Time Dependent Electrochemical Effect of Saturated Area in Capillary and Gel Pores of Concrete on the Corrosion Rate of Embedded Steel Reinforcement

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This paper aims at measurement of time dependent electrochemical corrosion rate in reinforced concrete under the effect of varying moisture content in the gel zone and capillary pores acting as an electrolyte. From the experimental measurements of the concrete-corrosion electrochemical cells for one year, an interesting descending trend in the corrosion rate measurement was observed which has been further explored in this paper and modeled by using a constitutive equivalent FEM electrochemical model based on mass and energy transfer through the porous media for corrosion measurement under various environmental conditions. The reason for decrease in measured corrosion rate with time was found to be dependent on the saturated area of concrete acting as electrolyte for the corrosion process which becomes gradually smaller with the passage of time and age of concrete. The electrolyte present in gel and capillary pore zones reduces with successive reduction in porosity and saturation over a certain time interval and finite control volume.

Keywords: Electrochemistry, electrolytic saturated area, capillary zone, gel zone, porosity, saturation, time dependency, corrosion, reinforced concrete, electrochemical modeling.

1. INTRODUCTION

The corroding reinforced concrete structures have always been an issue of great concern for professional civil engineers and researchers all over the world. Reinforced concrete structures are corroded under the effect of various electrochemical and environmental actions such as chloride, carbonation, temperature etc. During the last so many years, corrosion of reinforcement induced by chlorides, carbonation of the concrete or low-quality concrete cover has caused a lot of damage to concrete structures all over the world necessitating repairs or replacement.



Figure 1. Comparison of corrosion rates after six months and one year duration [11, 12]

For the design of durable new concrete structures and for the development of effective and

durable repair measures, especially when using new repair methods and materials, proper understanding of the mechanisms and influencing factors of the corrosion process is necessary.

However, the various environmental actions can cause corrosion only if enough amount of electrolytic saturated area is available in the vicinity of corroding reinforcement bar in concrete. Therefore, it is necessary to understand and predict the effect of electrolytic solution on corrosion of RC structures. Few researchers have investigated the effect of electrolytic saturated area in pores on corrosion of RC structures [1-5]. The influence of w/c ratio, concrete cover thickness and degree of water saturation on the corrosion rate of steel in concrete has been discussed [6]. Moisture migration [7], pore water profile [8], diffusion of dissolved oxygen [9] and depth of moisture transport [10] has been discussed in the past. But, time dependent effect of electrolytic saturated area in capillary and gel pores of concrete on the corrosion rate of embedded steel reinforcement remained as a scope for future research which became the basis for this research paper.

In this research, consideration is given on electrochemical time dependency of corrosion rate in RC structures qualitatively as well as quantitatively for which the previous research data is limited. Deep investigations have been carried out in order to clarify the involved mechanisms of corrosion under varying electrolytic saturated area by incorporating realistic electro-chemical modeling as well as multi variable laboratory controlled experimentation. In the past, experimentation was conducted by the authors of this paper and the effect of several parameters on the corrosion rate of steel in concrete was reported case by case in detail. The figure 1 shows the experimental corrosion rates obtained for different cases referred from the past research reported by the authors [11, 12]. It can be seen from the experiment results that the corrosion rate decreases with time for almost for all the cases and exposure conditions used in the research. However, the reason for this decrease of corrosion rate with time was not fully explored and remained as a scope for future research. Therefore, in this paper the marked decrease in corrosion rate with the age of concrete has been investigated in detail with the help of numerical modeling and verified by existing scientific laws and principles.

2. EXPERIMENTAL PART

Deformed round carbon steel bars 13 mm in diameter were used as reinforcing material in the experiment specimens. Ordinary Portland cement (OPC) as per JIS R5210 specifications was used. 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/cm³ and 2.21%, respectively. Crushed sandstone with a maximum size of 20 mm was used as coarse aggregate with density of 2.70 g/cm³ and water absorption 0.59%. The air content was kept around 3.5 ± 1 %. Pure Sodium Chloride (NaCl) was used as a source for chloride ions to produce chloride induced corrosion.

The specimen size was prismatic (200x140x150mm) with two 13mm diameter deformed mild steel bars. Uniform chloride content (from NaCl compound) has been used as corrosion initiator considering the corrosion cell as a fused anode cathode system. The oxygen concentration available for corrosion at the surface of rebar embedded in concrete was limited by varying water to cement ratios, cover depths and chloride concentrations. The bare ends of bars were coated with think epoxy to

prevent any atmospheric corrosion and enhance the reliability and accuracy of measurements. The test consisted of eighty specimens. Eight specimens were made for each case and two specimens were placed in four environmental exposure conditions in duplicate for six months and one year duration. All the specimens were allowed to set and harden in mold for 1 day before being de-molded and then cured for the next 28 days in the environment control chamber in sealed condition at 20°C. After that the specimens were epoxy coated on the top face edges of plastic containers in order to avoid any possible oxygen penetration. Corrosion rate and half-cell potential was measured according to ASTM C-876. Further details can be obtained from the author's previous research [11, 12].

3. FEM ELECTROCHEMICAL COMPUTATIONAL MODELING APPROACH:

The methodology adopted in this research is based on a 3D finite element model developed by our research group [13-17]. It is a computational program for the evaluation of various durability aspects of concrete such as concrete hardening (hydration), microstructure formation and several associated phenomena, from casting of concrete to a period of several months or years (Fig. 2a). As such this tool can be utilized to study the effect of ingredient materials, environmental conditions as well as the size and shape of the 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 phenomena ensures that the effects of changing environmental conditions are easily integrated into the overall simulation scheme.





Figure 2. (a). Flow chart and inter linkage of the model (b). Schematic clarification of the model for electrolytic saturated area in concrete

4. ELECTROLYTIC SATURATED AREA OF CONCRETE

Initially, the model is adopted from the previous research [13-15] already incorporating the effect of other important variables that have not been considered in this paper, such as oxygen [16], chloride and temperature [17-19], mass and energy [20], carbonation [21] etc. Corrosion is an electrochemical phenomenon which requires electrolyte for the occurrence of corrosion reaction. Therefore, when it comes to corrosion evaluation of reinforced concrete structures, it is necessary to calculate the effective corrosion current $icorr_{eff}$ in the system with reference to saturated area of concrete only which acts as an electrolyte in the saturated pores of concrete (Eq. 1).

$$icorr_{eff} = i_{corr.} A_{fr.}$$
$$A_{fr} = (\Phi_{cp} S_{cp} + \Phi_{gl} S_{gl})^* (1.0 - \alpha_{Vf} V_f)$$
(1)

Where;

A _{fr}	: Effective corrosion current reduction factor for saturated area of concrete
i _{corr.}	: Corrosion current
icorr _{eff}	: Effective corrosion current
Φ_{cp}	: Capillary porosity
\mathbf{S}_{cp}	: Saturation of capillary pores
Φ_{gl}	: Gel porosity
\mathbf{S}_{gl}	: Saturation of gel pores
$V_{\rm f}$: Volume fraction of fine aggregate

 $\alpha_{\rm Vf}$

: Fraction of fine aggregate present in the vicinity of rebar.

As the hydration proceeds, new products are formed and deposited in the large water-filled spaces known as capillary pores. Moreover, the gel products also contain interstitial spaces, called gel pores, which are at least one order of magnitude smaller than the large voids of capillary pores. Theoretically and numerically, the saturated area depends on the capillary porosity, gel porosity and their respective degree of saturation in the aggregate free volume of concrete which is a heterogeneous material in nature. Thus it is essential to estimate the saturated area of concrete which is the only portion which takes part in the corrosion reaction as dry areas of reinforced concrete without electrolytic conductivity cannot corrode. Consider Fig.2b in this model, the volume fraction of fine aggregate (V_f) and the factor ' αV_f ' representing the percentage of fine aggregate present in the vicinity of rebar varying from 0 to 1.0 depending on parameters such as fineness modulus of sand, particle size distribution profile of fine aggregate etc. and needs to be further investigated as scope for future research. In this study the value is tentatively taken as 1.0.

5. DISCUSSION AND COMPARISON OF EXPERIMENT RESULTS WITH THE ELECTROCHEMICAL MODEL



Figure 3. Model simulation for variation of electrolytic saturated area of concrete factor "A_{fr}" as a function of time.

The reason for decrease in the corrosion rate with time lies in the fact that as the time passes on gradually the saturated area of concrete factor " A_{fr} " becomes smaller. As the hydration of cement proceeds with time, the electrolyte of the concrete reduces with change in capillary porosity, gel porosity and saturation over a certain time interval.Figure 3 and Figure 4 show the variation of saturated area of concrete factor " A_{fr} " with time for a typical case selected for illustration purpose along with change in porosity and saturation of gel and capillary zones. Similar trend can be found in case of variation of corrosion rate with time.



Figure 4. Model simulation for variation of capillary and gel porosity and saturation as a function of time



Figure 5. Time dependent Corrosion model analysis

Figure 5 shows the corrosion model simulation for estimation of corrosion rate with time. It can be seen that the corrosion rate varies with time in the same fashion as the electrolytic saturated area of concrete shown in Figure 3 and 4. Another interesting point which is found from the corrosion rate profile with time is that the corrosion rate falls very rapidly with time during the first 28 days. Afterwards the decrease in corrosion rate with time is less speedy. After about 200 days of time interval, onwards the decrease in corrosion rate with time becomes very small and after two years the rate tends to become constant with negligible variation.



Figure 6. (a) Corrosion rate variation for 5% total chloride concentration; b) Corrosion rate variation for 5% total chloride concentration (Enlarged view); c) Corrosion rate variation for 10% total chloride concentration

The above phenomenon was found when the chloride concentration is low (for example 0.5% total chlorides by mass of binder in the above case). But, when the chloride concentration is much higher for example 5% or 10% then the corrosion rate variation with time is like as shown in Figure 6. The corrosion rate remains very low under sealed conditions of curing (28 days in this case). This is because of the fact that due to high chloride concentration in concrete, all the electrolyte/saturated area present in the sealed concrete specimen is consumed very fast and after that the corrosion rate falls to a minimum value (almost zero) due to the further unavailability of electrolyte. After the end of curing the sealed specimen is opened and exposed to air. Therefore, the corrosion rate suddenly rises just in one day to its peak value.



Figure 7. Time dependent corrosion model analysis for alternate wetting-drying

Then it falls to a much lower value in 75 days due to the variation in the concrete electrolyte related to the gel/capillary porosity and saturation as already explain above. After 75 days, the corrosion rate seems less variable with time. It must be noted over here that these time dependent corrosion rate model simulations have not been verified yet and remain as scope for future research, but seem to be very much reasonable and can be used for understanding of corrosion rate variation with time. Variation of corrosion rate in alternate wetting drying conditions is also shown in Figure 7.

6. CONCLUSION

Electrochemical time dependent effect of electrolytic saturated area in the gel and capillary pores on the corrosion of steel rebar embedded in concrete has been successfully investigated in this paper. The trends observed in the past experimental measurements have been resolved, compared and verified with the model simulations in this paper. Similar trend has been observed in the graphical measurements of A_{fr} , gel and porosity, as well as the corrosion rate measurement profiles with the conclusion that the reasons for the decrease in corrosion rate measurement with time has been successfully sorted out. This was found to be dependent on the saturated area of concrete acting as electrolyte for the corrosion process which becomes gradually smaller with the passage of time and the

age of concrete. As the hydration of cement proceeds with time, the electrolyte of the concrete present in the gel and capillary pore zones reduces with successive reduction in the capillary and gel porosity and saturation over a certain time interval and finite control volume measurement. This phenomenon was investigated quantitatively considering and simulating the actual field conditions such as by varying concrete cover depth, relative humidity, water-cement ratio etc. This comprehensive modeling investigation involving a variety of materials and environmental variable measurements will help in profound understanding of the electrolyte (saturated area of concrete at the gel and capillary zone) controlled time dependent corrosion reaction in reinforced concrete structures and will enhance the estimation of corrosion rates over the life time period of steel rebars embedded in concrete.

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