Influence of the Marine Environment on Reinforced Concrete Degradation Depending on Exposure Conditions

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Chloride ion, present in marine breeze and seawater is considered the main external agent to damage reinforced concrete in marine environments. It affects the passivity of steel film and provokes the initiation of corrosion. This study analyzes the changes in concrete contour and interface steel-concrete on samples exposed to continuous immersed seawater, alternated wet in seawater/dry at atmosphere and continuous weathering at atmosphere. The next elements: chloride, calcium, iron, oxygen and magnesium were determine by using SEM/EDX analysis. Immersed concrete specimens show high amount of chloride at the steel-concrete interface, followed by those exposes to alternated wet-dry cycles, while atmospheric samples practically do not present this ion. Similar sequence of chloride concentration was obtained for the contour of specimens. The noticeable presence of high quantity of magnesium at contour evidence the formation of particular compounds such as brucite and dolomite in those samples exposed to total immersion and alternated wet-dry alternated cycles. Monitoring of electrochemical impedance spectroscopy, shows passivity for steel embedded bars for concrete samples exposed to atmosphere, activity to immersed specimens and transition passive-active for wet-dry cycles. The effect of the exposure conditions on concrete degradation in marine environment is presented.

Keywords: Concrete, degradation, marine environment, SEM, DRX.

1. INTRODUCTION

Concrete is a very important construction material. It is highly resistant to compression forces, but week under traction forces. To improve its properties, it is combined with steel bars, highly resistant to traction. Concrete offers corrosion protection to carbon steel. It acts like a physical barrier
that partially isolates steel surface from the external environment and establishes an alkaline pH that facilitates steel passivity.

Durability of a reinforced concrete structure depends on the environment in which it is exposed, as also on the time and properties of concrete. Permeability is an important property in determining sensibility of concrete to external factors. For high durability, concrete should have low permeability that is strongly linked to porosity of the concrete paste. The extent of the damage depends on concrete quality [1].

Inner causes of damage are chemical reactions occurring inside concrete, volume changes caused by differences in physical and chemical properties of aggregates and cement paste and particularly to its water permeability [2].

Damas on concrete induced for environment are due to the migration across the net of pores in concrete, of aggressive agents as chloride (Cl\textsuperscript{-}), sulfate (SO\textsubscript{4}\textsuperscript{2-}) and others ions, as well as oxygen (O\textsubscript{2}) and carbon dioxide (CO\textsubscript{2}) dissolved in pore solution. When these deleterious substances reach critical concentrations at the surface of steel reinforced, the corrosion process starts. Nevertheless, during the migration of harmful substances into the pore net of concrete, many reactions may be carried out, which delay the process and the arriving of these substances as far as the concrete-reinforced interface.

At marine exposure, it is common the formation of a layer of aragonite and brucite on the concrete surface which reduces the chloride penetration.

This effect is particularly relevant in the submersed and tidal zone where the concrete is in contact with sea water. The formation of this protective layer and its effect on the reduction of concrete permeability has been reported by others researchers [3-6]. Freidel’s salts have been reported as product of aluminates reaction with chlorides [7].

This decreases the chloride concentration in the pore [8]. Limestone aggregates containing dolomite may produce an alkali-carbonate reaction which induce the brucite (Mg(OH)\textsubscript{2}) formation and alkali regeneration. When it is exposed to humidity increase their volume, inducing traction internal stresses and consequently generates fissures, which affects the migration of substances inside of the concrete [9].

Many authors have reported elemental composition and phase identification of corrosion products at interface concrete-rebar[10], such as Iron oxyhydroxides (FeOOH) which vary in chemical compositions and present different morphologies, according to which they can be categorized as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), or akaganeite (Fe\textsuperscript{3+}(O,OH,Cl)) [11]. Also, elemental analysis have been reported for concrete-reinforced interface and relate it with electrochemical essays to estimate the corrosion condition [12,13].

This study presents the analysis of contours of test cylinders by using scanning electron microscopy (SEM) coupled to elemental analysis (EDS) and X-Ray Diffraction (XRD). Effect of exposure type is observed on the concrete paste near to the contour. Also SEM and EDS analysis was carried out to steel-concrete interface.

Electrochemical tests show good relation with element distribution, relative to the corrosion condition of reinforced steel.
2. EXPERIMENTAL PART

2.1. Sample preparation and exposition

A set of cylindrical concrete samples sizing 7.5 cm diameter and 15 cm height were prepared using ordinary Portland cement type I (OPC-I), sand and river coarse aggregates (maximum size 1.25 cm). Water/cement (w/c) ratio was 0.46. Samples were cured during 28 days in saturated water with Ca(OH)$_2$. Design of the concrete mix is presented on Table 1. Four samples were used for each exposure conditions. One reinforced bar was embedded in every sample.

Table 1. Mix concrete dosage.

<table>
<thead>
<tr>
<th>Cement (kg/m$^3$)</th>
<th>Sand (kg/m$^3$)</th>
<th>Gravel (kg/m$^3$)</th>
<th>Water (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>443</td>
<td>805.98</td>
<td>887.95</td>
<td>204.81</td>
</tr>
</tbody>
</table>

Samples were exposed to three different types of environments:

a) Natural atmospheric exposure (ATM) in coastal environment. Samples placed at the test station existing at Corrosion Research Center (CRC), at San Francisco de Campeche City, located at about 200 m from the shoreline. Cylinders were located with no shelter in vertical position over the ceiling of CRC about 4 m height. Samples were under the effects of natural weathering agents: rain, dew, wind, marine aerosol, gaseous pollutants and so on.

b) Permanent immersion in sea water (IMM). Sea water was collected every week in a site located at 500 m from at San Francisco de Campeche harbor. Samples were submitted to natural sea water under static conditions in cylindrical recipients of 20 liters capacity. No significant changes in temperature should occur. Sea water was considered stable up to one week of test. Also, the influence of biological agents was considered negligible.

c) Alternating cycles (ALT). Were developed in two stages. The first 2 years (730 days) were exposed to immersion during the nights and atmosphere at the day. The second stage consisted of 3 days of immersion in sea water and 4 days outdoors. It was a combination between conditions recently described for ATM (four days) and IMM (3 days).

2.2. Carbonation test.

Carbonation depth was determined using an acid-base indicator [14]. From each set of samples, one was selected for carbonation test. The sample was cut in axial direction to the bar using an electric emery machine. This cut was used as a guide for the application of pressure and fracture the sample in two pieces (see Figure 1). The reinforced bar remain in one of the two pieces obtained. The part having no reinforced bar was selected to determine the carbonation front. Acid base indicator was applied by spray on the surface. After application, the long of the uncolored zone was measured by using a ruler.
2.3. Scanning electron microscopy (SEM).

After exposure, one of the samples (from each set) was selected for observation in Scanning Electron Microscope (SEM). The sample was cut into slices 2 cm thickness. Then, the transverse surface section was polished with emery paper beginning on number 200 up to 1200. A scanning electron microscope JEOL model JSM-5600-LV was used. Two parts of the surface were studied: environment-concrete interface and concrete-steel bar interface. Calcium (Ca), chloride (Cl), Iron (Fe), magnesium (Mg) and oxygen (O) were mapped.

![Figure 1. Carbonation test. a) Cut of cylinder. b) Acid-base indicator application.](image)

2.4. X-Ray Diffraction (XRD).

Concrete powder was extracted by using a chisel from 2, 4 and 6 mm depth from the specimen surface. The samples obtained were grinded and sieved up to 200 mesh. Samples were kept under dry conditions until XRD analysis was carried out. A portion of each sample (0.1 g) was introduced in a Bragg-Brentano Geometry X-ray diffractometer (Siemens D5000). The equipment operated with a CuKα radiation (λ = 1.5416 Å °), with a step size of 0.01° (2θ) every 5 seconds.

2.5. Electrochemical measurements.

Potentiostat/galvanostat PARC-273A and Solartron Frequency Response Analyzer (FRA) model 1250 from Schulemberger, were used for electrochemical measurements. Half cell potential (Ecorr) was measured always before starting EIS measurement according to ASTM-C 876-91[15] standard, using a calomel electrode as reference electrode. Electrochemical Impedance Spectroscopy (EIS) were measured in an interval sweep from 100 kHz to 1.5 mHz, with 5 measures by each decade.
A 316-L stainless steel foil was used as counter electrode. A wet sponge was placed between concrete sample and the electrodes.

3. RESULTS AND DISCUSSION

Carbonation - After a period of 44 months of exposure, changes in pH in all the analyzed samples (ATM, IMM and ALT) were determined using an acid-base indicator, where only was observed at two millimeters depth from the external surface. It indicates that, at this exposure time, concrete degradation caused by CO₂ is very low, almost negligible.

3.1. SEM/EDS Analysis.

3.1.1. Concrete border surface.

Figure 2 shows the images of concrete samples exposed to each test media during the study. On the other hand, a comparative mapping about the elemental distribution in concrete samples is presented in Figures 3 (Ca), 4 (O), 5 (Cl), and 6 (Mg).

![Figure 2](image1.png)

**Figure 2.** Concrete samples borders. a) ATM (130x), b) ALT (250x), c) IMM (1500x).

![Figure 3](image2.png)

**Figure 3.** (Ca). Calcium distribution at the borders. a) ATM (130x), b) ALT (250x), c) IMM (1500x).
Ca (Figure 3) is distributed on concrete paste on the surface of the samples exposed in the three different conditions. Dark zones should correspond to fragments of aggregates, mainly composed by Si. Oxygen distribution (Figure 4) should be mainly due to the presence of Ca(OH)$_2$, silicates and other hydrated compounds in the concrete paste.

The presence of Cl (Figure 5) is not observed on the surface of samples exposed in atmospheric conditions (ATM). Since these samples were exposed to natural weathering, perhaps chloride ions were dissolved and washed by rain. Also, chloride ions could have migrated inside the concrete
through the porous structure, because the test zone is submitted to wet-dry cycles. It should be also considered that chloride deposition rate is not high in Campeche, so the amount of deposited Cl could be low [16], ALT and IMM samples show the presence of Cl at the entire surface. In these cases, they were immersed in sea water, so the presence of Cl is warranted.

Mg is present in the three types of exposure conditions, Figure 6. This element is a constituent of cement as MgO. Also it is present in sea water and sea aerosol. Maximum content of Mg allowed for Portland cement according to[17] is 6%. It is reported an expansive effect of Mg[18]. Under atmospheric exposure (ATM), only scattered points of Mg are observed in the surface, whose probably source is the cement. Under ALT and IMM conditions, higher accumulation of Mg was observed. This accumulation is attributed to the calcareous layer formed in the concrete surface known as “skin” [4] as a consequence of the exposure to sea water. This layer acts as a barrier and plays an important role since slows down the migration of chloride ions inside the sample. Its effect should be considered for the surface concentration calculation and modeling of chloride ion diffusion.

3.1.2. Concrete-steel reinforced bar interface.

![Figure 7. Concrete-steel interface. a) ATM (130x), b) ALT (110x), c) IMM (130x).](image)

![Figure 8. (Ca). Calcium distribution at concrete-steel interface. a) ATM (130x), b) ALT (110x), c) IMM (130x).](image)
Concrete-steel reinforced interface image is presented in Figure 7. Comparative mapping of the surface elements distribution at the interface concrete-steel reinforced in samples exposed under three different exposure conditions is presented on Figures 8 (Ca), 9 (O), 10 (Cl), and 11 (Fe).

**Figure 9.** (O). Oxygen distribution at concrete-steel interface. a) ATM (130x), b) ALT (110x), c) IMM (130x).

**Figure 10.** (Cl). Chlorine distribution at concrete-steel interface. a) ATM (130x), b) ALT (110x), c) IMM (130x).

**Figure 11** (Fe). Iron distribution at concrete-steel interface. a) ATM (130x), b) ALT (110x), c) IMM (130x).
According Figure 8, Ca distribution seems to be similar to that observed at the borders of the concrete paste. Ca(OH)$_2$ produces an alkaline pH that induce passive conditions allowing the protection of steel rebar against corrosion. Oxygen is an element included in the composition of cement, aggregates, and corrosion products of steel. A lower distribution of oxygen is present on steel bar surface of ATM samples (Figure 9). It could indicate the absence of corrosion products in this surface; however, oxygen is observed in the surface of steel in samples submitted to immersion (IMM) and humid/dry cycles (ALT). It indicates the presence of corrosion products on these surfaces and, consequently, corrosion of the steel bar. The corrosion over the iron surface could probably be caused by contamination during the polishing process.

Figure 10 shows the distribution of Cl in the interface concrete-reinforced bar. It is important to highlight that Cl is not detected in the sample corresponding to atmospheric exposure. Respecting samples exposed under ALT and IMM conditions, it was observed the presence of Cl in the interface concrete-rebar. The presence of Cl over the rebar surface could be due to contamination during polishing process.

Samples exposed under ALT and IMM conditions shown presence of iron at the concrete-steel interface (Figure 11). It was not the case of the ATM samples. In the case of IMM conditions, a diffuse and disperse iron layer was detected closer to the interface; perhaps it indicates that corrosion products are migrating towards the concrete external surface (indicated by arrow).

3.2. X-Ray Diffraction

![Figure 12. DRX diffractograms corresponding to samples exposed to ATM conditions.](image-url)
Figure 13. DRX diffractograms corresponding to samples exposed to ALT conditions.

Figure 14. DRX diffractograms corresponding to samples exposed to IMM conditions.
Figures 12-14 shows the XRD diffractograms obtained from powder of concrete samples obtained at 2, 4 and 6 mm depth. A comparative analysis of their mineral phases is presented on this...
section. Ratios were obtained based on the measurement of the main peak from the net area of principal reflection in arbitrary units, (A. U.).

**Figure 17.** Aragonite content at the contours of concrete samples.

**Figure 18.** Dolomite content at the contours of concrete samples.
Figure 19. Brucite content at the contours of concrete samples.

Quartz - The profile of SiO$_2$ content in the samples was determined considering three penetration depths for each exposure conditions. Its concentration is presented at Figure 15. The three types of samples showed a similar behavior. The external layer (2 mm) shows lower quartz content, indicating that quartz content decreases due to the influence of the external environment. The sample corresponding to atmospheric exposure (ATM) shows the higher quartz content, followed by the sample ALT and finally the lower content corresponds to IMM sample. Quartz is one of the main components of concrete and is responsible of mechanical resistance. If the environment aggressiveness increases, a higher loss of quartz could occur in the surface.

Calcite - The higher calcite content was determined in the concrete external layer under atmospheric exposure. Calcite is considered a reaction product between hydrated cement components and CO$_2$. The reaction with CO$_2$ is facilitated in the external layer. Calcite content increases when penetration depth decreases.

Aragonite - Aragonite was observed at the external layer of ALT and IMM samples, but in opposite tendency to calcite. The higher content is reported for IMM samples. It is reported that aragonite is stable in seawater[11]. Transformation of aragonite into calcite is possible in an aqueous environment. Calcite is more stable on ATM samples, while in presence of sea water, the probability of calcite transformation into aragonite increases.

Dolomite - This phase should be present in the samples since the cylinder fabrication. The higher content is reported for ALT samples. In this case, the drying process could contribute to stabilize the presence of dolomite.

Brucite - It is reported that in an alkaline solution, Mg(OH)$_2$ is more stable than MgO. Aragonite and brucite precipitate when the solution is saturated in calcium carbonate and magnesium hydroxide.
The samples submitted to complete immersion (IMM) and in lower proportion ALT could suffer the influence of magnesium chloride and magnesium sulfate presents in sea water according to the following chemicals reactions [19, 20]:

\[
\text{MgCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + \text{Mg(OH)}_2
\]

\[
3\text{MgSO}_4 + 3\text{CaO.2SiO}_2\cdot\text{H}_2\text{O} + 9\text{H}_2\text{O} \rightarrow 3(\text{CaSO}_4\cdot2\text{H}_2\text{O}) + 3\text{Mg(OH)}_2 + 6\text{SiO}_2\cdot\text{H}_2\text{O}
\]

These reactions produce gypsum and magnesium hydroxide, both dangerous compounds for concrete. The diminution of quartz content is higher in more aggressive conditions (IMM) followed by ALT and ATM. It is evident that the influence of sea water decreases quartz content in the external surface of concrete.

Corrosion of rebar - Corrosion of rebar was determined by measuring corrosion potential and application of EIS.

Half cell potential (Ecorr).- Changes in Ecorr of steel rebar on samples exposed at the three different exposure conditions vs exposure time is presented on Figure 20. Ecorr of steel rebar corresponding to ATM samples lie always in the passive zone according to [15]. It means that no corrosion process was not detected in these samples. On samples exposed under ALT conditions, the probability of corrosion of rebar is higher because corrosion potential shows more negative values in comparison to ATM samples. It is important to note that from the exposure of 1238 day, the corrosion potential reach values indicating high corrosion probability. For IMM samples, corrosion potential values oscillate in the zone of high corrosion probability. According to these results we can have information about corrosion probability, but not related to the corrosion intensity.

![Figure 20. Half cell potential vs time.](image-url)
The order of corrosion probability, according to corrosion potential measurement was IMM>ALT>ATM.

*EIS analysis* - Corrosion of steel rebar.

Nyquist diagrams of EIS show clear differences respect to condition of steel rebar, Figure 21. At ATM exposed samples, capacitive response was predominant over the resistive, an arc with high resistance value is evidence of passive rebar as can be observed at Figure 21a. ALT exposure (Figure 21b) show changes in the capacitive arc behavior from high resistance with a tendency to less resistance than 500,000 Ωcm². This represents a transition active-passive at concrete-steel interphase and consequently an increase of corrosion rate. The importance of these changes is the evidence of the starting of corrosion process. Figure 21c shows arcs with a less magnitude order in resistance, undoubtedly is signal of an active interphase concrete-rebar [21-24].
Figure 21. EIS diagrams vs time.

Figure 22. icorr vs time.

Experimental results of EIS were adjusted by using a commercial software, to obtain value of $R_{tc}$. Corrosion current ($I_{corr}$) was calculated based on charge transfer resistance (considered equivalent to polarization resistance ($R_p$)) using the following Stern-Geary equation:

$$I_{corr} = \frac{B}{R_p}$$

Where:

$B = \text{constant} = 0.052 \text{ V (for passive conditions)}$ for ATM samples and $= 0.026 \text{ V (active conditions)}$ for ALT and IMM samples.
The behavior of corrosion current vs time for samples exposed at different exposure conditions is presented on Figure 22. Values corresponding to ATM samples are lower than 0.1 µA/cm² (passive conditions). In the case of ALT samples, corrosion current values are also low, but sometimes are over 0.1 µA/cm² (active-passive conditions). Data corresponding to IMM samples are higher (active zone), showing a higher corrosion in this exposure conditions. Similar tendency with the ones results of corrosion potential was obtained. The order of corrosion current corresponds with the corrosion probability. Half cell potential (Ecorr) vs corrosion current (icorr) determined by EIS is presented on Figure 23. The points corresponding to ATM samples lie in a zone of low corrosion current and passive conditions, but points corresponding to ALT samples are located in a zone that corresponds to the corrosion probability, but in general has a low corrosion current (active-passive conditions). Points for IMM samples show the most negative values of Ecorr and higher values of corrosion rate. The results show that the most aggressive conditions correspond to IMM samples, followed by ALT samples. No significant corrosion of rebar is detected for ATM samples.

![Figure 23. Ecorr vs icorr distribution.](image-url)

Electrochemical results obtained are in accordance with the chloride distribution at interphase concrete-steel reinforced. ATM has the lower chloride concentration (almost insignificant), by this reason the reinforced steel remains passive, as indicate by the values of Ecorr and icorr. Chloride is higher for ALT samples than ATM, however by its exposure condition, when were located to atmosphere the chloride migrates inside the sample and the corrosion process diminishes. Since the samples were continuously immersed in IMM, the chloride ions migration was faster than of ATM and
ALT and therefore they show the highest chloride quantity. As a consequence, the activation of steel reinforced started faster than ATM and ALT and its corrosion rate is higher.

This study shows the relation of exposure condition with deterioration of concrete paste and corrosion of embedded steel reinforced.

### 4. CONCLUSIONS

After 44 months of testing, concrete degradation occurred in the external surface of the samples. The most aggressive conditions correspond to IMM exposure, followed by ALT and ATM. It means that porosity and other properties of the samples together with environmental influence do not allow to CO$_2$ and other possible gaseous contaminants to reach deeper sites in the concrete volume.

The influence of atmospheric CO$_2$ is higher in ATM samples, followed by ALT and IMM. No significant influence of chlorides in corrosion or degradation is determined in ATM samples.

Changes in concrete phases are determined mainly in the external layer due to the influence of atmosphere and sea water. The influence of CO$_2$ increases calcite content while the influence of sea water favors transformation of calcite into aragonite.

The results of natural tests carried out on ATM samples show no significant corrosion or degradation of concrete of these samples in Campeche coastal site.

Electrochemical EIS tests define clearly the corrosion status of steel reinforced embedded in concrete.

Related to the corrosion of rebar, the same order in environmental aggressivity for the three types of exposure conditions is obtained: IMM>ALT>ATM. No external signs of corrosion are observed after 44 months of exposure.

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