Effect of tropical marine microclimates on depassivation and corrosion-induced cracking of reinforced concrete

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The objective of the present work is to discuss the electrochemical monitoring and corrosion-induced cracking propagation obtained from small reinforced concrete cylinders exposed to three natural tropical marine microclimates. Tests were performed with reinforced concrete cylinders (7.5 x 15 cm) exposed for 16 years at three different tropical marine microclimates (50, 100 and 780 m from the seashore) in the city of Progreso, Yucatan, Mexico. The concrete used in these cylindrical specimens was fabricated with four different water/cement ratios (0.50, 0.53, 0.70, and 0.76), and three different curing periods (1, 3, and 7 days). Electrochemical techniques were used to monitor the corrosion performance of the reinforcing bar during the exposure time (16 years). After corrosion damage was achieved by the appearance of surface cracks, the morphology of such cracks were surveyed and recorded. The results observed indicate a direct effect of distance from the seashore on the depassivation time of the reinforcing steel: the higher the distance from seashore, the longer is the corrosion initiation period. Regarding crack width propagation, stress attenuation was observed in the seashore specimens. In addition an apparent exponential relationship was observed between depassivation time and the water/cement ratio.

Keywords: tropical marine microclimate, cracking, reinforced concrete, corrosion.

1. INTRODUCTION

Corrosion of reinforcing steel is one of the must important causes of reinforced concrete structures degradation [1-3]. The environment and climate change effects contribute also to the acceleration of this deterioration. The humidity and different concentrations of sea chloride ions in the

environment enhance its deposition on the concrete surface and the degradation rate significantly depends on the seashore distance [4].

Between the different damages caused by the reinforcing steel corrosion process, concrete surface cracking is the most common, and it is produced by the corrosion products expansion [5, 6]. Therefore, it has been presented elsewhere empirical relationships between corrosion-induced cross-section loss of the reinforcing steel and damage symptoms such as concrete cracking to monitor service life reductions of reinforced concrete structures [7-9]. The study of any possible relationship between concrete cover cracking and reinforcing steel corrosion parameters will help to structural inspectors to define possible repair strategies.

Such relationships between structural distress and corrosion from accelerated corrosion tests performed in laboratory have been presented [10-16], while natural corrosion investigations are scant due to its complexity on data analysis, which may include various parameters involved in this corrosion phenomenon [16]. In the case of structures exposed in a marine environment, chloride ions are deposited on the surface of the concrete and penetrate until they reach the surface of the reinforcing steel, causing the breakdown of the passive layer [17-19]. Once reinforcing bar corrosion starts, corrosion products starts to build up around the reinforcing bar, causing volumetric expansions that will result in concrete cover cracking (Figure 1) [20].

The literature has reported important investigations related to the concrete cover cracking in reinforced concrete structural elements, but under controlled conditions in the laboratory [21]. The methods that have been used in these investigations to accelerate the corrosion of the steel reinforcement include chloride contamination of the concrete during mixing water, or by spraying saline water on the surfaces of the specimens. Another accelerated method includes not only chloride contamination but also accelerated electrochemical methods by applying anodic currents or potentials, among others [22-28].



Figure 1. Scheme of concrete cover cracking.

The objective of this work is to discuss some of the results obtained with an experimental program, which included the fabrication of several reinforced concrete cylinders with five different water/cement ratios, direct tropical marine exposure of these reinforced concrete specimens to three

different microclimates (Figure 2, main variable was the distance to the seashore: 50, 100 and 780 m), the time of steel reinforcement depassivation (corrosion initiation stage), and cover concrete crack propagation.

2. EXPERIMENTAL PROCEDURE

2.1 Concrete mixtures

For concrete fabrication, typical fine and coarse aggregate was used (crushed limestone) and ordinary Portland cement. Concrete mixes were fabricated using four different water/cement ratios: 0.50, 0.53, 0.70 and 0.76. Another concrete fabrication variable was the curing time: 1, 3, and 7 days. The concrete cylinders were exposed since 1993 in a tropical marine environment, at the north coast of the Yucatan Peninsula (Figure 2). The concrete cylinders were placed in front of the beach in the Progreso Port, Yucatan State, distributed to three different microclimates, with distances from the seashore of 50, 100 and 780 m.



Progreso City, Yucatán, México

Figure 2. Distribution and location of the concrete specimens

2.2 Specimens

90 reinforced concrete cylinders, 7.5 cm in diameter by 15.0 cm in length, with a deformed reinforcing steel bar (9.5 mm nominal diameter and 20.0 cm long), placed in the center of the cylinder were evaluated (Figure 3a). Cylinders and the reinforcing bars (also called working electrode or WE)

were covered with coal tar paint and duct tape at the ends (of both, concrete and steel bar) to have an exposed length of approximately 12.0 cm, which was considered as the exposure area.

It was also placed an activated titanium/ titanium oxide bar (5 cm long and a diameter of 3 mm), which was used as a reference electrode (RE) in the electrochemical measurements.

2.3 Electrochemical monitoring

Two were the electrochemical techniques used to determine the corrosion performance of the reinforcement steel inside the concrete cylinders: corrosion potential measurements (E_{corr}) and linear polarization resistance (Rp) [29, 30]. Electrochemical measurements were performed using the cell configuration as shown in figure 3b, which has been characterized and calibrated in previous studies [31].

Corrosion potentials of the reinforcing steel were measured using a multimeter (MULTISCOPE Opening Screen RMS True 179) and a calomel reference electrode (ECS), with the purpose to verify the performance of the internal ATR.



Figure 3. Schematic representation showing (a) dimensions and assembly of the specimens, (b) the cell configuration.

Rp measurements were performed using a Gamry's Potentiostat/Galvanostato/ZRA (Reference 600 model). The test included a 20 mV cathodic potential application starting from open circuit potential, and a 0.06 mV/s sweep rate. Polarization curves were analyzed with specialized software (from Gamry Instruments) just after each of the measurements were made. The concrete resistivity was estimated using a soil resistance meter (Nilsson, model 400), and this value was subtracted from the Rp analysis result [31, 32].

All Rp values were used to estimate the apparent corrosion rate (i_{corr}) using the well known relation:

$$i_{\rm corr} = \frac{B}{Rp} \tag{1}$$

Where B is a constant equal to 0.026 V when steel is active and equal to 0.052 V when steel is passive; Rp is the apparent polarization resistance in ohm-cm².

During the experimental period, all cylinders surfaces were inspected to observe possible corrosion-induced crack formations. When corrosion crack appeared at the concrete cylinder surface, the date was recorded and the cylinder was retrieved from the test station for crack survey and returned afterwards to the test station. For the registry of the crack's shape and size, special crack comparators were used (transparent plastic card of 5.0 cm x 8.0 cm, from Construction Technology Laboratories, Inc. CTL reference card). Also, transparent acetate sheets were used to draw the crack configuration and morphology with respect to the cylindrical specimen geometry. Figure 4 shows a concrete cylinder with the presence of typical concrete cover cracking (corresponds to a 0.53 water/cement ratio, 1-day curing, and exposed to 100 m from the seashore).



Figure 4. Typical concrete cracking after exposure to tropical marine environment.

Cylinders that reached severe damage (cracks width larger than 5 mm) were removed from the exposure site to analyze the reinforcing steel. The cleaning was done on the reinforcing bar to determine the gravimetric steel mass according to the procedure described in ASTM G-1-03 [33] using an analytical balance (Analytical Standard AS200S). With the mass loss estimations using this

procedure, the average corrosion penetration (x_{prom}) was estimated, similar to the reported in the literature [26].

$$x_{\text{prom}} = \frac{\mathsf{D}W_g \cdot 10^3}{r\rho fL} \tag{2}$$

Where x_{prom} is given in mm, ΔW_{g} is the reinforcing bar gravimetric mass loss in grams (g), ρ is the steel density (7.86 g/cm3), ϕ is the reinforcing steel bar diameter (9.5 mm), and *L* is the anodic length of the reinforcing steel. The reinforcing steel loss ratio is defined in this investigation as the relationship between x_{prom} and the initial radius of the reinforcing steel bar r_{o} .

3. RESULTS AND DISCUSSION

Figure 5 shows two typical examples of the polarization curve that were used to extract the polarization resistance, which was used to obtain the corrosion rate from the equation (1). The examples correspond to both microclimates, Armada (ARM SR) and Bachilleres (BACH SR) which are exposed at 100 m and 780 m from de seashore respectively.



Figure 5. Example of the polarization curve that was used to extract the polarization resistance.

3.1 Time of corrosion initiation, T_1 , at the different marine microclimates.

The corrosion initiation stage (T₁) was considered as the time between the concrete cylinders were placed at the test station and time which reinforcing steel depassivation occurred. In this investigation, depassivation is reached when i_{corr} values measured is $\geq 0.1 \ \mu\text{A/cm}^2$ [34]. Figure 6 shows typical performance of all w/c ratio concretes, 1-day curing (TC), and exposed to 50, 100, and 780 m test sites. This figure displays i_{corr} measurements vs. time of exposure (in months). It also shows two horizontal dotted lines (at 0.1 and 0.5 $\mu\text{A/cm}^2$), which correspond to the corrosion activation range. Therefore, the time estimate of active corrosion is reached when i_{corr} values were higher than this two horizontal threshold. Using these activation values, Figure 6 was built, showing the results (average of three cylinders per mixture) of corrosion initiation stage for all mixtures and exposure sites.

It is important to mention that the T_1 period was obtained in this investigation quite easily due to the fact that i_{corr} estimates were continuously obtained. Even though, the best way to get T_1 is through the cumulative slope of i_{corr} as stated in a previous investigation [35].





Figure 6. Corrosion rate to determine T1, 1-day curing concrete.

As observed in Figure 7a (concrete with 1-day curing), an apparent exponential correlation between T_1 and the water/cement ratio is observed regardless of the exposure site distance from the seashore: T_1 decreases by increasing the water/cement ratio. It was also possible to observe that in the cylinders at the 100 m and 780 m exposure sites, T_1 was quite larger than the 50 m exposure site results: 5 times higher at the 100 m site and 11 times higher at the 780 m than 50 m site.

A similar effect was observed for the 3-day curing time concrete (Figure 7b): T_1 values were 5 times greater for the 100 m and 780 m exposure sites than the 50 m exposure site. Same for the 7-day curing time (Figure 7c): T_1 values were 5 and 8 times greater for 100 m and 780 m exposure sites, respectively, than the 50 m exposure site. Arrows shown in figures 7a and 7b for 0.5 water/cement ratio at 780 m exposure site, indicate that the reinforcing steel still remains in a passive state.

On the other hand, by comparing the average T_1 estimates for the different curing times at same microclimate, it was observed that by increasing the curing time period for each water/cement ratio, T_1 tends to increase. However, at this moment it is unclear why the cylinders exposed at the 780 m site, and with 7-day curing, showed a smaller T_1 than their counterparts for 1-day and 3-day curing time.

At the larger water/cement ratio, 0.76, T_1 occurred at 6 and 46 months for the 50 m and 780 m exposure sites, respectively.

 T_1 values obtained from cylinders placed at the 780 m exposure site are related with various factors associated with parameters of the microclimate (environment), and to those associated with the concrete quality. Among them might be the temperature and relative humidity, which will lead to concrete maintain its moisture inside, thus small humidity changes in its interior. On the other hand, the parameters that can be related to the quality of the concrete includes the water/cement ratio, the electrical resistivity, and/or i_{corr} , which may be related to the penetration density or corrosive agents flow (chloride ion) inside the concrete during the experimental period.







(c)



Figure 7. Average value of time (months) of depassivation, *T*₁, for specimens exposed to 50, 100 and 780 m from the seashore, different w/c ratios (0.50, 0.53, 0.70 and 0. 76), and three times of curing: (a) 1 day; (b) 3 days; (c) 7 days.

It is well known the effect observed on T_1 decrease by increasing the water/cement ratio, and has been attributed to an increase in concrete porosity at high water/cement ratio values, allowing easily entrance of pollutants (chlorides, water, oxygen) which accelerate corrosion of the reinforcing steel. But, the pollutant transport inside the concrete cover depends also on the internal humidity of the concrete and ambient temperature.

A correlation analysis was performed between T_1 and the water/cement ratio with the results obtained. This analysis used the following empirical correlation: $(T_1 = ae^{-b(w/c)})$, where *a* and *b* are constants. Results of these empirical correlations are shown in Table 1.

1-day curing			
Distance (m)	a	b	R^2
50	72.12	3.5	0.42
100	3305.3	6.84	0.79
780	5133.2	6.26	0.98
	3-day	curing	I
50	116.2	4.08	0.86
100	14086.0	9.78	0.95
780	6996.3	6.95	0.95
	7-day of	f curing	
50	168.7	4.56	0.95
100	2609.0	6.46	0.86
780	3377.8	6.00	0.98

Table1. Correlation parameters between T_1 and the water/cement ratio for different curing periods, and distances from the seashore.

As observed from the parameters in Table 1, there is a good correlation (see R^2 factor) between T₁ and water/cement ratio, with exception of the test pieces to 50 m and 1-day curing. The constants a and *b* apparently are associated with the volumetric electric charge density during the exposure time and the stress attenuation factor in the concrete cover, respectively. The first constant, *a* could be understood as the concrete capacity to allow the aggressive agent transport during the exposure time, in addition to the amount of corrosion products generated by the reinforcing steel. While the parameter *b*, or attenuation factor, corresponds to the ability of concrete to absorb the tensile stresses generated by the expansion of the corrosion products.

It is important to mention that the validity of this type of empirical correlation is restricted to similar concrete properties and microclimates, and to obtain a general relationship, additional investigation is needed. It is then possible, with some precautions, extrapolate to different water/cement ratios to obtain the expected T_1 estimate.

3.2 Effect of the distance from the sea

Figure 8 shows cross section ratio (x_{prom}/r_o) vs. maximum crack width (MCW) data measured on all the specimens evaluated in this research that have shown concrete cover cracking. Same figure shows the empirical correlations between x_{prom}/r_o and MCW according to the exposure site distance from seashore (50, 100, and 780 m), with the purpose of evaluating the effect of distance from seashore on these two parameters. As observed in Figure 8, x_{prom}/r_o values were located between 0.03 to 0.1 (3% to 10 %), regardless of exposure distance from the seashore.

As observed from this figure, the effect of seashore distance had a significant influence on cover concrete crack propagation (MCW), being the maximum values obtained at the 780 m exposure site, while the smallest MCW values correspond to the 50 m test site. With the trend lines can be seen that behavior, although the data collected so far are not sufficient to describe more clearly a general behavior. It is suggested that this behavior is influenced by the effect of concrete quality and the capacity to absorb internal stresses caused by the expansion of the corrosion products [36, 37]. The term, which relates this, is known as attenuation factor. The attenuation factor is define in this research as the ability of concrete to absorb expansive stresses, depending on the quality of the concrete, the mechanisms of corrosion and the environment in which exposes the concrete.



Figure 8. Comparison of the maximum width of crack against the loss of radio reinforcement for the different microclimates.

From data in Figure 8 it is clear to observe that this attenuation factor for the 780 m test data is higher than the one for the 50 m exposure site. This might be due to the fact that the corrosion product kinetics is a slower process, allowing the concrete to absorb a certain amount of tensile stresses generated by the expansion of the oxides. While in most of the accelerated corrosion experimentation, the generation of oxides is more rapid and concrete has almost no opportunity to absorb the expansion stresses generated, what gives rise to a sudden cracking. This is how the 50 m exposure site specimens performed, similar to an accelerated corrosion experimental procedure. In accordance with the foregoing, the evidence for natural corrosion from this investigation shows that the distance from the seashore has an effect on the crack width propagation, which could be related to the attenuation factor.

Perhaps this is due to the presence of moisture in the concrete, which may contribute to the migration of corrosion products away from the steel/concrete interface through the pore network, reliving the concrete from the corrosion expansion stresses. Figure 9 shows photographs of the corrosion products penetration in concrete around the reinforcing steel. Therefore, when moisture content in the concrete cover decreased at distances far from the seashore (780 m), i_{corr} may decrease also as compared with i_{corr} at shorter distances from seashore (50 m).



(a) 50 m, 1-day TC and 0.76 w/c



(b) 100 m, 1-day TC and 0.46 w/c



(c) 780 m, 3-day and 0.76 w/c

Figure 9. Migration of the corrosion products transported through the concrete cover pore network, for cylinders exposed in the various microclimates (50 m, 100 m and 780 m).

Another possible reason for this crack attenuation performance of cylinders at the 780 m exposure site is that for less water in the pore network increases the pressure buildup at the steel/concrete interface because the corrosion products accumulate rapidly without escaping from this interface, thus cracks widen more easily at an exposure site less humid.

The cracking process of concrete could be represented as a four-stage mechanism: (I) generation and corrosion product expansion; (II) first crack generation; (III) crack propagation; and (IV) oxide transport ease through the concrete and crack coalescence and concrete delamination. Linking these stages with the parameters mentioned above, the stage I would be controlled by the porosity of the concrete, the current charge density, and the volumetric cross section loss of the reinforcing steel (x_{prom}/r_o). Stage II would be controlled by the attenuation factor of the concrete; and stages III and IV would be controlled by the spread and transport ease of the corrosion products away from the steel/concrete interface.

4. CONCLUSIONS

These conclusions apply only to the conditions of study, any extrapolation to other environments or conditions must be carefully established. Based on the results obtained in the present investigation, the following conclusions were obtained:

With corrosion rate data obtained from the measurement in this long term investigation, it is confirmed that there is a direct influence of seashore distance on the electrochemical behavior of the different types of reinforced concrete mixtures, giving shorter steel reinforcement depassivation periods (8 times less) for concrete specimens exposed at 50 m from seashore, as compared with same specimens exposed to a site 780 m away from seashore.

The steel reinforcement depassivation stage (T_1) obtained from results of this investigation showed an apparent exponential correlation with respect to concrete quality: higher concrete quality gave longer depassivation stage. This was observed regardless of microclimate.

Based on the results obtained, the curing time did not affect the depassivation performance of the reinforcement steel at a long term exposure. However, this natural corrosion procedure at three different microclimates (50 m, 100 m, and 780 m away from the seashore), corroborate the effect of the seashore distance on the crack width propagation that could be related to the stress attenuation factor due to internal concrete humidity.

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References

- 1. Y. Yuan, Y. Ji and S. P. Shah. ACI Structural Journal. 104 (2007) 344.
- U. Angst, B. Elsener, C. K. Larsen and O. Vennesland. *Cement and Concrete Research*. 39 (2009) 1122.

- 3. C. Fang, K. Lundgren, L. Chen and C. Zhu. Cement and concrete Research. 34 (2004) 2159.
- 4. P. Castro-Borges and J. M. Mendoza-Rangel. *Corrosion Engineering Science and Technology*. 45 (2010) 61.
- 5. M. D. Meyer, L. S. Watson, C. M. Walton and R. E. Skinner. *Control of cracking in concrete. State of the art.* Transportation Research Circular. No. E-C107. Washington DC. (2006).
- 6. S. J. Jaffer and C. M. Hansson. Cement and Concrete Research. 39 (2009) 116.
- 7. S. Ahmad. Cement and Concrete Composites. 25 (2003) 459.
- 8. R. E. Weyers. ACI Materials Journal. 95 (1998) 445.
- 9. S. J. Kwon, U. Jin Na, S. S. Park and S. H. Jung. Structural Safety. 31 (2009) 75.
- 10. O. Poupard, A. Aït-Mokhtar and P. Dumargue. Cement and Concrete Research. 34 (2004) 991.
- 11. J. M. Chi, R. Huang and C. C. Yang. Journal of Marine Science and Technology. 10 (2002) 14.
- 12. C. H. Simpson, C. J. Ray and B. S. Skerry. Journal of Protective Coatings & Linings. 8 (1991) 28.
- 13. C. L. Meade. Metal Finishing. 97 (1999) 526.
- 14. T. A. El-Maaddawy and K. A. Soudki. Journal of Material in Civil Engineering. 15 (2003) 41.
- 15. L. Li and A. A. Sagüés. Corrosion Science. 57 (2001) 19.
- 16. T. Vidal, A. Castel and R. François. Cement and Concrete Research. 37 (2007) 1551.
- 17. M. F. Montemor, A. M. P. Simoes and M. G. S. Ferreira. Cement and Concrete Composites. 25 (2003) 491.
- 18. M. Moreno, W. Morris, M. G. Alvarez and G. S. Duffó. Corrosion Science. 46 (2004) 2681.
- 19. S. Caré, Q. T. Nguyen, V. L'Hostis and Y. Berthaud. *Cement and Concrete Research*. 38 (2008) 1079.
- 20. Y. Zhao, J. Yu, B. Hu and W. Jin. Corrosion Science. 55 (2012) 385.
- 21. C. Q. Li. ACI Materials Journal. 97 (2000) 690.
- 22. J. G. Cabrera. Cement and Concrete Composites. 18 (1996) 47.
- 23. A. A. Torres-Acosta, P. Castro-Borges and A. A. Sagües. *Effect of corrosion rate in the cracking process of concrete,* in Proc., XIVth National Congress of the Mexican Electrochemical Society. 1999: Spanish.
- 24. C. Andrade, C. Alonso and F. J. Molina. Materials and Structures. 26 (1998) 453.
- 25. J. Rodriguez, L. M. Ortega and J. Casal. Construction and Building Materials. 11 (1997) 239.
- 26. A. A. Torres-Acosta and M. Martínez-Madrid. *Journal of Materials in Civil Engineering*, 15 (2003) 344.
- 27. P. S. Mangat and S. Elgarf. *Materials and Structures* 32 (1999) 89.
- 28. Y. Hernández-López, et al. *Relationship between loss of reinforcement section and width of cracks in concrete beams* (Spanish), in CONPAT, Mexico (2009).
- 29. P. Garcés-Terradillos, M. A. Climent-Llorca and E. Zornoza-Gómez. *Corrosion of Reinforcement in Concrete Structures* (in Spanish). Editorial Club Universitario, Spain, (2000).
- 30. M. Stern and A. L Geary. Journal of the Electrochemical Society 104 (1957) 56.
- 31. M. A. Pech-Canul, A. A. Sagüés and P. Castro. Corrosion 54 (1998) 663.
- 32. M. A. Pech-Canul and P. Castro. Cement and Concrete Research 32 (2002) 491.
- ASTM G1-03. Standard practice for preparing, cleaning, and evaluating corrosion test specimens. (2011)
- 34. K. Tuutti, *Corrosion of steel in concrete*. Swedish Cement and Concrete Research Institute, Stockholm, Sweeden (1982).
- 35. P. Castro-Borges, M. Balancán-Zapata, A. López-González. Journal of Chemistry. (2013) 8.
- M. Z. Jumaat, M. H. Kabir and M. Obaydullah. *Journal of Applied Science Research*. 2 (2006) 317.
- 37. A. A. Almusallam. Construction and Building Materials. 15 (2001) 361.
- S. Bastianoni, A. Galli, V. Niccolucci and R. M. Pulselli. *The ecological footprint of building construction*. In The Sustainable city IV. Urban regeneration and sustainability. WIT Press. UK 93 (2006).

- 39. J. L. Doménech Quesada. *Ecological footprint and sustainable development* (Spanish). AENOR. España (2007).
- 40. H. Yazici, H. Yigiter, A. S. Karabulut and B. Baradan. Fuel. 87 (2008) 2401.
- 41. G. Menéndez, V. Bonavetti and E. F. Irassar. Cement and Concrete Composites. 25 (2003) 61.
- 42. J. M. Khatib and J. J. Hibbert. Construction and Building Materials. 19 (2005) 460.

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