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- Technical paper -

MACRO-CELL CORROSION AND ITS TIME DEPENDENCY UNDER NON-UNIFORM CHLORIDE ENVIRONMENT

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ABSTRACT

Concrete specimens with a divided steel bar were cast having non-uniform chloride contents in a single specimen representing a non-uniform environmental conditions of chloride ion ingress. Generated macro-cell corrosion currents were periodically monitored. It was observed that macro-cell anodic and cathodic reactions change their status towards the cathodic and anodic reactions respectively. Transformations of reactions occur in a non-uniform way with respect to the distance and time and also it was assumed to be occurred due to the heterogeneous properties of concrete which is described in this paper.

Keywords: macro-cell corrosion, corrosion currents, time dependency, non-uniformity

1. INTRODUCTION

Reinforcement is naturally protected by the alkaline medium of concrete. Even in this condition, steel is corroded at the rate of less than 0.1μm/year [1] which can be neglected. However, ingress of Chloride ions (Cl^-) from surrounding environment may exceed its threshold to destroy the passive layer and start the corrosion.

Corrosion is an electrochemical process mainly governed by the electrochemical potential difference creating basic types of corrosion patterns are as micro-cell or macro-cell corrosion [2]. The diffusion rates of Cl^- ions into concrete become non-uniform as concrete obviously behaves as a heterogeneous material and also due to the variation of surface Cl^- contents along a member [3]. Hence, a comparatively higher potential difference occurs along the steel bar which can generate macro-cell corrosion.

Therefore, this study concentrates about the macro-cell corrosion variation along the steel bar under the non-uniform chloride environment. Although the corrosion process occurs as a combination of anodic and cathodic reactions, the effect of anodic locations are only important for analysis on rust production. However, anodic and cathodic locations are electrically combined so that a particular reaction rate is directly affected to the other. Hence there may be opportunity to transform anodic and cathodic locations, which is also mainly investigated in this study.

2. METHOD OF MACRO-CELL CORROSION CURRENT MEASUREMENT

A method of using a divided steel bar [4] for the purpose of measuring actual macro-cell corrosion current passing from one steel element to the other was used for this study. When the corrosion occurs, the electrons pass from anode to cathode, and therefore an electronic current is produced in the direction of cathode to anode. Providing a divided steel bar where all adjacent steel elements are connected by wires facilitates to measure actual current passing from element to element (as in the Fig. 1). These currents are used to evaluate the current absorbed or current produced by each element. However, when the steel elements are not in the same size, the current of each element is further converted to the current density which is more appropriate to represent the corrosion rates as shown in the equation 1.

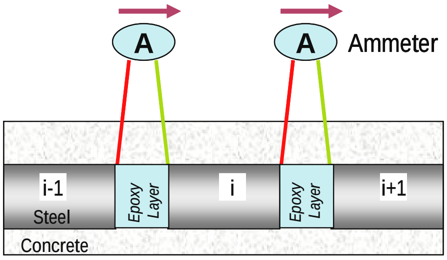

Fig.1 Measurement method of macro-cell corrosion current

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$$\mathbf{a}_{\mathbf{i}} = \frac{\mathbf{I}_{\mathbf{i,i+1}} - \mathbf{I}_{\mathbf{i-1,i}}}{\mathbf{S}_{\mathbf{i}}} \quad (\mu\,\mathbf{A/cm^2}) \qquad (1)$$

Where, a_i is the macro-cell corrosion current density of steel element [i]. $I_{i,i+1}$, $I_{i-1,i}$ are corrosion currents passing through element [i] to [i+1] and [i-1] to [i] respectively (in μA). S_i is surface area of element [i] (in cm^2).

Note: Anodic or negative(-) current represents the locations of rust is produced.

3. TEST PROGRAMS

3.1 Materials

(1) Concrete

Ordinary Portland Cement (OPC) was used for the concrete mix of W/C 0.55. Maximum size of 15 mm course aggregate was used keeping s/a as 45%. To represent Cl^- penetrated concrete members, Cl^- ions were deliberately added to concrete mix.

(2) Divided steel bar

Plain 10mm diameter divided steel bar is symmetric as in the Fig. 2, where one side (side A) from the symmetric line consists 2 No's15 mm (1A, 2A), 1 No's 30 mm (3A), 1 No's 45 mm (4A), 1 No's 68 mm (5A) length elements in the order. 15 mm or shortest elements were kept near the middle of the specimen to obtain more accurate results assuming that macro-cell corrosion effect is high at the region of higher potential difference. The epoxy length between two steel elements was 3 mm, but it was 6 mm only at the centre of the divided steel bar. Each and every steel elements were connected together with lead wires for making the steel bar continuous to flow macro-cell corrosion current. Th etotal resistance of the divided steel bar was measured and maintained as less than 0.5 Ω.

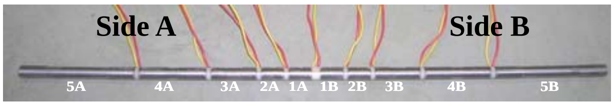


Fig.2 A view of the divided steel bar

3.2 Preparation of specimen

100x100x376 mm concrete specimens were made with two sides named as side A and side B as shown in the Fig. 3. Different sides were cast in two consecutive days with different Cl^- ion contents. However, specimens with uniform Cl^- ion content were cast as a single unit though they were named as side A and B for the clarity. Table 1 represents the Cl^- ion content variation of side A and side B with the specimen name. Divided steel bar was placed with the cover thickness of 20mm from the bottom and additional steel bar was used as the reinforcement. Except the bottom of the specimen, all other area was epoxy coated so that O_2 and H_2O penetrate only through the bottom side.

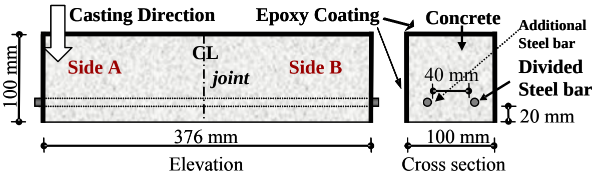


Fig.3 View of concrete specimen

Table 1 Cl^- content variation in side A and B

Specimen No	Chloride ion content (kg/m^3)		
	Side A	Side B	Difference (B-A)
U1	2.4		0
U2	4.8		0
1	0	1.2	1.2
2	0	2.4	2.4
3	0.6	2.4	1.8
4	0.6	4.8	4.2
5	1.2	2.4	1.2
6	2.4	4.8	2.4

Specimens with different Cl^- content were subject to cyclic exposure conditions for 28 cycles while it is 22 cycles for specimens with uniform Cl^- content . It was wet condition of Relative Humidity (RH) 90% and Temperature (T) 60°C for 3 days and dry condition of RH 65% and T 15°C for 4 days. One cycle was corresponds to 7 days, data were taken at the end of dry cycle.

4. EXPERIMENTAL RESULTS

4.1 Corrosion current density variation - Uniform Cl^- contents

Measured macro-cell corrosion currents were converted to the corrosion current density (in $\mu A/cm^2$) along the steel bar. Periodic corrosion current densities of specimens with uniform Cl^- content are presented in the Fig. 4. It represents the corrosion current density against the time durations also with chloride content. The locations of anodic reactions (where rust produced) are represented by negative corrosion currents while cathodic reaction represented by positive currents.

A uniform Cl^- ion concentration generates a uniform electrochemical potential along the steel bar. Therefore it can be assumed that, if the Cl^- ion contents are uniform throughout the steel bar, it may avoid the macro-cell corrosion phenomenon.

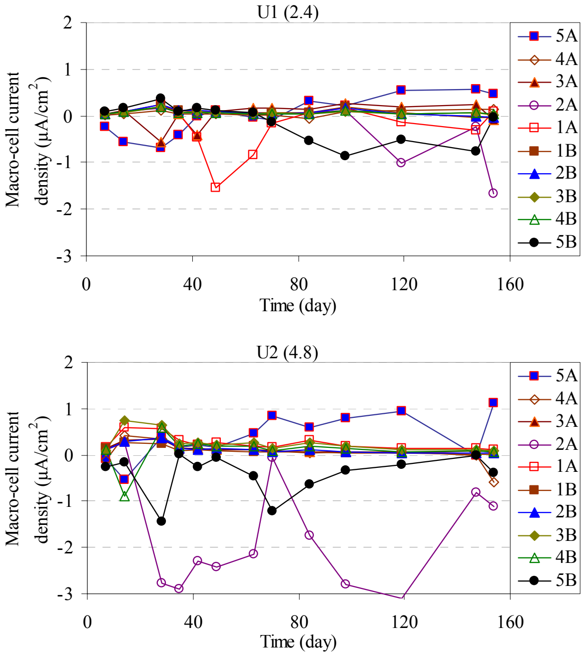


Fig.4 Current density variation – Uniform Cl^- content

First, in reality, Cl^- penetration into concrete is no longer uniform due to the heterogeneous properties of concrete pore structure. Although the Cl^- concentrations are uniform along the steel bar (especially in experiments), this research study observed that the macro-cell corrosion can be observed as presented in Fig. 4.

Substances required for corrosion process, oxygen (O_2) and water (H_2O) should also reach to the steel bar level to start the corrosion process. O_2 and H_2O penetration is mainly governed by the profile of concrete pore structure. Due to the availability of course aggregates in concrete, its penetration speed or else its penetration amount is directly affected. Therefore, it is clear, although uniform chloride contents are available, oxygen and water amount may not be uniform along the steel bar at a time and hence macro-cell corrosion may be generated.

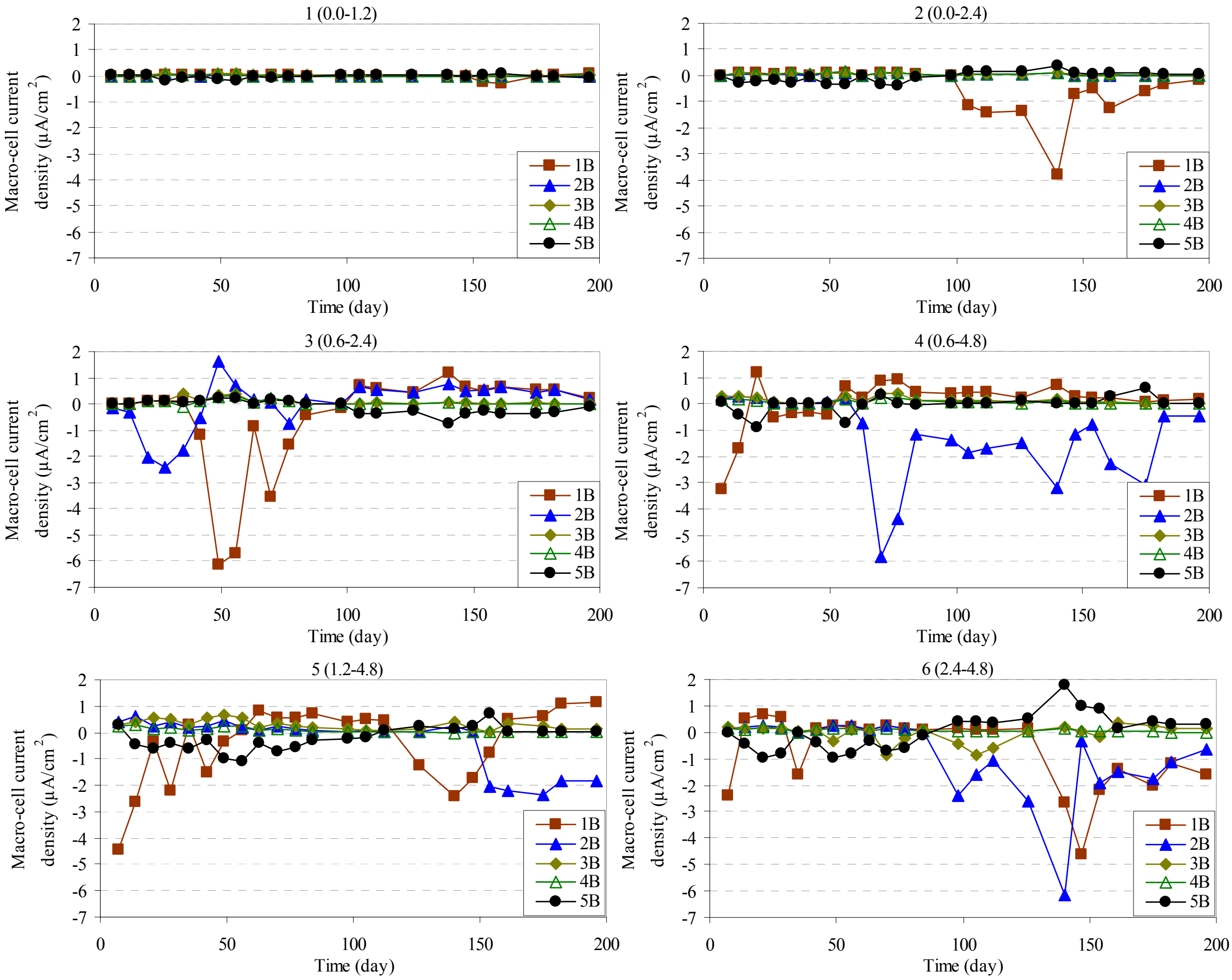


Fig.5 Current density variation – Non-uniform Cl^- content

Corrosion activity was observed as negligible when the uniform Cl^- content is 1.2kg/m^3; hence current density variation is not shown. However, when the Cl^- content is increased, the macro-cell corrosion activity is increased. But, still specimens with uniform Cl^- contents have low corrosion current densities compared to specimens with different Cl^- contents as shown in the Fig.5. Therefore, it may be assumed that the contribution of Cl^- ion to produce an electrochemical potential difference is higher than the contribution of O_2 and H_2O.

4.2 Corrosion current density variation – Non-uniform Cl^- contents

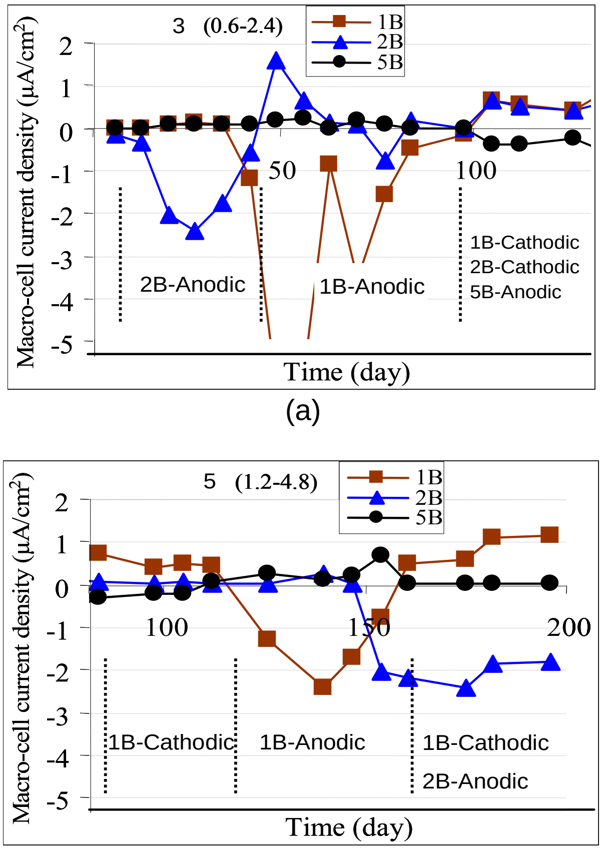
Variation of macro-cell corrosion along the steel bar was investigated using 6 concrete specimens as tabulated in Table 1. Side A always contains less Cl^- content than side B of all specimens. Corrosion current density of low Cl^- content side of all specimens showed a negligible macro-cell corrosion activity; hence those curves are not shown in the Fig. 5.

Current density curves in specimen 1 of Fig. 5 clarify that low Cl^- environment show negligible macro-cell corrosion effect even though Cl^- content is non-uniform along the steel bar. It was also observed that, although a comparatively high Cl^- environment available in side A (specimen 6), it does not show a higher macro-cell corrosion activity when the side A is combined with the side B which is having a high Cl^- environment than side A. Hence, it is confirmed that macro-cell corrosion in different Cl^- environment mainly occurs in high Cl^- content region. Additionally, it can be observed that most of the cases show highly active steel elements are either 1B or 2B or both together which are located within 40mm from the center. 1B and 2B steel elements only shows the corrosion electricity exceeding 80% of total electricity produced by all elements in a particular specimen. This mechanism may be explained by the theory of electrochemical potential difference where in this experiment, a higher potential difference occur in the region of different Cl^- content and in the high Cl^- content side.

According to the current density variations of all specimens, neither of elements shows a uniform corrosion process throughout the exposure period though the measured environmental conditions were constant. Current variation of a particular steel element is, however, acceptable if it varies behaving as either anodic or cathodic throughout the period. But, most of the steel elements (mainly 1B, 2B and 5B) show, their corrosion process changing from anodic to cathodic, and cathodic to anodic with the time.

4.3 Anodic-cathodic transformation

The corrosion process of any steel element was not observed as uniform with respect to the time. It means a steel element may transfer from anodic to cathodic while the cathodic element transfers to an anodic element. This particular time dependent behavior of corrosion process can be clearly observed in current density curves of Fig. 6 (a) and (b). In Fig. 6(a), element 2B changes its behavior several times during the exposure period. Similar observation occurs in the steel element 1B in the Fig. 6(b). Additionally, it was noted that, although elements in side B behave as anodic elements, their cathodic contribution is mainly taken by another steel element in side B itself rather than elements in side A.



(a)

(b)

Fig.6 Anodic-Cathodic transformation

4.4 Peak currents due to anodic-cathodic transformation

The anodic (negative) current densities are visible for a particular time period and anodic reactions transfer to cathodic reactions at a time due to the above explained anodic-cathodic transformation mechanism or time dependent variation of corrosion process. However, there is a

Table 2 Peak anodic current density and particular exposure cycle

Specimen	**Peak anodic current density (μA/cm^2)** (*cycle*)								
	1B			**2B**		**3B**		**5B**	
	1st	**2nd**	**3rd**	**1st**	**2nd**	**1st**	**2nd**	**1st**	**2nd**
1 (0.0-1.2)	-	-	-	-	-	-	-	-	-
2 (0.0-2.4)	3.8 (*20*)	-	-	-	-	-	-	-	-
3 (0.6-2.4)	6.1 (*7*)	-	-	2.4 (*4*)	0.7 (*11*)	-	-	0.7 (*20*)	-
4 (0.6-4.8)	3.3 (*1*)	0.5 (*4*)	-	5.8 (*10*)	-	-	-	0.9 (*3*)	0.8 (*8*)
5 (1.2-4.8)	4.5 (*1*)	1.5 (*6*)	2.4 (*20*)	2.4 (*25*)	-	-	-	1.1 (*8*)	-
6 (2.4-4.8)	2.4 (*1*)	1.6 (*5*)	4.6 (*21*)	6.2 (*20*)	-	0.8 (*10*)	0.8 (*15*)	1.0 (*3*)	0.9 (*7*)

possibility of occurrence this mechanism again and again until the complete deterioration occurs. Several anodic-cathodic transformations create current density peaks of a particular steel element. Using the results of all specimens which are in the Fig. 5, the peak currents were tabulated for side B steel elements as shown in Table 2. However, the element 4B did not show any peak value (its current density was always smaller than 0.5 μA/cm^2 during 28 cycles for all specimens); 4B element was not included to the Table 2. The Table 2 shows the peak current density with the relevant exposure cycle (1 cycle=7 days). Small current densities (smaller than 0.5 μA/cm^2) were not taken into consideration.

Current density becomes negligible when chloride contents are small and hence effective peaks are rarely visible. However, the corrosion activity is increased with considerable number of peaks when the total chloride contents are increased. In that situation, it can also be observed that these higher numbers of peaks are shared by majority of steel elements rather than one or two elements only. Higher numbers of peaks are interpreted as higher frequency of anodic-cathodic transformation. Considering the peak current density of elements 2B, 3B and 5B, 1st peak current is higher than the second peak (in 3B, it is equal) and in most cases 2nd peak was not observed for those elements. This fact is not clearly visible in element 1B. This result clarified that, the activity of anodic-cathodic transformation decreases with the distance from the region of highest electrochemical potential difference.

Fig. 7 shows the accumulated mass loss rate variation against the time (specimen 6). The rate of rust production is a similar representation to the rate of steel mass loss ($100 \mu A/cm^2/year$ = $914 mg/cm^2/year$). A sudden initiation of corrosion process or the rust accumulation is clearly observed in steel elements such as 1B&2B due to the sudden transfer of corrosion status of elements from cathodic to anodic. The cathodic or neutral period of mass loss rate of elements are represented by the zero gradients of curves where the rust is not produced.

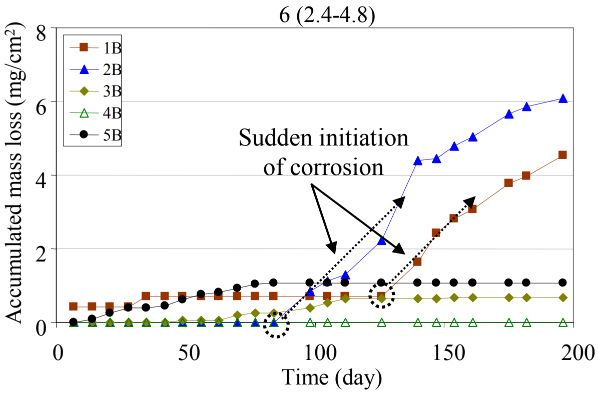


Fig.7 Accumulated mass loss rate

4.5 Discussion on anodic-cathodic transformation

Reinforced concrete is not contaminated any vulnerable material (such as Cl^- or CO_2) just after the casting, therefore it is assumed that steel corrosion will not occur due to the alkaline properties of concrete. However, with the time, the above mentioned corrosive materials may penetrate into concrete, but it is definitely in a non uniform way as experimentally established based on the heterogeneous properties of concrete. Therefore, an electrochemical potential difference occurs along the steel bar and hence the corrosion process starts as macro-cells else local corrosion.

The corrosion process is an electrochemical reaction, which is a combination of Cl^- ions, O_2 and H_2O. The potential difference is affected not only by Cl^- ions but O_2 and H_2O is also accountable since they are directly related with the corrosion reactions. It has been experimentally found that macro-cell corrosion is visible even the Cl^- contents are uniform along the steel bar. Therefore, it would be an evidence to mention that, macro-cell corrosion is possible even with uniform chloride contents.

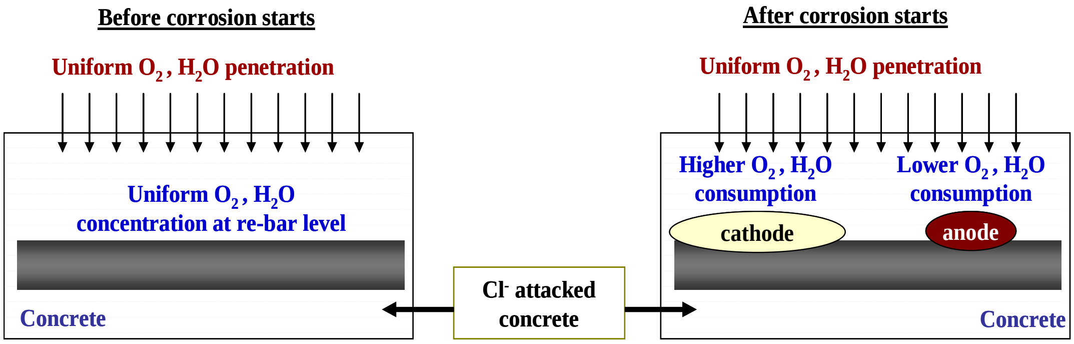


Fig.8 Possible mechanism for anodic-cathodic transformation

Above discussion clarified how the macro-cell corrosion initiate even with uniform Cl^- ions. Discussion is to be directed to clarify how the initiated macro-cell anodes and cathodes transformation is occurred. Different Cl^- ion contents were deliberately added to concrete for the purpose of making macro-cells at reasonably known locations. Therefore it can be assumed that the potential difference is not changing at steel elements from time to time (since no Cl^- ions enter from surrounding) provided that O_2 and H_2O concentrations are uniform throughout the steel bar level. Although additional Cl^- ions do not enter to concrete section, O_2 and H_2O frequently enter but it has a maximum penetration speed depend on the properties of concrete. However, once the corrosion process starts (refer the Fig. 8), the cathodic locations consume O_2 and H_2O in a higher consumption rate than anodic locations. Therefore with the time, the O_2 and H_2O concentration decreases at cathodic locations if the consuming speed is higher than the penetration speed. A lack of O_2 and H_2O create an additional potential difference which is more local than the potential difference created by Cl^- ions. O_2 and H_2O fewer areas are vulnerable to become anodic regions; hence the cathodically activated areas may be transferred to anodically active areas or neutral areas with the time. This may facilitates to convert the anodic areas into cathodic areas.

5. CONCLUSIONS

Uniform Cl^- ion concentrations may not generate a potential difference. However, this research found that the macro-cell corrosion is still visible even with the uniform Cl^- ions.

If specimens are subject to different Cl^- environment, more local macro-cell corrosion can be clearly observed in the region of different Cl^- concentrations. Also, the macro-cell corrosion in high Cl^- region is more active while the macro-cell corrosion in low Cl^- region is negligible even the low Cl^- concentration exceed its threshold value or critical chloride concentration for initiation of steel corrosion which can be taken as $1.2kg/m^3$ as JSCE recommendations.

In this research, it was also found that initially generated macro-cells (i.e. anodic and cathodic locations) may change their status with the time. Hence it can be concluded that macro-cell corrosion is time dependent where the macro-cell anodic locations may transfer to cathodic locations while cathodic locations transfers to anodic locations. The anodic-cathodic transformation may be observed periodically. As a result, the rust production on the steel bar surface is no longer uniform in short term condition (considering 28 week results only).

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