Theta}_{02}+((RT/z_{02}F)\ln(P_{02}/P^{\Theta})-0.06\,\mathrm{pH} \qquad (1)$$

where E_{Fe} is the standard cell potential of Fe, anode (V, CSE), E_{02} is standard cell potential of O_2, cathode (V, CSE), E^{Θ}_{Fe} is standard cell potential of Fe at 25 °C (−0.44 V), E^{Θ}_{02} is standard cell potential of O_2 at 25 °C (0.40 V), z_{Fe} is number of charge of Fe ions (2), z_{02} is number of charge of O_2 (2), P^{Θ} is atmospheric pressure [6]. Next, based on thermodynamic conditions, the state of passive layers is evaluated by the Pourbaix diagram [7]. The existence of a passive layer reduces the corrosion progress and the phenomenon is described by changing the Tafel gradient in this corrosion model as shown in Fig. 5.

The relationship of electric current and voltage for the anode and cathode can be expressed by the following Nernst equation as,

$$ɲ^a=(2.303RT/0.5z_{Fe}F)\log(i_a/i_o), ɲ c^c c^C$$
$$=-(2.303RT/0.5z_{02}F)\log(i_c/i_o) \qquad (2)$$

where $ɲ^a$ is the overvoltage at anode [V], $ɲ^c$ is overvoltage at cathode [V], F is Faraday's constant, i_o is equilibrium current density (A/m^2), i_a is electric current density at anode (A/m^2), i_c is electric current density at cathode (A/m^2). The corrosion potential Ecorr. and corrosion current Icorr. can be obtained as the point of intersection of the two lines [6]. In the model i_a=1.0E−5 and i_c=1.0E−10. The effect of chloride on corrosion has been incorporated by varying the Tafel gradient of anodic reaction with chloride concentration as shown in below equation.

$$\mathrm{ba}=(2.303\,\mathrm{RT}/0.5Z_{\mathrm{Fe}}F)\mathrm{fp},\quad \mathrm{ba}=\text{anodic Tafel gradient} \qquad (3)$$

where $fp=0.4/C_{Cl}$ if $0.04<C_{Cl}<0.4$; $fp=1$ if $C_{Cl}\geq 0.4$; and fp=1.0E+4 if $C_{Cl}\leq 0.04$

In the model, this semi-empirical-theoretical factor '*fp*' accounts for the change in anodic Tafel slope gradient. When the free chloride concentration becomes very low or zero (0.04–0.0%), the Tafel slope co-efficient '*fp*' becomes very large approaching infinity (10−∞). Considering the rebar to be in a perfect passive condition represented by a 90° perpendicular anodic line of the Tafel diagram, when the free chloride concentration is equal to or less than 0.04% the value of Tafel slope co-efficient '*fp*' is ideally assumed to be very large (1.0E+4) approaching infinity. As the chloride concentration increases, the passive layer starts breaking simulated by a decrease in the Tafel slope co-efficient '*fp*' resulting in the decline of anodic gradient moving the point of intersection of anode and cathode lines towards a more negative corrosion potential and increase in corrosion current until the value of 0.4% free chloride by mass of binder is reached and the passive layer is considered to be completely destroyed. At this stage the Tafel slope co-efficient is assumed to become 1.0 and the gradient of anodic reaction in the Tafel diagram becomes equal to the actual Tafel gradient as given by Nernst equation. Fig. 5 explains the physical and logical working of anodic Tafel slope co-efficient.

The cathodic Tafel gradient was fixed to a constant value (bc=0.12) in the model by previous literature survey which has been improved (bc=0.14) especially for the effect of temperature on corrosion by utilizing the experimental results of this research. By extensive previous literature survey and experimental data it was observed that the corrosion potential and current are under estimated especially for free chloride content more than 0.4% by mass of binder. Therefore, an empirical factor 'FMacro' is introduced to enhance the model for the above said as shown in Eq. (4) below:

$$E_{\mathrm{Fe}} = E_{\mathrm{Fe}}Q + ((\mathrm{RT}/Z_{\mathrm{Fe}}F)\ln h_{\mathrm{Fe}}{}^{2})\mathrm{FMacro},$$
$$E_{02} = E_{02}Q + 0.826 + ((\mathrm{RT}/Z_{02}F)\ln(P_{02}/\mathrm{PQ})) - 0.06\,\mathrm{ph}$$

$$\mathrm{FMacro} = 0.142\ln(C_{Cl}) + 1.13, \quad \text{for } C_{Cl} > 0.4 \tag{4}$$

where T is the surrounding temperature in Kelvin's scale, F is Faraday's constant, R is universal gas constant, E_{Fe} is standard cell potential of Fe, anode (V,SHE), E_{O2} is standard cell potential of O_2, cath. (V,SHE), $E^{\ominus}_{Fe}$ is standard cell potential of Fe at 25 °C (−0.44 V), $E^{\ominus}_{O2}$ is standard cell potential of O_2 at 25 °C (0.40 V), Z_{Fe}: the number of charge of Fe (2), z_{O2} is the number of charge of O_2 (2), C_{Cl}: free chloride concentration as a weight percentage of binder/cement, pH is power of hydrogen ion concentration, P_{02} is partial pressure of oxygen and P^{Θ} is atmospheric pressure.

Please refer to the Tafel diagrams shown in Fig. 6(a) and (c) for further illustration of this enhancement. In the original model as shown in the Fig. 6(a), the anodic gradient becomes constant beyond 0.4% free Cl; hence, under estimates corrosion potential for higher vales of Cl. This has been taken care in the enhanced model by varying the anodic curve with the increase of chloride content even at very high concentrations with satisfactory accuracy. For the purpose of illustration only five cases of chloride concentration variation are shown in the Fig. 6(c). The empirical factor 'FMacro' causes the anodic curve to shift downwards with the increase in the chloride content, thus moving the point of intersection of cathode and anode polarization curves towards the more negative potential side.

6. Verification of the computer based corrosion evaluation model:

The enhanced corrosion model shows good agreement with the experimental results as shown in Fig. 6(b) for the effect of chloride, and in Fig. 7 for the effect of temperature for the corrosion of reinforcement embedded in concrete. Thus, providing evidence for the efficiency and accuracy of enhanced corrosion model of DuCOM. The model though simple but predicts well taking into account the influential parameters involved in the process of corrosion in R.C structures. The conversion of free Cl to bound Cl and vice versa is done using the chloride equilibrium empirical equation given by LanAnh [8].

7. Conculsions

Vital parameters on evaluation of corrosion in RC structures involving chloride concentration and temperature variation are determined by NDT and numerically evaluated through parametric study. Appropriate parameters for material modeling evaluation of corrosion on the basis of already developed computational scheme were successfully identified. It is shown that the Tafel slope co-efficient has a great influence on the evolution of corrosion

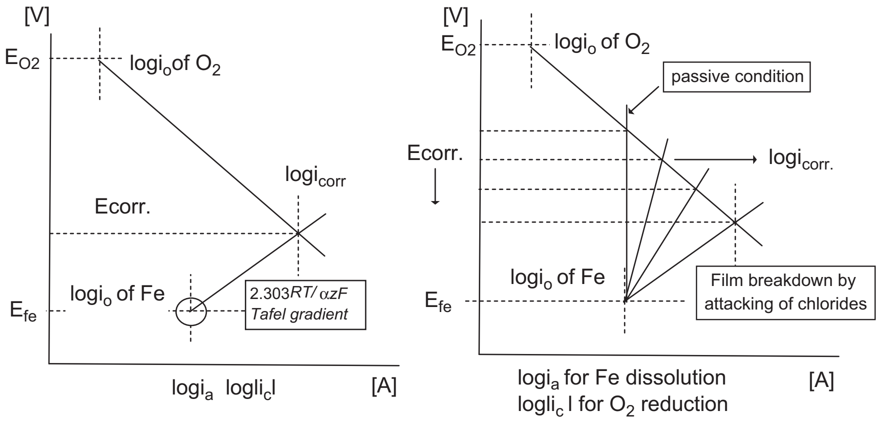

Fig. 5. Relationship of current and voltage with rate of corrosion accelerated by Cl migration.

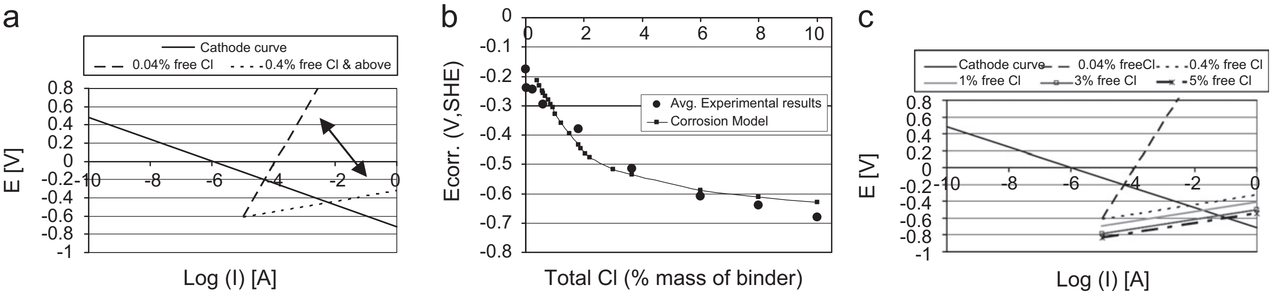

Fig. 6. Evaluation of corrosion model by comparison with NDT: (a) original model, (b) half-cell potential vs. Cl(T=20°C) and (c) enhanced model.

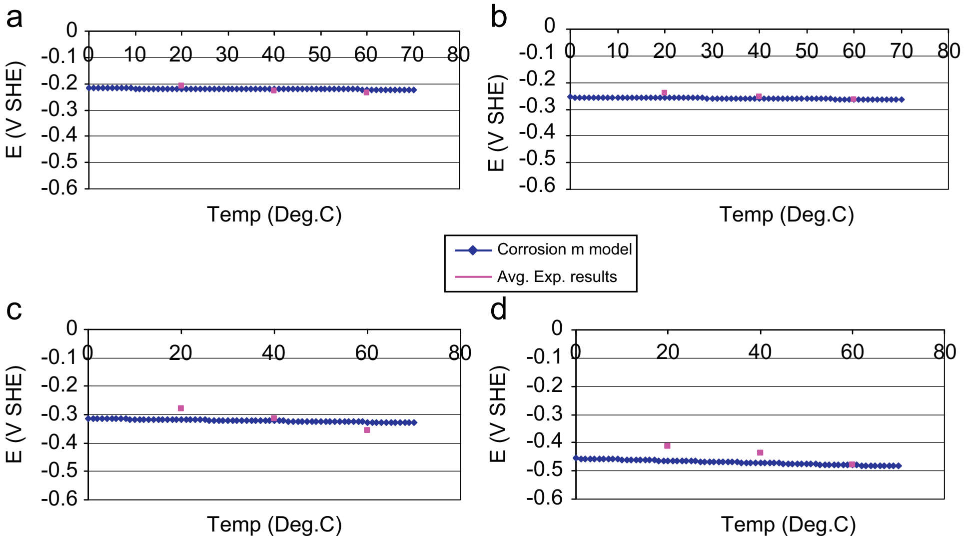

Fig. 7. Variation of half-cell potential with temperature: (a) 0.04% NaCl, (b) 0.4% NaCl, (c) 1.0% NaCl and (d) 3.0% NaCl.

in reinforced concrete structures especially for the coupling of chloride and temperature. The NDT results for the effect of chloride and temperature on corrosion are found to be in reasonably good agreement with the DuCOM [9] thermodynamic corrosion model evaluation with enhancement of the model parameters proposed in this paper.

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