Analysis of the Infiltration of Chloride Ions into Concrete Samples and Its Role in the Corrosion Onset of Embedded Steel Rebars

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Profiles of samples infiltrated by chloride ions are analyzed in this study. The samples were made of simple concrete, cylindrical shape with water/cement (w/c) ratios of 0.6 and 0.46, without chloride, and the 3.5% of its weight of chloride in the mixing water for both w/c ratios. Systematic monitoring of electrochemical parameters on samples with steel rod in the center at the same proportions was done in parallel. The concrete samples were exposed under three media: natural atmosphere, total immersion and to alternating wetting-drying cycles in natural sea water. Profiles of chloride concentration after an exposure of 90 to 365 days were obtained and processed assuming a diffusion mechanism in a finite porous medium, according to the equation of Fick´s second law. The time considered to reach the critical chloride threshold (0.4% by weight of cement) in rebar-concrete interface was calculated by using a lineal approximation for the diffusion coefficient. Chloride concentrations were also calculated at the time that electrochemical measurements reported the onset of corrosion. On the other hand, the electrochemical impedance spectroscopy diagrams show the depassivation of rebar at exposure times that do not correspond to a critical threshold of 0.4 % by weight of cement. Electrochemical techniques suggests that depassivation of embedded steel rebar in concrete occurs at different thresholds to 0.4% by weight of cement; therefore, the critical time is also modified. It is clear that the elaboration and exposure conditions are determining in the onset of the corrosion process of steel rebar.

1. INTRODUCTION

Mexico is a country with approximately 10,000 km of coastline, where a considerable part of Mexican economic activities are developed. Consequently, an important port, industrial, and tourism infrastructures are settled. Some of the problems of maintaining this infrastructure are directly related to deterioration resulting from its interaction with the environment. Reinforced concrete structures that are exposed to a tropical marine atmospheres often suffer damage caused by the corrosion of reinforcing steel, mainly as a result of its direct interaction with chloride ions content in seawater, or indirectly through its contact with the marine breeze in airborne particles transport[1,2]. It is feasible to asses the level of damage and characterize a region in which the same concrete and similar exposure conditions exist. In the Yucatan Peninsula, concretes are elaborated generally with a high water/cement (w/c) ratio, and aggregates of calcareous origins are also used. Due to the nature of these aggregates (angular shape and low resistance to abrasion) it is very difficult to obtain low w/c ratios[3,4]. On the other hand, besides of the structural damages usually assigned to an inadequate design and bad construction practices, the importance of the influence of environment on the corrosion of embedded steel is not considered. This entails the production of specific concretes vulnerable to the infiltration of chloride ions that eventually would cause corrosion to reinforcing steel.

To analyze this issue experimentally, cylindrical concrete test-probes were manufactured with aggregates made with river w/c ratios of 0.46 and 0.60. The concrete samples were exposed under three media: natural atmosphere, total immersion and to alternating wetting-drying cycles in natural sea water. They were used to approximate the natural conditions of a marine environment which a reinforced concrete structure might be exposed to. The electrochemical evaluation was carried out by using the technique of electrochemical impedance spectroscopy (EIS), which have proved to be useful tool to determine the starting point of the corrosion process. Measurement of penetration of chloride ions was made in order to know the critical concentration that triggers start the corrosion process. Chloride ions profiles were introduced into a mathematical model based on Fick´s equation, assuming the penetration of chloride as a phenomenon of diffusion in a porous medium [5]. Results from the mathematical model indicate that the critical concentration of chloride ions (0.4% by mass of cement) reported by several authors[6-9] does not correspond to the depassivation of steel observed by the EIS. It was also determined that the period of time in which the reinforcement is depassivated, the chloride concentration is higher than the reported as critical.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Specimens.

Concrete cylinder specimens of 7.5 cm diameter and 15 cm height made with Ordinary Portland Cement type I (OPC-I), coarse (1.25 cm maximum size) and sand river aggregates were manufactured for this study. Two w/c ratio, 0.60 and 0.46, with a variation of cement content were established. Dosages of concrete mixtures are shown in Table 1. In samples that are marked with the

extension Cl⁻ , the mixing water used to mix the concrete, contained 35 gl^{-1} of NaCl (3.5 % wt NaCl). The concrete cylinders were cured by continuous immersion during 28 days [10].

Table 1. Concrete mixture design. f'c = compressive strength of concrete (MPa) after 28 days of curing.

Water / cement ratio (c/w)	cement (kgm^{-3})	water (kgm^{-3})	sand (kgm^{-3})	Gravel (kgm^{-3})	f'c (MPa)
0.60	350	206.5	880.6	888.0	19.20
0.60 Cl⁻	350	206.5	880.6	888.0	16.30
0.46	443	204.8	806.0	888.0	25.74
0.46 Cl⁻	443	204.8	806.0	888.0	22.43

For each exposure media and condition of manufacturing, four-cylinder series of simple concrete and four concrete with centered steel rod in the longitudinal direction, were casting. Commercial corrugated steel bars of 0.95 cm diameter were used. The chemical composition is detailed in Table 2.

Table 2. Chemical composition of the steel bars.

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	Nb	Ti	Pb	Fe
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0.3515	0.0997	1.094	0.0224	0.0260	0.3528	0.0489	0.0888	0.0106	0.0094	0.4570	0.0018	0.0031	0.0054	97.4

The specimens were exposed to 3 different environments: a) permanent immersion in sea water (IMM), b) alternating cycles of sea water soaking at night and drying in the atmosphere during the day (IMM-DRY) and, c) continuous exposure to the atmosphere (ATM).

2.2. Electrochemical impedance spectroscopy (EIS)

A monitoring of corrosion potential (Ecorr) and electrochemical impedance spectroscopy (EIS) during 500 days at intervals of 15 days made using a conventional cell of three electrodes[11] connected to a potentiostat PAR 273 coupled to a frequency response analyzer (FRA). The steel rod was employed as working electrode was and as a counter electrode a graphite bar was used, as well as a saturated calomel electrode (SCE) as a reference electrode. EIS sweeps were conducted in a

frequency interval of 100 kHz to 1mHz, AC amplitude of 10 mV with 5 measurements per magnitude order.

2.3. Measuring the infiltration of chloride ions.

For these measurements, simple cylindrical concrete specimens without rods were fabricated with the same characteristic and dosages that those destined to electrochemical assays. Both sides of the specimens sections were sealed with a coating of coal tar in the longitudinal direction of the cylinders to prevent the penetration of aggressive species.

To obtain samples for the chloride ions analysis, a slice of 1 cm thick cylinder of concrete was cut. Then, samples of concrete powder at different radii of the slice[12] (0-5mm, 5-10mm, 10-15 mm, 15-20 mm, 20-25 mm, 25-30 mm, 30-35 mm) were obtained under dry conditions by using a drill. Each sample was prepared to make it pass through the mesh No. 200. A solution of 0.06 M HNO_3 at 20 °C was used to chloride ion extraction and the quantification of chloride was carried out using a selective ion analyzer[13]. The chloride concentration profiles in the radial direction were determined at 90 and 365 days[14]. The obtained experimental chloride ions concentration was used to determine the concentration profile as an adjustment to the Fick´s Law. The adjustment parameters considered in Fick´s Law are the surface concentration and the diffusion coefficient. They were obtained with the Downhill-simplex method[15], using the square mean root as a test function. To determine the time at which the chloride concentration was 0.4% by weight of cement, Boltzmann function and a linear function were used. The Boltzmann function consider the surface concentration as a function of time due to its capacity to reproduce the asymptotic behavior at a saturation value on the surface; while a linear approximation was used to calculate the diffusion coefficient in relation to time. Both, the adjustment function of surface concentration and the diffusion coefficient were obtained from the experimental values for 1, 90 and 365 days of exposure.

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance spectroscopy.

Figure 1 shows the monitoring of corrosion in the specimens series with a w/c ratio 0.6, 3.5 % chloride by weight in mixing water (0.6 Cl), which was the first to show signs of corrosion. Nyquist diagrams, Bode–phase angle and Bode – impedance module showed significant changes in its shape and values of charge transfer resistance R_{ct}. It can be observed that the system goes from a passive to an active state of the reinforcement. It is evident that after 259 days, the rod is in a passive state, as reflected by a capacitive arc in the Nyquist plot, a value that is greater than 10^4 Ωcm^2 in the |Z| module of impedance and a phase angle close to 75 degrees. The following measurement after 280 days reveals a change in the interface, which is manifested by the decrease of the semicircle in the Nyquist diagram on the order of 10^3 Ωcm^2 and a decreasing phase angle up to 25 degrees. The measurement of 322 days shows an increase on the order of 40000 Ωcm^2, but, after 336 days, the graph shows a clearly

active interface with a defined semicircle closer to 10^3 Ωcm^2 value. Similarly, the impedance modulus is closer to that value and the phase angle is less than 10, and tends to zero, that means an active process of corrosion[16-19].
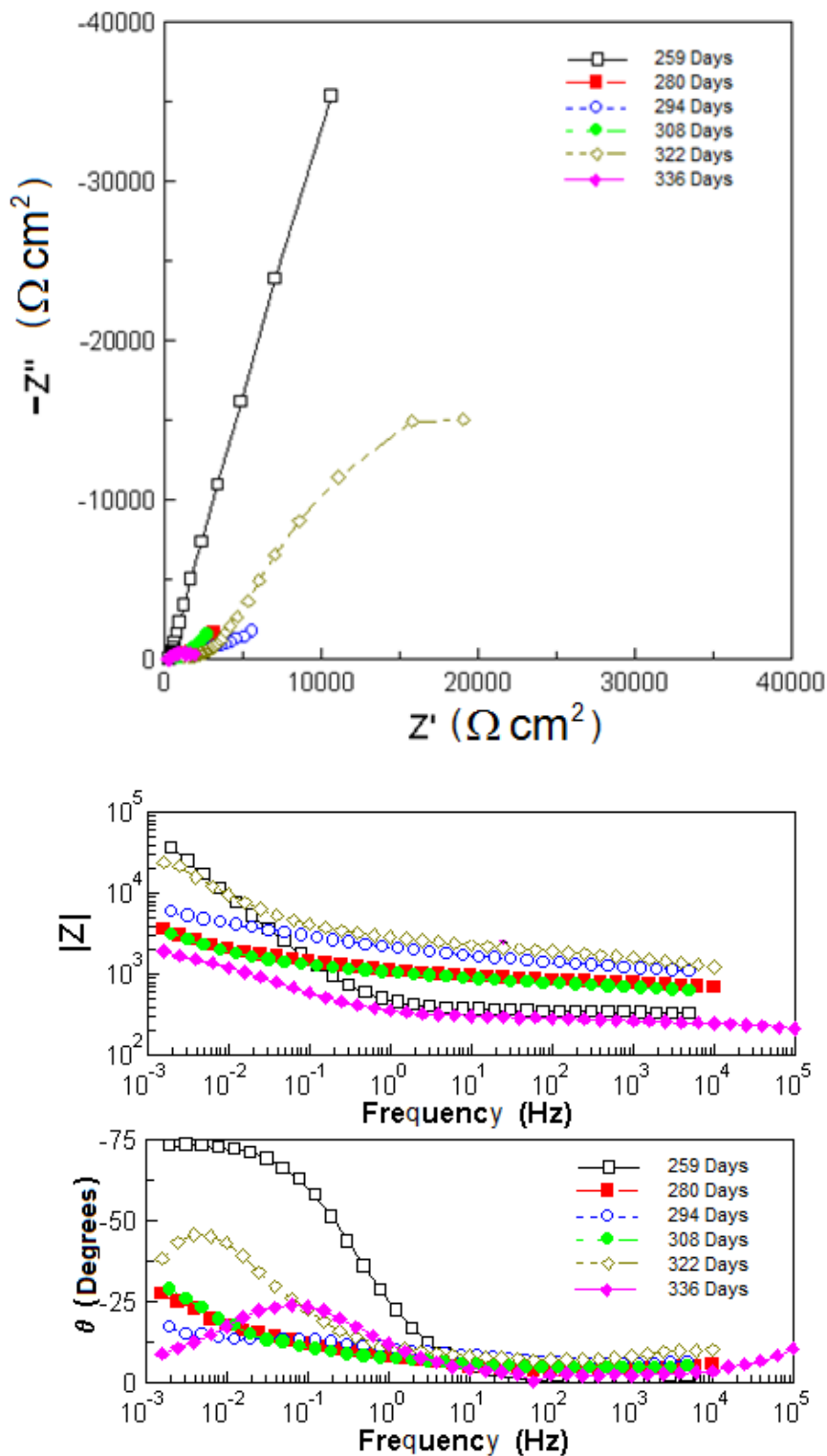
Figure 1. Nyquist diagrams, Bode and Bode-phase. Type of exposure: atmosphere-immersion. 0.6 Cl⁻ series. Exposure time: from 259 to 336 days.

The stability of the passive film on the reinforcement surface is affected by the presence of chloride ions that, at reaching a critical concentration in the interface, it induces the breakdown of iron oxides which give protection; thus, the metal is exposed to an aggressive environment and the corrosion process starts. Given that the depassivation of the rod is associated with a critical concentration of the chloride ion, the EIE monitoring shows that the days indicated in the diagram are determining in the corrosion process start, hence the importance of knowing the chloride concentration and establishing its relationship with the breakdown of the passive layer.

3.2. Penetration of chloride ions.

The chloride penetration profiles for 90 and 365 days of exposure are illustrated in Figures 2 to 5. They show the effect of the exposure medium and the w/c ratio on the chloride penetration profiles. After 90 days, the amount of chloride reported in % by weight respect to cement on the specimens' surface is higher for the 0.60 w/c ratio, because its porosity is higher. During this period, the profiles describe a behavior that tends to be parabolic, suggesting a diffusive pattern in both exposure conditions: immersed permanently and subject to wetting-drying cycles. This behavior is observed both in the samples that were prepared with chloride in the mixing water and in the samples without chloride in the mixing water. The specimens under atmospheric conditions describe a diffusive profile into the cylinder, away from the surface, due to the limited penetration of chloride ions and to the thickness near the surface, which is subject to wetting and drying cycles. Profiles can be explained as a result of the weather conditions in the exposure site, the City of Campeche, where the prevailing winds are from the East; that is in land to sea. The result is a low concentration of chlorides in the marine aerosol and, therefore, a poor penetration of the ion in the samples[20].
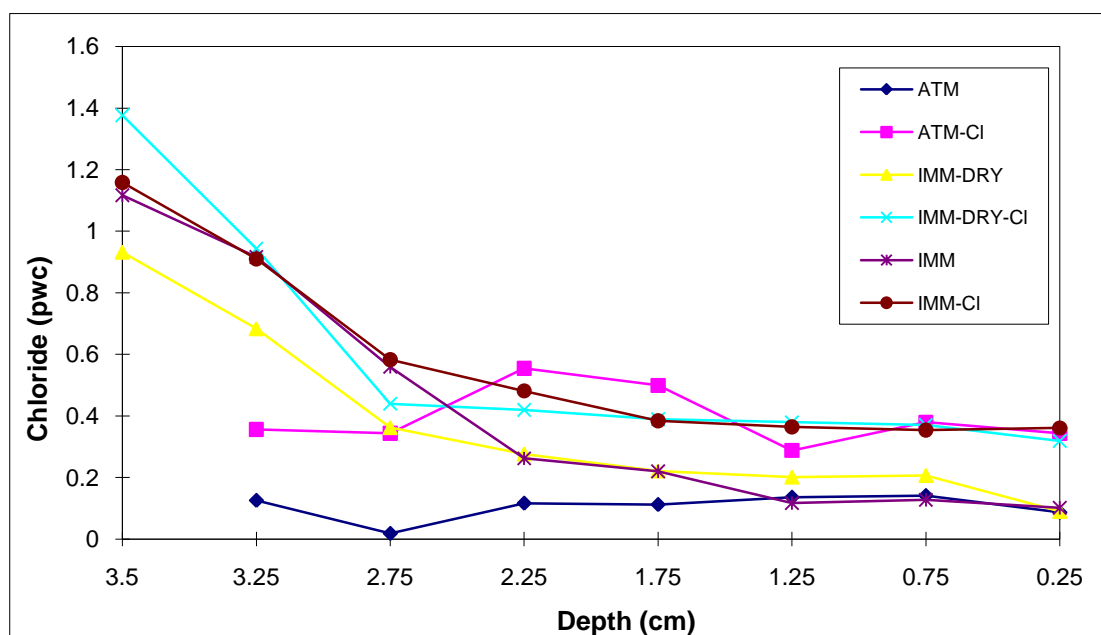

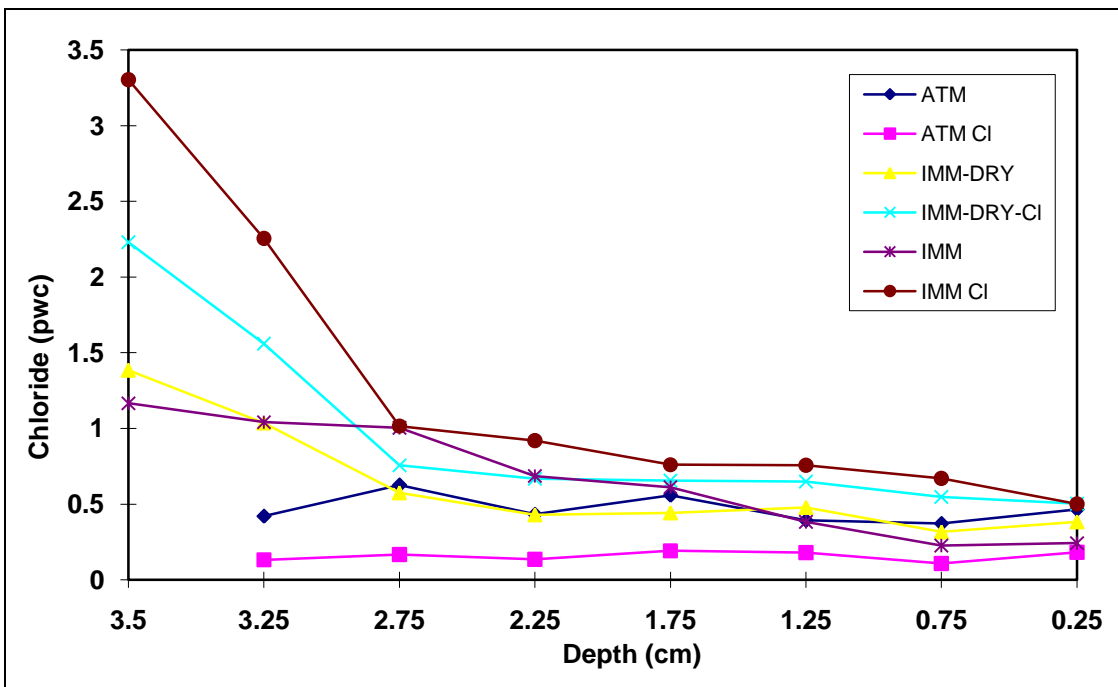**Figure 2.** Cylinders w/c = 0.46 after 90 days of exposure.

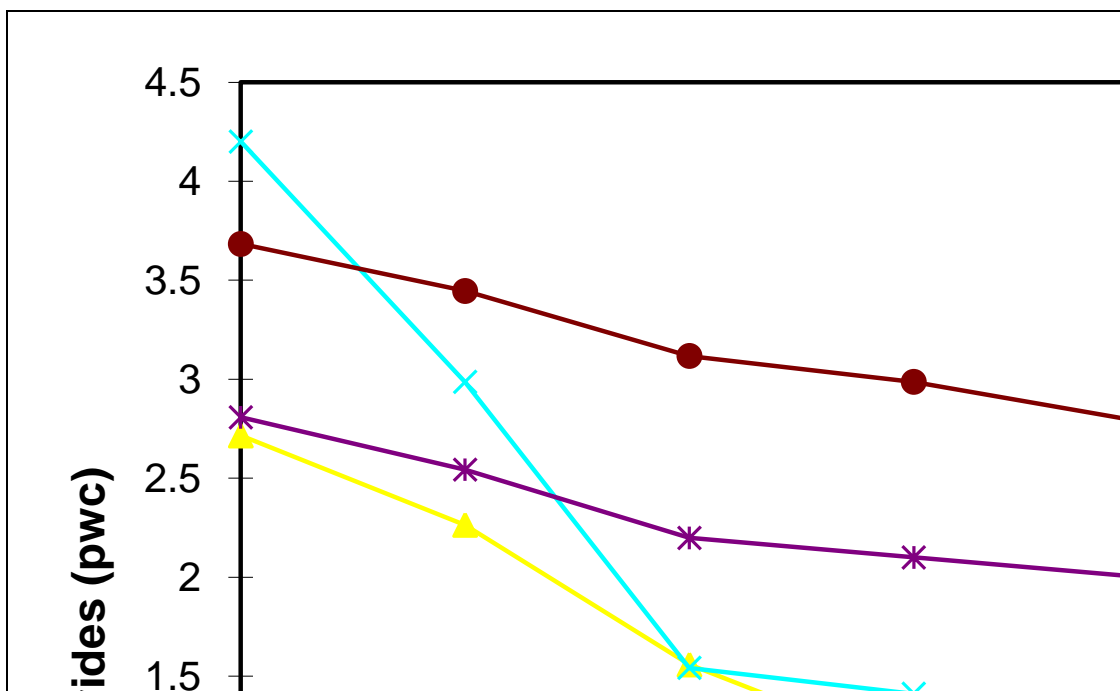**Figure 3**. Cylinders a/c = 0.6 after 90 days of exposure.

Figure 4. Cylinders wc = 0.46 after 365 of exposure.

The profiles of samples in both ratios show more clearly the influence of exposure conditions and the w/c ratio on the process of penetration of chloride ions after 365 days. The diffusive profile is repeated in the samples immersed permanently, regardless of the addition of chlorides in the mixing water. In the specimens exposed to drying-immersion cycles, the concentrations are closer to those at

permanent immersion only at 0.25 cm from the surface. At greater depths the concentration of chloride decreases, establishing that alternating cycles of immersion and drying affect the diffusive process and thus the entry of the chloride ion.
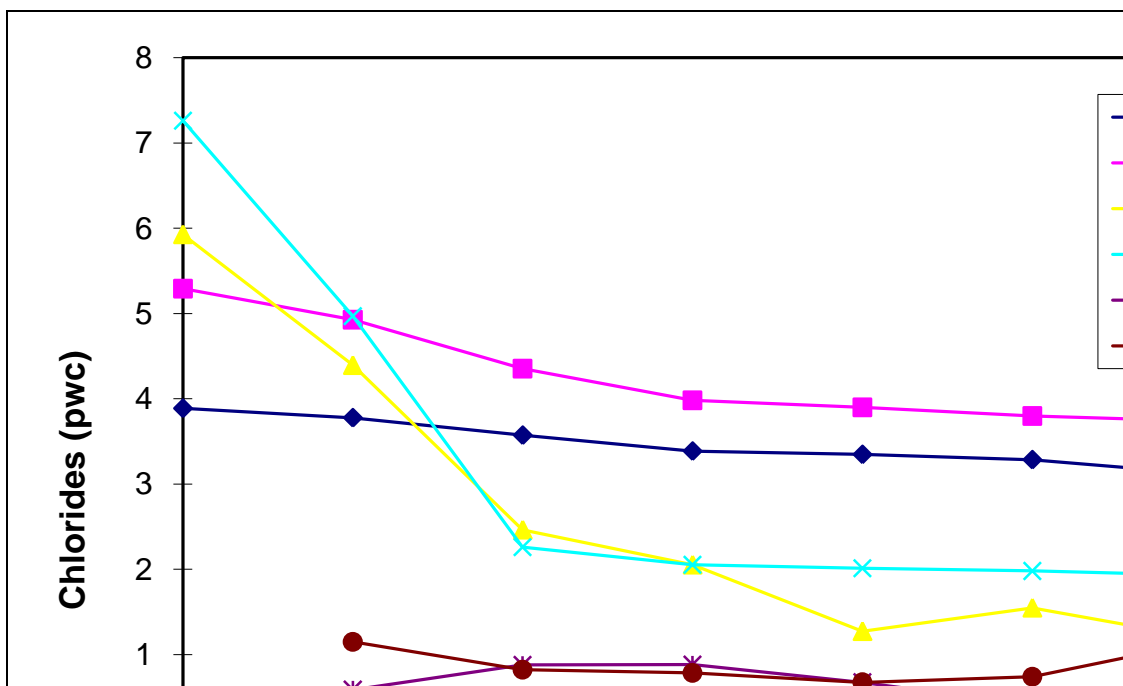

Figure 5. Cylinders w/c = 0.60 after 365 days of exposure.

Table 3 shows the values of surface concentration (Sc) and the apparent diffusion coefficients (D) obtained with a mathematical model for the conditions of permanent immersion and immersion drying-cycles. The specimens exposed to the atmosphere were discarded due to its horizontal behavior (not diffusive).

Table 3. Values obtained with the adjustment to the Fick's Law with respect to the experimental values available after 90 and 365 days.

Exposure Condition	Ratio a/c	Sc (Cl^- (%wc))		D (cm^2s^{-1}) E-8	
		90 days	365 days	90 days	365 days
Immersed	0.46	1.12	2.46	4.69	12.30
Immersed	0.46 Cl^-	1.06	3.44	3.57	11.16
Immersed	0.60	1.23	3.84	13.97	13.24
Immersed	0.60 Cl^-	1.22	4.24	22.52	20.00
Imm-dry	0.46	0.50	1.80	9.14	5.60
Imm-dry	0.46 Cl^-	0.49	1.80	19.39	7.36
Imm-dry	0.60	0.62	3.06	29.09	5.19
Imm-dry	0.60 Cl^-	0.85	2.34	28.14	12.46

The diffusion coefficient is higher for specimens with 0.60 w/c ratio than for the 0.46 w/c, which was expected as a consequence of their higher porosity that facilitates the entry of the chloride ion.

After 365 days of exposure, the values of the diffusion coefficient (D) tend to be higher in the specimens that are immersed they remain in the order of 10^{-8} cm^2s^{-1}. D values of immersion-drying cycles decrease, also being within an order of magnitude of 10^{-8} cm^2s^{-1}[3, 21, 22]. Table 4 shows the values of surface concentrations (Sc) and calculated diffusion coefficients after 259 and 336 days. Taking D for 259 days, was calculated the critical time to achieve a 0.4% weight of cement concentration. Also were calculated the concentration of chloride ions at the depth of the embedded steel rod for 259 and 336 days.

Table 4. Values calculated after 259 and 336 days taking into account that the surface concentration and the diffusive coefficient vary over time.

Exposure Condition	Ratio a/c	Cs $_{Cl^-}$ (%wc)		D (cm^2s^{-1}) E-8		Critical period of time (days)	C $_{Cl^-}$ (%wc)	
		259 days	336 days	259 days	336 days		259 days	336 days
immersed	0.46	2.23	2.42	9.37	11.50	191	0.99	1.66
immersed	0.46 Cl^-	2.53	3.19	8.23	10.36	172	1.10	2.10
Immersed	0.60	3.01	3.63	20.97	20.27	109	1.94	2.76
Immersed	0.60 Cl^-	3.10	3.92	13.52	13.32	50	2.63	3.57
imm-dry	0.46	1.31	1.67	6.96	5.97	253	0.42	0.60
imm-dry	0.46 Cl^-	1.33	1.65	12.00	8.63	100	0.88	1.01
imm-dry	0.60	2.16	2.79	14.40	7.71	84	1.48	1.37
imm-dry	0.60 Cl^-	1.78	2.19	18.50	14.11	49	1.46	1.77

It is noticeable that the value 0.4% weigh of cement chloride is exceeded in periods of time less than 259 days, when it manifests depassivation of steel in the series with the most aggressive conditions as observed in the diagrams of electrochemical impedance spectroscopy. This indicates that the concentration reported to be critical is not enough to start the process of corrosion in all cases.

Column labeled as critical period of time shows the time required to get the 0.4% weight cement chloride.

With the approximation of a mathematical model, the starting concentration is 2.63% weigh of cement of Cl-, which is in the range reported by other authors under similar exposure conditions[6,23].

The analysis shows that the corrosion onset process of steel rods embedded in concrete is complex and depends on several variables, not only on the concentration of chloride in steel-concrete interface.

4. CONCLUSIONS

Electrochemical Impedance Spectroscopy technique was an useful tool in order to monitoring the performance of embedded steel reinforced concrete specimens under experimental conditions. It allowed the determination of the critical steps on rebar corrosion condition: passive, passive-active transition and active. Those conditions depend strongly on chloride concentration.

The exposure medium is crucial in the penetration of chloride ions in concrete structures. Significant differences were seen in the profiles of samples under permanent immersion with respect to those under alternating immersion-drying cycles due to the thickness of the edges of drying cylinders, which modifies the permanent inflow of chloride ions and therefore the concentrations at different depths.

In this order, atmospheric penetration of chloride ion is not a key factor in onset corrosion mechanisms under the particular atmospheric condition of Campeche City, such as was observed during immersion/dry cycles, being diffusion coefficient higher in those samples under immersion conditions.

The onset of corrosion is determined by the conditions of manufacture and exposure. Mathematical model used in this study confirming that penetration pattern mechanisms of chloride ion are consequence of both factors. The critical concentration of chloride ions is decisive for the depassivation of the rod, and its value is not fixed. It also modified the critical time to reach a depassivation stage.

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