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- Technical Paper -

ELECTRO-CHEMICAL MODELING OF CORROSION IN REINFORCED CONCRETE AND THE EFFECT OF CHLORIDE AND TEMPERATURE

Raja Rizwan HUSSAIN[*1] and Tetsuya ISHIDA[*2]

ABSTRACT

The electro-chemical reaction of chloride induced corrosion at variable temperature is influenced by several variables and some of them still need to be further investigated more deeply. Different school of thought exists between past researchers and the data is limited in the high temperature and high chloride concentration range. The objective of this paper is to investigate the detrimental effects of chloride and temperature on corrosion of RC structures by incorporating realistic thermodynamic model namely 'DuCOM' developed by our research group and actual field condition experimentation.

Keywords: reinforced concrete, corrosion, chloride, temperature, modeling.

1. INTRODUCTION

The high alkaline environment of good quality concrete forms a passive film on the surface of the embedded steel which normally prevents the steel from further corroding. However, under chloride attack and high temperature, the passive film is destroyed, and the steel spontaneously corrodes. Therefore, it is necessary to conduct in-depth investigations in order to further understand the mechanisms of corrosion in concrete influenced by chloride and temperature.

2. OBJECTIVE

Investigation of the severe environmental effects of chloride and temperature on corrosion of steel in concrete both by experimentation and modeling approach by clarifying the mechanisms involved is the major objective of this research paper. The corrosion phenomenon is influenced by several factors and some of them have been overlooked in the past research works and have difference of opinion among themselves. Also it was found that the experimental data for the coupled effect of chloride and temperature on corrosion of reinforcement especially in the high temperature range and high chloride concentration is limited [1].

3. ELECTRO-CHEMICAL-THERMO-HYDRO -DYNAMIC MODEL 'DuCOM

A three dimensional finite element model developed by our research group is implemented in this research as a general framework for corrosion assessment and numerical analysis of RC structures subjected to severe environmental conditions such as chloride. A general frame work of mass and ion equilibrium equations and an electro-chemical reaction model of corrosion in reinforced concrete has been presented [2,3]. Thus the influential parameters on the theorem of corrosion process for severe environmental effects are determined experimentally and simulated in numerical terms for the enhancement of existing model in this research. The reliability of this model is verified through comparison of simulation with experiment 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 severe environmental effects along with various connected sub-routines to acquire the parameters necessary for the computation of corrosion are taken into account automatically in the unified framework of this program which is the beauty and originality of this model. Please refer to Fig. 1 below for further explanation of the above said DuCOM thermodynamic model.

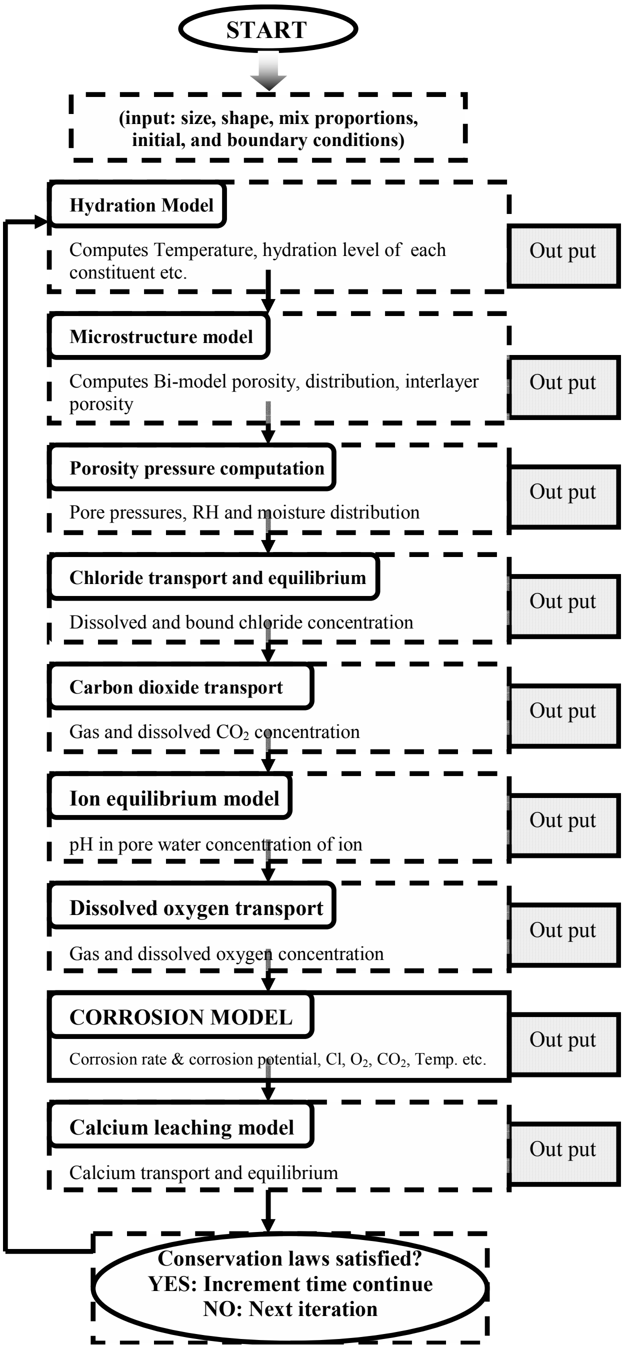

Fig.1 Visualization of the unified frame work of DuCOM

4. EXPERIMENTATION

4.1 Materials and mix proportions

Ordinary Portland cement (OPC) as per JIS R5210 specifications was used throughout this research. Natural river sand passed through JIS A1102 sieve No. 4 (4.75-mm openings), was used as fine aggregate for all concrete mixes. Its density and water absorption were 2.65 g/cm^3 and 2.21%, respectively. Crushed limestone with a maximum size of 20 mm was used as coarse aggregate with density of 2.70 g/cm^3 and water absorption 0.59%. It was retained on the sieve No.4 (4.75mm-openings) and cleaned before being used. Deformed round carbon steel bars 13 mm in diameter were used as reinforcing steel. The surface of steel bar was polished by sand paper No.200. Finally, steel bar was degreased by acetone just prior to being placed in the mould. The W/C ratio was kept 0.45 with an air content of 3.5±1 %. Mix proportions are shown in the following Table 1.

Table 1 Mix proportions

Specimen	W/C	Binder Kg/m^3	Water Kg/m^3	Sand Kg/m^3	Agg. Kg/m^3
Concrete	0.45	386	174	629	1122

4.2 Specimen preparation and scheme

Schematic diagram and original picture of the prismatic concrete specimen (100x100x400 mm and 100x100x200 mm) with two 13mm diameter steel bars (one bar completely embedded and other coming out from both faces, both having a clear cover of 15mm) cast in steel molds are as shown in Fig. 2.

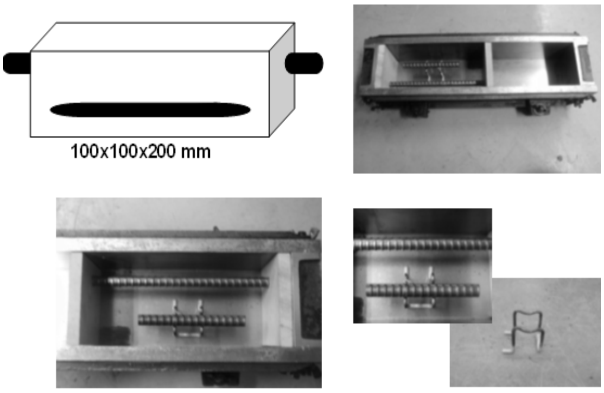

Fig.2 Schematic and actual diagram

The reason for using two steel bars is to make it possible to measure corrosion potential and corrosion mass loss using the same specimen which is the originality of this experiment scheme. The clear cover was kept 15mm because it was reported that that measured half-cell potential values at concrete surface could be considered as actual value at steel surface, if cover depth was within 20 mm [4]. The test consists of 24 specimens having a total Cl concentration varying from 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. Half-cell potentials were measured for all specimens using a copper-copper sulfate reference electrode (CSE), in accordance with

ASTM C-876. Refer to Fig.3 for further illustration.

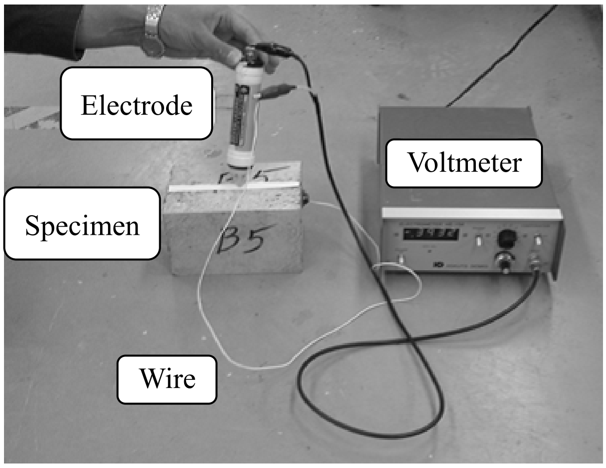

Fig.3 Half-Cell Potential Measurement

Finally the specimens were broken and corrosion mass loss was determined by gravimetric method after standard chemical cleaning of the corrosion products as shown in Fig. 4 below.

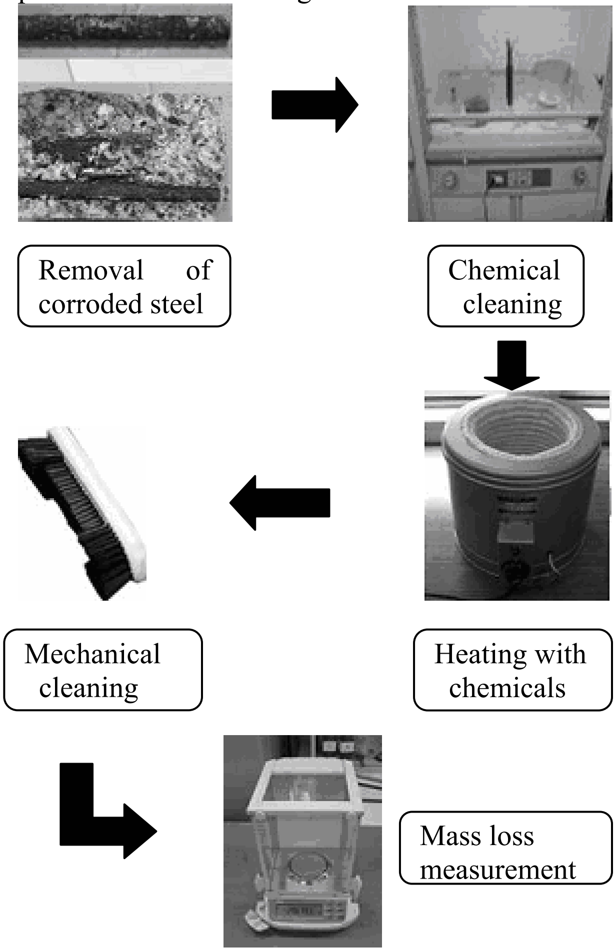

Fig.4 Gravimetric weight loss determination

5. MODELING OF CORROSION

5.1 Governing laws & tafel diagram technique

The corrosion model in the DuCOM system was firstly adopted from the previous research [2,3]. In the model a general scheme of micro-cell corrosion is introduced based on thermodynamic electro-chemistry. Initially, 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 subroutines in the system. The half-cell potential can be expressed with the Nernst Equation. Tafel Diagram [5] is a useful tool for simulating the corrosion phenomenon of metals. Corrosion potential 'Ecorr.' and corrosion current 'Icorr.' can be obtained as the point of intersection of the two lines in the model.

5.2 Corrosion in concrete and the effect of Cl

Although most corrosion takes place in water, corrosion in non-aqueous systems is not unknown. When it comes to the modeling of corrosion in concrete like steel reinforcement embedded in concrete under the effect of severe environment such chloride attack, then need arises to introduce some semi-empirical equations which logically satisfy the existing corrosion science laws, principals and these equations are also verified by experiments. In modeling of large scale real structures, pure theory becomes insufficient and somehow theory and practice has to be combined together in the form of a semi-empirical-theoretical approach.

5.3 Anodic Tafel Gradient Factor 'fp'

The effect of chloride on corrosion being anodic controlled in nature has been incorporated by varying tafel gradient of anodic reaction 'ba' with free chloride concentration (C_{Cl}) given in Equation (1) and Fig.5. 'i_a'and'i_c' are electric current densities at anode and cathode respectively

$$ba=(2.303RT/0.5z_{Fe}F)fp,\ fp=3.17x\ 10^{-2}\ C_{Cl}^{-0.826} \quad (1)$$

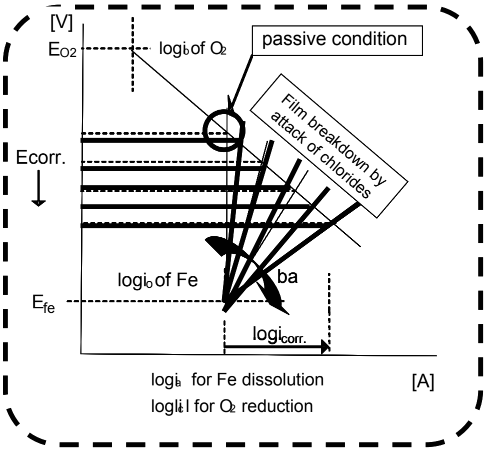

Fig.5 Potential and Current Increment by Cl Migration and Breakdown of Passive Layer

In the model, this semi-empirical-theoretical factor 'fp' accounts for the change in anodic gradient. When the chloride concentration is zero, the factor 'fp' becomes infinity and the rebar is considered to be in perfect passive condition represented by a 90° perpendicular anodic line of the tafel diagram as shown in the Fig. 5. As the chloride concentration increase, the passive layer starts breaking simulated by decrease in 'fp' resulting in the fall of anodic gradient moving the point of intersection of anode and cathode lines towards the more negative corrosion potential and increase in corrosion current until the threshold chloride value is reached and the passive layer is completely destroyed. At the threshold chloride value, the passive layer is completely destroyed, thus the factor 'fp' becomes 1.0 and the gradient of anodic reaction in the tafel diagram becomes equal to the actual tafel gradient as given by Nernst equation. In the light of past research works the threshold chloride value has been fixed as 0.4% total chlorides by mass of cement [6-11]. Since the model is based on the amount of free chloride existing in the pore water, conversion of free Cl to bound Cl and vice versa is done using chloride equilibrium model [12].

5.4 Anodic Potential Factor 'F_{Cl}'

It was observed from the experiment results (refer to Fig. 9 & 10) that corrosion rate and potential continuously increases even after the threshold chloride value is reached and the passive layer is completely destroyed. Based on this experimental observation and the theoretical scientific fact that the chloride induced corrosion reaction is anodic controlled in nature [13], a semi-empirical factor F_{Cl} is introduced in order to initiate anodic potential variation as a function of chloride content as shown in Equation 2.

$$E_{Fe} = E_{Fe}^{\Theta} + ((RT/z_{Fe}\,F)\ln h_{Fe}^{2+})\,F_{Cl} \tag{2}$$

$$F_{Cl} = 1 + 3\text{x}10^{-3}\ln(10^{4}C_{Cl}+1) + (1.2C_{Cl}/(C_{Cl}+1))$$

. This factor 'F_{Cl}' shifts the anodic curve diagonally 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 and higher corrosion current direction. In the absence of chloride the factor F_{Cl} is equal to one and the anodic potential is equal to the original anodic potential of the tafel diagram given by the Nernst equation as already explained. As the chloride attack becomes active, the factor F_{Cl} starts increasing more than 1.0 with the increase in chloride concentration in a non linear path. Refer to Fig.6 and Fig.7 for further illustration of working of the anodic potential factor 'F_{Cl}'.

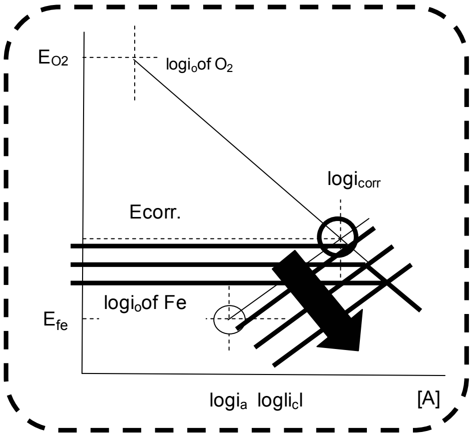

Fig.6 Illustration of 'F_{Cl}"

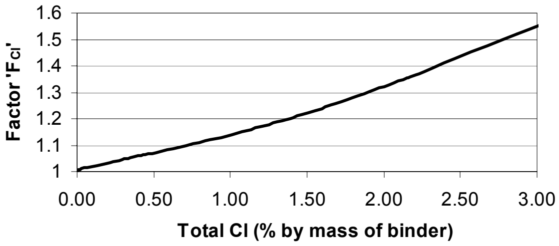

Fig.7 Anodic Potential Factor 'F_{Cl}'

In this research the model is enhanced from the previous research [14], by combining potential and tafel slope models to execute at the same time as both the tafel anodic slope and potential are influenced by chloride migration. Refer to Fig. 8 for physical meaning and illustration of this enhancement. The adjacent figure shows coupled maneuver path of anodic potential and tafel slope as a function of chloride concentration and breaking of passive layer.

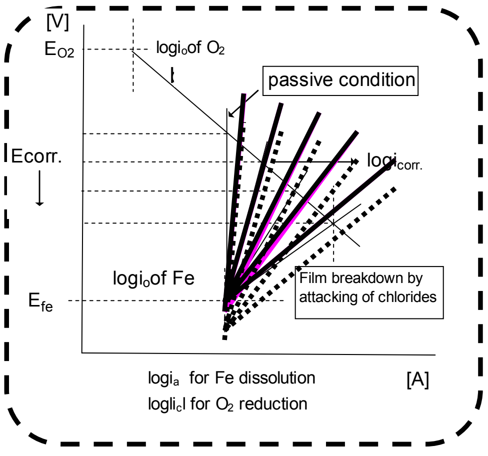

Fig.8 coupling of 'fp' and 'F_{Cl}"

6. RESULTS AND DISCUSSIONS

Results of half-cell potential and corrosion rate measurements for ordinary Portland cement concrete mixed with 0.0, 0.025, 0.25, 0.6, 1.0, 1.82, 3.65, 6.0, 8.0 & 10.0 percent chloride by mass of binder and three temperature conditions of 20, 40 and 60°C respectively are shown in Fig. 9 & 10. The half-cell potential values for various cases have a tendency to increase in early age and then approach to certain less variable values but not strictly constant. In general the corrosion potential and corrosion rate shows a non-linear increase with the increase of chloride content and temperature as shown in Figure 9 & 10. But, only in the case of the specimens having the high concentration of Cl and highest 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 specimens. Thus causing the loss of moisture needed for corrosion process and discontinuity of the specimen materials between steel and concrete along the crack.

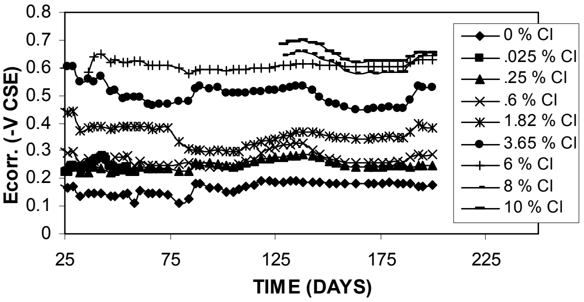

Fig.9 Variation of Half-Cell Potential with age, Cl and temperature (OPC, W/C=0.45) (Representative results for 20°C temperature)

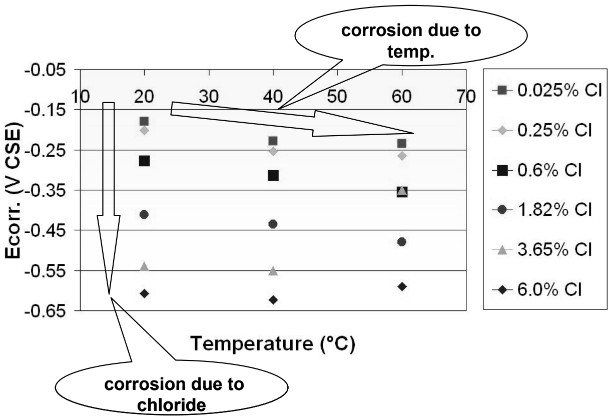

Fig.10 (a) Corrosion Potential

Coupled effect of chloride and temperature

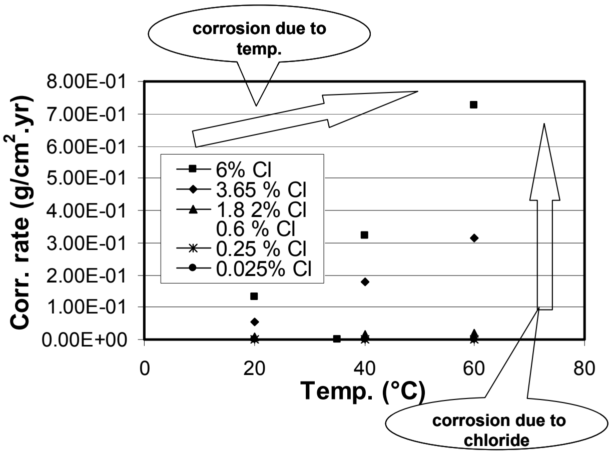

Fig.10 (b) Corrosion Rate

Coupled effect of chloride and temperature

7. VERIFICATION OF THE MODEL

DuCOM model for corrosion shows good agreement with the experiment results as shown in Fig. 11 & 12 for the effect of chloride on corrosion of steel reinforcement embedded in concrete for both corrosion potential and corrosion current. Thus, providing evidence for the efficiency and accuracy of the model. The model though simple but predicts well taking into account influential parameters involved in the process of corrosion in R.C structures. Modeling and verification for the effect of temperature is in the pipeline and will be published soon.

According to ASTM standard C-876, the reinforcement steel bar in concrete is prone to be under the attack of corrosion if the half-cell potential value is below -0.2 Volts. Above that value the steel is in satisfactorily safe condition. The same criterion is also verified by the corrosion model under discussion. In case of chloride induced corrosion, the initiation of corrosion takes place at the threshold value which is mostly considered to be around 0.4% total chlorides by mass of binder and the model under discussion gives a corrosion potential of -0.21 Volts at this value which is just below the value of corrosion potential specified by standards for the detection of initiation of corrosion. Therefore, the corrosion model of DuCOM is also verified by the ASTM Standards in addition to the experimental verification provided in this paper. The corrosion model gives the value of corrosion potential 'Ecorr.' in SHE (Standard Hydrogen Electrode) or NHE (Normal Hydrogen Electrode) units. Therefore, in order to compare it with experiment results which are in CSE (Copper-Copper Sulfate Electrode) units, a standard conversion factor

(CSE (V) = SHE (V) +0.316 V) is employed.

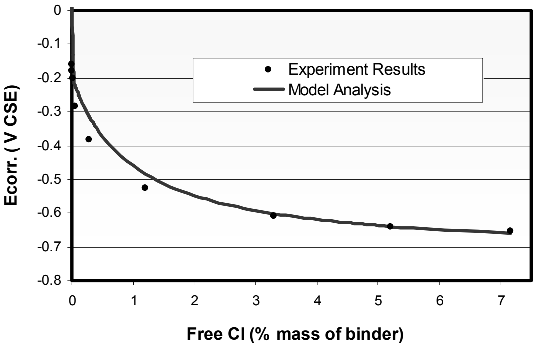

Fig.11 Cl Vs Corrosion potential profile (T=20°C, W/C=0.45)

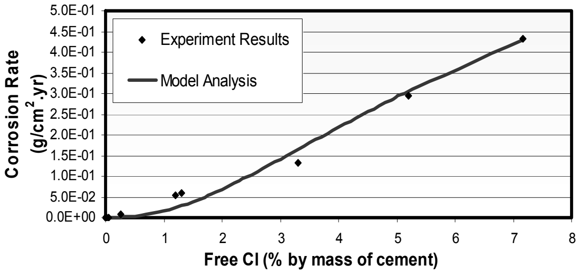

Fig.12 Cl Vs corrosion current profile (T=20°C, W/C=0.45)

8. CONCLUSION

Corrosion in RC structures continuously increases in a non uniform manner even at high chloride concentration in high temperature range. It is found that the gradient of corrosion profile with temperature becomes significantly steep with the increase in chloride concentration. Influential parameters on prediction of corrosion in R.C structures involving the severe environmental loadings of chloride and temperature variation are experimentally determined and numerically discussed through parametric study. Appropriate parameters for material modeling of corrosion on the basis of already developed computational scheme are successfully identified. The model being in close agreement with the experiment results predicts the corrosion rate and potential with good accuracy and precision.

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