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Short Communication

Electrochemical Behavior and Dependency of Anodic Current Density on Chloride Concentration and Temperature Based on Reverse Corrosion Modeling Approach for Steel Reinforced Concrete

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This paper elaborates the electrochemical behavior and dependency of anodic current density on chloride concentration and temperature based on reverse corrosion modeling approach for steel reinforced concrete. This research presents a semi-empirical corrosion modeling approach which obeys the basic mathematical laws and is also verified by the test results involving a wide range of chloride and temperature variations. The numerical modeling task has been incorporated by the use of computer based finite element model as a computational platform on which the coupled temperature-chloride induced corrosion throughout the life of reinforced concrete structures is examined in both space and time domains. This article contains advances in the development and use of computational methods for the solution and simulation of corrosion problems in civil engineering. In this paper a back calculation mathematical model has been developed and its numerical solution along with testing verification is presented. This article makes use of computers and numerical methods to model and solve the temperature induced corrosion problems in concrete structures. The paper provides a unique combination of strong numerical experiments, mathematical analysis, and comparisons with the test data. In this paper an automatic solution of mathematical models has been developed for corroding structures presenting algorithms for optimization and simulation which will help in profound understanding of temperature controlled corrosion reactions in reinforced concrete structures based on primary scientific laws and principles for complete life cycles. Investigations revealed that in fact anodic current also varies as a function of chloride concentration and temperature. This relation has been successfully extracted in this paper from the past research. It was interesting to observe the similarity present in the profiles of anodic current at different temperature conditions of 20°C, 40°C and 60°C.

Keywords: Electrochemistry, Material modeling, FEM computations, Anodic current, temperature, chloride, corrosion, reinforced concrete.

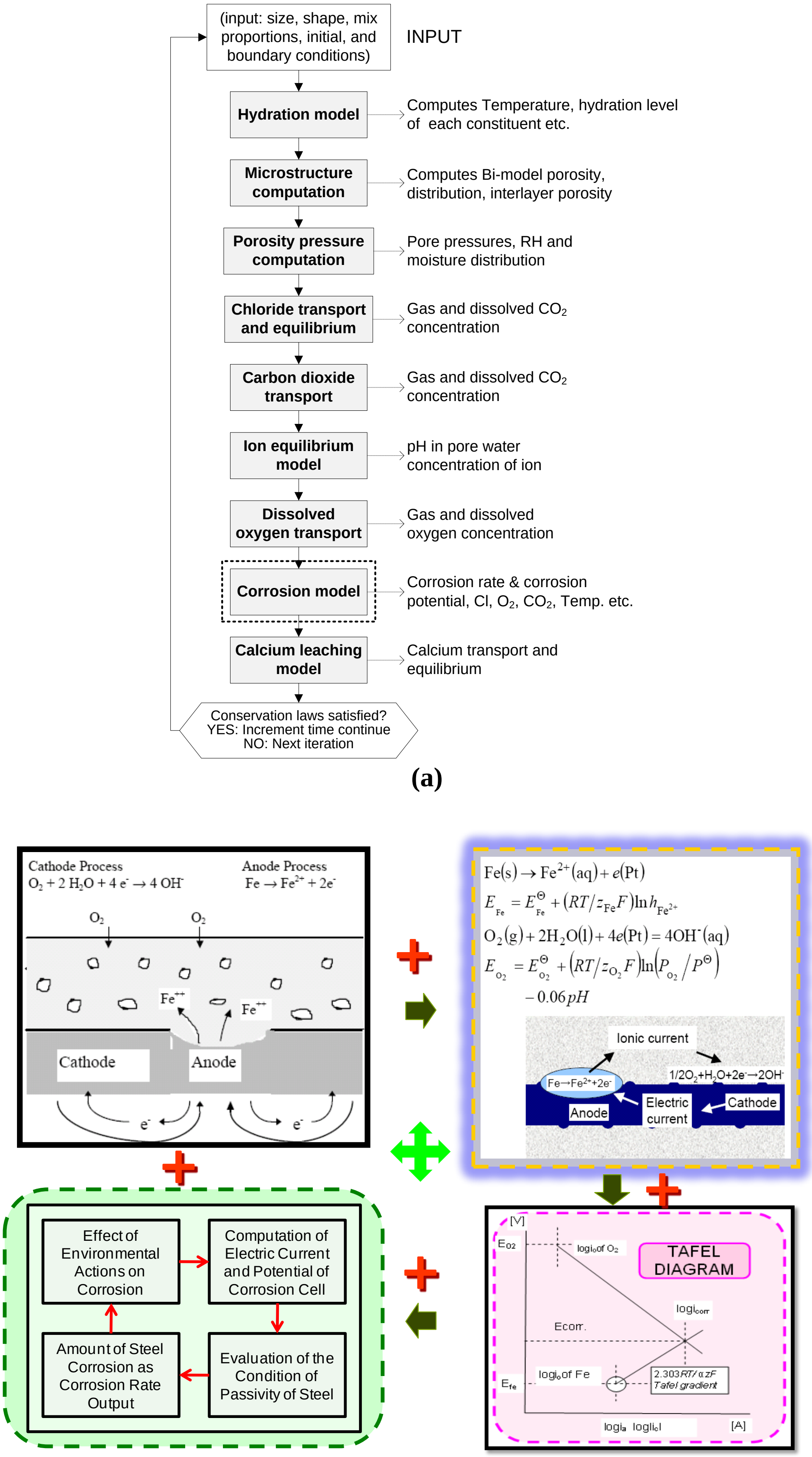
1. INTRODUCTION

Under chloride attack, the passive film is destroyed, and the steel spontaneously corrodes. This phenomenon is much more accelerated when the climate is hot. Many researchers have computed the effect of temperature on chloride induced corrosion of RC structures [1-8]. The effect of temperature on corrosion is influenced by several computation factors and some of them have been overlooked in the past research works having difference of opinion. Some researchers believe that corrosion rate is directly proportional to the increase in temperature while, others are of the opinion that the rate of increase in corrosion varies exponentially with the temperature rise. Yet some other researchers computed that corrosion has very non linear or no specific relation with temperature and their computations showed a widely scattered trend. The anodic current density dependency on chloride and temperature is also not clear. This leads to the objectives of this research.

2. RESEARCH METHODOLOGY: COMPUTER-AIDED COMPUTATIONAL SIMULATION FEM MODEL

The methodology adopted in this research is based on durability concrete model [9, 10], a 3D finite element numerical model. It is a computational computer based program for the evaluation of various durability aspects of concrete such as concrete hydration, microstructure formation and several associated phenomenon, from casting of concrete to a period of several months or years. As such this tool can be utilized to study the effect of ingredient materials, environmental conditions as well as the size and shape of structure on the durability of concrete. The term durability considered here takes into account both the fresh concrete problems as well as matured concrete exposed to environment. This tool can be used to analytically trace the evolution of microstructure, strength and temperature with time for any arbitrary initial and boundary conditions. Since the main simulation program is based upon finite-element methods, it could be applied to analyze real life concrete structures of any shape, size or configuration. Furthermore, dynamic coupling of several phenomenon ensures that the effect of changing environmental conditions is easily integrated into the overall simulation scheme.

A general frame work of mass and ion equilibrium equations and an electro-chemical reaction model of corrosion in reinforced concrete has been presented elsewhere [9-11]. Thus the influential parameters on the theorem of corrosion process for the severe environmental effects are determined experimentally and simulated in numerical terms for the enhancement of existing model in this research. The reliability of this computational model is verified through comparison of simulation with test results. The constituent material models employed (Figure 1 (a, b)) 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 non-linearity in corrosion process and the effect of severe environmental actions is taken into account automatically in the unified framework of this computer program by the help of various connected sub-models within this system to acquire the parameters necessary for computation of corrosion.



(a)

(b)

Figure 1. Overall view of the simulation [9, 10, 15] (a) Unified framework of computer-aided FEM simulation model (b) Corrosion model for RC structures

3. NUMERICAL MODELING AND COMPUTER SIMULATION

The corrosion model is initially adopted from the previous research [9-11]. In the computational model a general scheme of micro-cell corrosion is introduced based on electro-chemistry and classical Tafel diagram technique. The electric potential and current of corrosion cell is obtained from the ambient conditions which are calculated by other subroutines in the system. The effect of temperature in previous corrosion model is considered from the original Nernst equations as temperature is one of the variables in these equations [9, 10]. The model does account for the variation in temperature as far as the calculation of electrical potential is concerned. But, the model was primarily designed for constant normal temperature conditions for the calculation of electric current. Consequently, from the comparison of experiment results and model analysis, it can be seen that the model underestimates at high temperature conditions more than 20°C and required improvement [11].

No doubt these Nernst Equations are used in the model to understand the stable phase and reactions to be occurred in E-pH diagram, or Pourbaix diagram and Tafel's diagram [12]. But in the previous model, only respective potentials and slopes are calculated with respect to temperature. The Tafel slope b_a in the previous model [11] increases with higher temperature and it causes reduction in the corrosion current i_{corr}. This is the reason for under estimation of temperature induced corrosion model. At a later stage it was found that in the previous model [11] not only the slope b_a but also the exchange electric current density at anode i_o^a also increases with higher temperature and needs to be incorporated in the model. From the past research works [13, 14], it is found that the effect of temperature is much higher on i_o^a than on b_a. As a result, even though the slope b_a increases with temperature causing decrease in i_{corr}, the increase in i_o^a is much higher. This results in overall increase in the corrosion current. So far in the previous model [11], a standard constant value of i_o^a was used as 1.0×10^{-5}A/m^2. This value is satisfactorily enough when one uses a constant normal temperature model for 20°C. But when it is intended to extend the model for variable temperature conditions in this paper, then need is felt to install the effect of temperature from the original Arrhenius Law as shown in Equation 1 [11] below.

$$i_{o\,(T)}^a = (i_o^a)_\infty \exp(-\Delta \mathrm{E_a}/RT) \qquad (1)$$

where;

$i_{o\,(T)}^a$:anodic current at temperature 'T'

$(i_o^a)_\infty$:ultimate reference anodic current at infinite temperature (an imaginary situation)

It is not easy to get the value of 'i_o^a' directly from experiment results only. Therefore, it was decided to back calculate the values of 'i_o^a' at 20, 40 and 60°C by the sensitivity analysis in comparison to the experiment data and drawing of the Arrhenius plot for checking the applicability of Arrhenius Law and the determination of activation energy. The referential temperature has been set at 20°C and the standard value of $i_o^a = 1.0\text{x}10^{-5}$A/m^2 which was used as a constant value of anodic current in the original model has been set as the referential value of anodic current at 20°C in the enhanced model in this paper. With reference to the previous literature review [15], the Equation 2 can be narrated as follows for the setting of referential values.

$$i_{o\,(T)}^{a} = i_{o\,(Ts)}^{a} \exp\left[-\Delta E_a/R\,(1/T - 1/T_s)\right] \qquad (2)$$

where;

$i_{o\,(Ts)}^{a} = i_{o\,(\infty)}^{a} \exp[-\Delta E_a/R(1/T_s)]$

Here in Equation 4 the value of referential anodic current '$i_{o\,(Ts)}^{a}$' is equal to $i_{o\,20^{o}C}^{a} = 1.0\text{x}10^{-5}$ A/m^2. This enhanced model derived from Arrhenius law gives the direct relation between the anodic current 'i_o^a' and any arbitrary temperature T. As there is no way to measure the value of 'i_o^a' directly from experimentation, therefore, the referential values of 'i_o^a' at 40 and 60°C are back calculated by using standard referential value of $i_o^a = 1.0\text{x}10^{-5}$A/m^2 at 20°C alongwith sensitivity analysis on the corrosion model. Originally the back calculation is done starting from the corrosion current and potential. Corrosion potential is obtained as direct measurement while corrosion current is obtained from the gravimetric mass loss measurement in the experiment by using Faraday's law. Then using Nernst Equation in the model and comparison of experiment results and analysis [11], the respective values of anodic current 'i_o^a' at 40 and 60°C are back calculated by performing sensitivity analysis, so that the model analysis and experiment results become coherent on averaged basis for all the available cases of variable chloride and temperature conditions.

The anodic current values 'i_o^a' obtained as above were plotted against the inverse of absolute temperature to obtain what is called Arrhenius plot. It was observed that the Arrhenius plot came out to be a straight line (Figure 2).

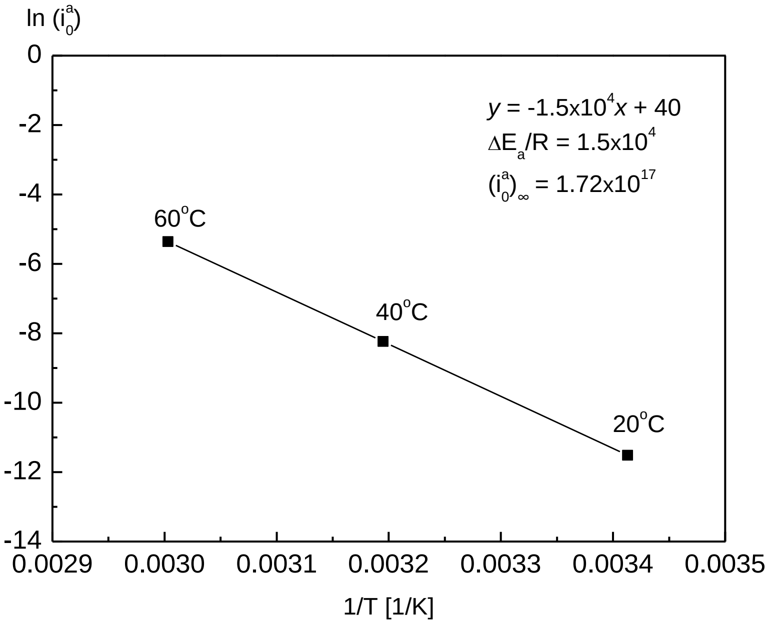


Figure 2. Arrhenius plot for referential anodic current 'i_o^a' model values at 20°C, 40°C and 60°C

Thus proving the fact that Arrhenius Law is applicable and the proposed enhancement method is valid. As it is evident from Figure 2 that the rate of increase of 'i_o^a' with temperature follows Arrhenius Law, activation energy can now be obtained. From this Arrhenius plot, activation energy of reaction came out to be '$\Delta E_a = 1.5x10^4xR$' and the referential value '$(i_o^a)_\infty$' which is the ultimate reference anodic current at infinite temperature is calculated as '$(i_o^a)_\infty = 1.72x10^{17}$'. Thus all the unknown parameters in Equation 2 have been identified. It was seen that the enhanced model shows good averaged agreement with the experiment results for the coupled effect of chloride and temperature on corrosion of RC structures [11].

4. BEHAVIOR AND DEPENDENCY OF 'i_o^a'

Investigations revealed that in fact i_o^a is also varying as a function of chloride concentration and temperature. This relation is extracted from Fig. 2 and presented in the Fig. 3. The above figure shows that i_o^a is not only a function of chloride but also a function of temperature as well. Yet it is very interesting to observe the similarity present in the profiles of i_o^a at different temperature conditions of 20°C, 40°C and 60°C. The anodic current is found to be maximum at the highest temperature of 60°C and lowest at 20°C providing the directly proportional relation between the temperature and anodic current density.

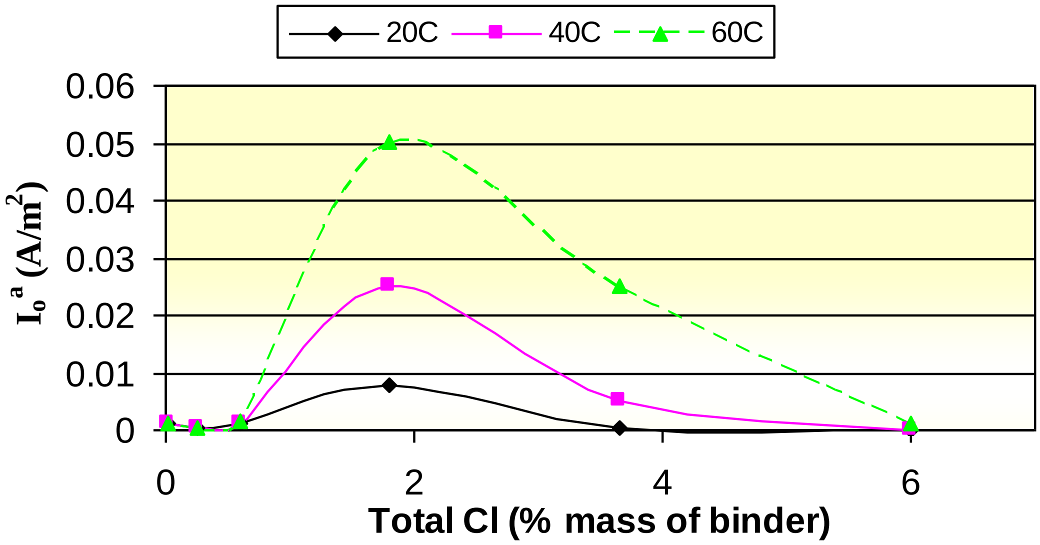


Figure 3. Relation between i_o^a and chloride concentration at variable temperature conditions of 20, 40 and 60°C

At low chloride values (less than 1% total chloride), the current density at the anode does not vary a lot with respect to temperature since the level of corrosion is not high. However, with the increase in chloride concentration, the current density at the anode significantly increases with the rise of temperature and vice versa at high level of corrosion. This behavior reaches its maximum limit around 2% chloride concentration (total) by mass of binder and then falls down once again. At the total chloride concentration of 6% the respective anodic current densities i_o^a become similar one again irrespective of the variation in ambient temperature conditions.

It is interesting to observe that the anodic current i_o^a reaches its maximum value exactly at the same chloride concentration irrespective of the variation in temperature conditions. It shows there also exists a strong relation between the anodic current and chloride concentration in addition to the relation between activation energy and chloride concentration which cannot be avoided while explaining the electrochemical behavior and dependency of anodic current on chloride concentration and temperature based on reverse corrosion modeling approach for steel reinforced concrete structures. The experimental verification of this phenomenon remains as a scope for future research.

5. CONCLUSIONS

The numerical model based on novel approach towards computation of averaged activation energy from the Arrhenius plot developed in this paper being in close agreement with the test results predicts and simulates the corrosion rate and potential for the coupled effect of a wide range of temperature and chloride conditions with good accuracy and precision. Tafel’s equation derived from Arrhenius Law has been semi-empirically modeled for the estimation and computation of the effect of temperature on chloride induced corrosion in RC structures. Thus the effect of temperature corrosion obeys the Arrhenius equation. Influential semi-empirical parameters for numerical modeling and prediction of the effect of temperature on chloride induced corrosion of steel in concrete are experimentally determined and numerically discussed in this paper for which the previous research data is limited. This article contains advances in the development and use of computational methods for the solution and simulation of corrosion problems in civil engineering. In this paper a back calculation mathematical model has been developed and its numerical solution along with testing verification is presented. This article makes use of computers and numerical methods to model and solve the temperature induced corrosion problems in concrete structures. The paper presents a novel technique into established methods and at the same time verifies the developed technique by comparing with known methods and experimental verifications. In this paper an automatic solution of mathematical models has been developed for corroding structures presenting algorithms for optimization and simulation which will help in profound understanding and prediction of temperature controlled corrosion reactions in civil engineering infrastructure based on primary scientific laws and principles. Investigations revealed that in fact anodic current also varies as a function of chloride concentration and temperature. This relation has been successfully extracted in this paper from the past research. It was interesting to observe the similarity present in the profiles of anodic current at different temperature conditions of 20°C, 40°C and 60°C.

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