Unique Declining Electrochemical Trend of Macro-Cell Half-Cell Potential with Increase in Temperature at Constant High Humidity for Corroding Steel Bars in Repaired Concrete Patches

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This paper aims at finding the coupled effect of hot and humid environment on the corroded repaired patches of chloride contaminated steel reinforced concrete. Chloride induced corrosion under coupled environmental effects of high humidity and high temperature often found in gulf marine environment is a very serious threat for durability of reinforced concrete structures. In the previous research, the authors experimentally corroborated re-corrosion in the repaired reinforced concrete patches in the form of macro-cells. But, whether this formation of macro-cell is influenced by the coupled effect of high temperature and high relative humidity remained a question and formed the basis of this research. This coupled effect is investigated by laboratory controlled experimentation at varying temperature at 30, 40 and 50°C and a high ambient relative humidity of 85% in environmental control chambers. Specimens were prepared having total chloride concentration in mixing water 3% and 5% by mass of binder. From the experiment results interesting and novel observations, trends and behaviors have been identified. A non-uniform and non-linear corrosion reaction was observed even after the breaking of passive layer. Furthermore, a decrease in electrochemical corrosion potential and corrosion mass loss at 50°C in comparison to 30 and 40°C temperature conditions was seen. This may be due to the reduction of oxygen solubility in the pore solution at high temperature and blockage of concrete pores at high relative humidity. It is expected that a stable oxide layer may have developed under limiting oxygen controlled corrosion reaction. This can form basis for the development of a new technique to passivate steel bar embedded in chloride contaminated concrete and improve the method of repairs.

Keywords: repair patches, macro-cell corrosion, electrochemistry, high temperature, high relative humidity reinforced concrete, coupled effect experimentation.

1. INTRODUCTION

The degradation of concrete structures due to corrosion of reinforcing steel gives rise to concerns about structural safety, integrity, and serviceability. The cost of rehabilitating such structures is very significant and it consumes too much money on construction. The deterioration of reinforced concrete (RC) structures due to the corrosion of reinforcement has been widely investigated, experimented, modelled and reported in the past [1-4]. The corrosion induced deterioration of reinforced concrete is significant under chloride attack [5, 6]. Since the chloride induced corrosion is investigated as an electrochemical thermodynamic process, its rate is influenced by temperature [6, 7] and humidity [8] which may vary from one place to another due to the difference in seasonal conditions. Patch repair is the most commonly used method for rectifying localized damage in concrete due to corrosion. It entails removal of loose concrete that has cracked, spalled, or delaminated; often, the application of a surface treatment on the steel; and replacement of the defective concrete with patching materials, which normally re-establishes the original profile of the member.

The presence of high chloride content aided by the severe environmental conditions not only break the passive film which protects steel from further corrosion but also accelerate the corrosion of reinforcement steel bars even in repaired reinforced concrete patches [9]. But, the magnitude of this corrosion for the effect of ambient relative humidity as high as 85% under varying temperature conditions relevant to the harsh environment found in the coastal gulf regions has not been investigated in the past which leads to the objectives of this research paper.

2. EXPERIMENTATION

Specimens	Total Chloride (%mass of binder)	W/C	OPC Kg/m ³	Fine aggregate Kg/m ³	Coarse aggregate Kg/m ³
#1, #2 at 50°C #3, #4 at 40°C #5, #6 at 30°C	5% at the ends	0.45	371	756	1031
#7, #8 at 50°C #9, #10 at 40°C #11, #12 at 30°C	3% at the ends	0.45	371	756	1031

Table 1. Mix proportions

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 [10] was used. Natural river sand passed through JIS A1102 sieve No. 4 (4.75-mm openings) [11], 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%. Table 1 will illustrate the mix proportion of the specimens.

2.1 Specimen Preparation and Experiment Scheme

This experimental investigation is an extension of the previous research finding [9] in which specimens were prepared for macro-cell corrosion experiment simulating the actual patch repair work in the construction field. The two sides of these specimens were cast first containing chloride 5% and 3% chloride content respectively at the extreme ends. The middle portion of these specimens was cast after 24 hours with no chloride content presuming to be the repaired portion in the actual construction repairs to stop or minimize the chloride movement from contaminated to non contaminated portion of these specimens. The purpose was to create an artificial macro-cell resembling the one developed originally in case of repair works in the actual field of concrete structures. The schematic diagram of these specimens is shown in fig.1.



Figure 1. Schematic representation of the macro cell specimens kept at 30°C, 40°C and 50°C.

The complete mixing procedure is shown in fig. 2.The test consisted of 12 specimens with two sets in duplicate having a total chloride concentration 3% and 5% in mixing water for 50°C, 40°C and 30°C temperature conditions and 85% relative humidity in environment control chambers. Half-cell potentials were measured for one year for all specimens using copper-copper sulfate reference electrode (CSE) in accordance with standard specifications which can be found elsewhere [13-17]. For further illustration of the measurement procedure adopted in this research consider the Fig. 3. A

standard Voltmeter with 0.0001V accuracy was connected with the RC specimens and the standard electrode through the specified wire in order to make a half-cell potential measuring circuit.



Mould with a separator for middle and end portions



Casting of the end portions in two layers without vibration



After casting in two layers



Fresh middle portion with already hardened end portions



Specimen with completely hardened middle and end portions





Figure 3. Half cell measurements assembly.

Finally the specimens were split along the position of steel in the concrete and steel bars were removed carefully from the concrete. After the photographic evaluation of the corroded steel reinforcement bars, the corrosion mass loss was determined by gravimetric method. This was done by chemical cleaning [14-17] of the corrosion products using standard systematic step by step method. During chemical cleaning treatment, care was taken that the base metal should not dissolve along with the corrosion products.

3. EXPERIMENT RESULTS

After one year of corrosion potential readings the results are compared with our previous study of macro corrosion in repaired patches of chloride contaminated concrete [9]. The following results are obtained on comparison;

1) At the middle non contaminated portion of the specimen having 5% chloride at the end portions and kept at 50°C (#1 and #2), maximum corrosion -0.35 Volts is found as compared to the high -0.55 Volts at 30°C in the middle no chloride portion of the same specimens (#5 and #6). This low corrosion potential value of -0.325 Volts at middle shows that there is decline in corrosion potential due to high temperature of 50°C and humidity. This is evident by comparing figure 4 and 5.



Figure 4. Corrosion potential of the 5% Cl contaminated end portion specimen at 30°C.

2) The maximum corrosion potential reading of the specimens #1 and #2 is found -0.490 Volts as compared to high chloride induced potentials of -0.62 Volts (figure 5) of the same specimens #5 and #6 at 30° C (figure 4). This shows that corrosion potential readings are lowered when the specimens were put in high temperature and humidity.

3) At the middle non contaminated portion of the specimen #3 and #4 which were put at 40 °C maximum corrosion -0.610 Volts was found as compared to -0.55 Volts at 30°C in the middle no chloride portion of the same specimens (#5 and #6). The corrosion potential -0.610 Volts at middle indicates that there is increase in corrosion potential due to high temperature. This shows that the macro cell is severe in the middle of the specimens #3 and #4. This comparison is evident from the figure 4 and figure 6.



Figure 5. Corrosion potential of the 5% Cl contaminated end portion specimen at 50°C.



Figure 6. Corrosion potential of the 5% Cl contaminated end portion specimen at 40°C.



Figure 7. Corrosion potential of the 3% Cl contaminated end portion specimen at 30°C.



Figure 8. Corrosion potential of the 3% Cl contaminated end portion specimen at 50°C.

4) The high corrosion potential of -0.720 Volts is found in specimens #3 and #4 as compared to -0.62 Volts at the two extreme ends of the specimen #1 and #2 due to the high temperature. This shows that due to formation of macro cell at high temperature, the corrosion potential of the end portions has also increased. Furthermore, it can be concluded from this result that at high temperature the repaired patches are more prone to high corrosion.

5) In the 3 % chloride contaminated specimens (#7 and #8) at the end, the corrosion potential of - 0.325 Volts is obtained as compared to high -0.44 Volts of same specimens (#11 and #12) which were kept at 30 C°. This result is the same as obtained in specimen #1 and #2 proving that corrosion

potential is lowered in both cases having 3% and 5% chloride at the end when the specimens were put in 50°C temperature and high humidity of 85%. The comparison is evident from figure 7 and 8.

6) In specimen #11 and #12, the corrosion potential of -0.305 volts at the middle non contaminated portion is obtained as compared to -0.31 Volt at 30 C°. This result is the same as obtained in specimen #1 and #2 proving that corrosion potential is lowered in both cases having 3% and 5% chloride at the end when the specimens were put in 50°C temperature and high humidity of 85%. The comparison is evident from figure 7 and 8.

7) In specimens #9 and #10, the corrosion potential at the end is increased, confirming the influence of formation of the macro cell at the middle uncontaminated portion as shown in figure 9. This result is the same as obtained in specimens #3 and #4.



Figure 9. Corrosion potential of the 3% Cl contaminated end portion specimen at 40°C.

4. DISCUSSIONS

From the above results it is inferred that in the case of the specimens having the highest concentration of Cl and highest temperature showed an interesting falling trend and reduction in the corrosion potential values with the increase in temperature. One reason can be reduction of oxygen solubility in the pore solution at high temperature resulting in oxygen controlled corrosion reaction at high chloride concentration. Another reason can be the blockage of concrete pores at high relative humidity and high temperature resulting in discontinuity of interconnected concrete pores and finally resulting in the shortage of oxygen at such a high R.H and high temperature condition.

This experiment data provides corrosion rates under extreme boundary conditions for which the data is very limited and hence can be used in the future for numerical modeling developments and successive experimental verifications. It is expected that this data would be used as a bench in high temperature environments as a bench mark for patch repairs of the reinforced concrete and the necessary mitigation techniques will be applied in accordance to this research data for successful repairs.

It is interesting and worth noticing that when various bars carefully removed from concrete specimens having varying chloride 0%, 3% and 5% and temperature 30, 40 and 50 °C conditions, a novel finding was observed. The surface of steel bars has corroded less at 50°C than at 40°C as shown in figure 10. One of the reasons could be the unavailability of oxygen at such a high temperature and R.H which are must for corrosion process to occur. Increased temperature results in decreased solubility of oxygen in the pore solution of concrete at the ITZ and high R.H creates disconnection in the concrete pores obstructing the oxygen path from the exposed surface up to the embedded steel bar corroding surface [1, 2, 8]. This may have resulted in reduced magnitude of corrosion.



Bar from the end portion of the 5% Cl specimen at 40° C

Bar from the end portion of the 5% Cl specimen at 50° C

TO LEAST CONTRACTOR AND A MANUAL CONTRACTOR

Figure 10. Steel Bars Removed from the 5% contaminated concrete at 40°C and 50°C.

The results provided in the Fig. 11 show a reversing behavior of corrosion under high relative humidity of 85% and coupled effect of varying chloride and temperature conditions which is also in agreement with the experiment results presented earlier in this paper. The corrosion mass loss usually increases with the increase in chloride concentration justified with the sample having 3% and 5%. However, the corrosion mass loss decreases on 50°C temperature condition. This interesting experimental observation can be explained theoretically in the sense that at high temperature, the solubility of oxygen in the pore solution is reduced and oxygen is compulsory for the corrosion reaction to occur. Furthermore, the high relative humidity conditions such as 85% R.H used in this experimentation can block the continuity of concrete pores making further it difficult for the oxygen to

reach the corroding steel bar embedded in chloride contaminated concrete resulting in limiting oxygen controlled corrosion reaction.

It can be inferred from this observation that under limiting oxygen controlled corrosion reaction conditions at higher chloride induced corrosion rate, a stable iron oxide layer could have been developed on steel bar which prevents further corrosion of steel until the oxygen limiting corrosion reaction conditions are maintained. This is a novel and useful finding which can lead to the development of a new technique to passivate steel bar embedded in chloride contaminated concrete.



Fig 11 a. The declining trend of corrosion mass loss at $50C^0$ and 85% humidity of the specimen having 5% at the end and 0% at middle portion



Fig 11 b. The declining trend of corrosion mass loss at $50C^0$ and 85% humidity of the specimen having 3% at the end and 0% at middle portion

Figure 11. The declining trend of the corrosion mass of 3% and 5% contaminated specimens at 50°C and 85% RH.

5. CONCLUSIONS

From the electrochemical experiment results of this research it is corroborated that the corrosion in RC structures develops in a non-uniform manner with the severe environmental loadings. The increase of temperature acts as a catalyst for the chloride attack on carbon steel reinforcement in concrete structures which needs further investigation and numerical model development for this coupled effect as a scope for future research in the light of experiments results and trends obtained in this research paper. However, it was interesting to observe the decrease in corrosion potential and corrosion mass loss at 50°C in comparison to 40°C temperature condition. One reason can be the reduction of oxygen solubility in the pore solution at high temperature resulting in oxygen controlled corrosion reaction at high chloride concentration. Another reason can be the blockage of concrete pores at high relative humidity and high temperature resulting in discontinuity of interconnected concrete pores and finally resulting in the shortage of oxygen at such a high R.H and high temperature condition. It is also observed that the corrosion mass loss decreases with the increase of chloride concentration from 3% to 5% total chloride concentration. It can be concluded from this observation that under limiting oxygen controlled corrosion reaction conditions at higher chloride induced corrosion rate, a stable iron oxide layer is developed on steel bar which prevents further corrosion of steel until the oxygen limiting corrosion reaction conditions are maintained. This is a novel and useful finding which can lead to the development of new techniques to improve the method of repairs of the corroded reinforced concrete.

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