CORROSIVIDAD DE LA ATMÓSFERA CON RESPECTO A LA BARRA DEREFUERZO DEL CONCRETO EN ZONAS COSTERAS. RESULTADOS DE DOS AÑOS DE EXPOSICIÓN

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RESUMEN

Se determinó la deposición atmosférica de cloruros y la penetración en concreto durante un año de exposición en siete estaciones cubanas y dos de la Península de Yucatán. Se utilizaron probetas de relaciones a/c 0,4, 0,5 y 0,6 en la Habana y 0,46 y 0,6 en Yucatán. Se proponen dos niveles fundamentales de corrosividad atmosférica de las barras de refuerzo: Muy alta para áreas a menos de un kilómetro de la costa (alrededor de 600 m) y Moderada para áreas más alejadas. Los resultados de dos años de exposición muestran que las probetas con relación a/c= 0,4 aún no presentan valores significativos de la corriente de corrosión; sin embargo, las probetas de relaciones a/c=0,5 y 0,6 ya presentan valores apreciables de la corriente de corrosión a distancias de la costa inferiores a 615 m. Los resultados coinciden con los pronósticos hechos durante el primer año de exposición.

ABSTRACT

Chloride atmospheric deposition and penetration into concrete were determined during one year of exposure in seven cuban stations and two of Yucatán Peninsula. w/c ratios of 0,4, 0,5 and 0,6 were used in Havana and 0,46 and 0,6 in Yucatán. Two main levels of atmospheric corrosivity of the reinforced bar are proposed: Very high for sites located at less than one km of the shoreline (about 600 m) and moderate for more distant sites. After two years of exposure, samples having w/c =0,4 does not show significant values of corrosion current, but samples having w/c 0,5 and 0,6 already show appreciable values of corrosion current at distances to the shoreline lower than 615 m. The results are in agreement with the prediction made after one year of exposure.

Key words: corrosividad, corrosión atmosférica, durabilidad, barras de refuerzo.
INTRODUCTION

Atmospheric corrosivity for metals reaches ranges from C3 to >C5 according to ISO 9223 standard \[^{1,2}\] in tropical coastal atmospheres. The influence of atmospheric parameters, Chloride deposition and other contaminants on metals in tropical climate have been extensively studied; however, in the case of reinforced concrete, atmospheric Chloride deposition is not directly related to corrosion of rebar because the rate of Chloride penetration into the concrete cover to reach the rebar surface depends on the concrete properties, particularly capillarity and porosity. The development of the pore structure of hydrating portland cement systems is fundamental to the behavior of concrete exposed to a variety of aggressive environments. It influences mass transport of ions into the material and their interaction with concrete constituents as well as the diffusion characteristics of concrete.

Atmospheric corrosion aggressivity for metals is established based in Weight Loss or environmental parameters\[^{2}\]. Respecting reinforced bar, localized corrosion (usually called as pitting corrosion) is the predominant type.

Concrete cover properties changes in a relatively wide range and they are very important for determining Chloride penetration, that is why it is a difficult task to establish a relative prediction of reinforced concrete durability in coastal and marine zones based on atmospheric salinity deposition.

Significant corrosion of rebar starts when Chloride threshold is reached and after this moment, corrosion damage of the structure very fast increases\[^{3}\]. Under this conception, the most important parameter to be determined respecting the influence of the environment in coastal and marine sites is the necessary time to reach the Critical Chloride content or Chloride Threshold. This time does not only depends on the Chloride Deposition in the atmosphere and other atmospheric parameters, but also on the properties of concrete, particularly capillarity, cover thickness and so on. It is the time in which corrosion initiates. After this time, corrosion propagates and its rate is relatively fast, depending on the environment and the properties of concrete cover.

Corrosion current could be an index about the influence of Chloride content in concrete corrosion but it should be applied considering the type of corrosion, because when generalized corrosion occurs, corrosion attack occurs in almost all the metallic surface, but when localized corrosion occurs there are areas of the metallic surface where corrosion attack is localized while other areas remain without significant corrosion. Usually, corrosion intensity is divided by geometrical surface value and corrosion current density is calculated. It is correct for uniform and generalized corrosion, but when localized corrosion occurs, corrosion intensity divided by geometrical surface does not represent an average value of corrosion rate.

Bastidas-Arteaga et al\[^{4}\] described the influence of the distance from the sea on the probability of corrosion initiation using a stochastic model. It was noted that for all locations, the probability of corrosion initiation is higher for the tropical environment.

To study the influence of atmospheric environment on different types of concrete was the main objective of the CYTED project DURACON, developed between 11 iberoamerican countries\[^{5}\]. The first results obtained showed that in marine atmospheres, Chloride content in the environment should be considered a decisive factor when evaluating the probability of reinforcement corrosion.

A decreasing tendency for the total amount of chlorides that penetrate into concrete structures built in coastal atmospheres as function of distance to the shoreline have been observed under natural exposures\[^{6}\].
A relative small atmospheric Chloride deposition is determined using the wet candle method in the coastal zone, where maxima oscillated around 60 mg/m²d; however, for Brasil, Meira reports that chloride deposition rate on the wet candle can be used as an environmental indicator, helping to preview the expectancy of service life of concrete structures or suggesting minimum concrete cover thicknesses for a required service life.

EXPERIMENTAL PROCEDURE

Two sets of experiments have been performed. Seven exposure sites were selected in Havana City, Cuba, at different distances to the north seashore. The city of Havana is located in the north seashore in the west side of the Island. In the present paper, results of two years of exposure are reported. The other experiment was carried out in the Yucatan Peninsula, Mexico. Two exposure sites were selected close to the Mexican Gulf shoreline. This experiment was performed only during one year of exposure. Concrete samples were prepared using aggregates of the surrounding region. It causes that concrete samples properties for Havana and Yucatan are significantly different.

Exposure sites in Havana. Seven exposure sites were selected in the city of Havana, at different distances to the shoreline (see Table I). According to the location of the sites, an extreme corrosivity (>C5) should be expected at Arandia site because it is located at less than 250 m of the Cuban north shoreline, followed by MINVEC and CEADEN in a lower level of corrosivity.

Exposure sites in Yucatan Peninsula. Two exposure sites were selected at Yucatan Peninsula: Puerto Progreso, located at Yucatan State, very close to the shoreline, and Campeche PCGM, located at Campeche State and also close to the shoreline, but under conditions of lower airborne salinity due to the wind pattern distribution.

Concrete Samples. Samples exposed in Havana sites. Nine samples of concrete and six of reinforced concrete were prepared for every Havana atmospheric exposure site. Dimension of the samples is 20 cm x 20 cm x 10 cm. Three w/c ratios were used: 0.4, 0.5 and 0.6. Three samples of concrete and two of reinforced concrete correspond to each w/c ratio.

Four reinforced bars were placed into every reinforced concrete sample, two reinforcement bar at 2 cm cover and two corresponding to 4 cm cover. Distance between reinforcement bars is 1 cm. The diameter of the reinforcement bars used was 12 mm. Previous introduction of the bars in concrete, chemical cleaning was carried out, in order to avoid any possible corrosion product in the surface and keep the surface in similar conditions.

Aggregates combination used was the following: cement-365 kg, sand-750 kg, gravel-1030 kg, water-depending on the w/c ratio to obtain, plasticizer admixture (water reducing)-depending on the w/c ratio to obtain. Slump, water volume and admixture per cent used in samples preparation, according to w/c ratio were measured. Slump was determined using the Abrams cone method. All samples were cured during 28 days of immersion in water.

Another group of samples was prepared to determine concrete physico-chemical properties, such as compression resistance, density, ultrasonic pulse rate, capillary absorption coefficient and effective porosity. Compression resistance was determined using a 2000 kN testing machine. Samples prepared for this test were of cylindrical shape (height = 30 cm and diameter = 15 cm) and cured for 28 days. Three values were determined for each w/c ratio. Capillarity absorption coefficient and effective porosity were determined based on the methodology established by Goran Fagerlund and according to Cuban standard.
Table 1. Characteristics of exposure sites in Havana City

<table>
<thead>
<tr>
<th>Site</th>
<th>Distance to the north sea shore (m)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arandia</td>
<td>10</td>
<td>Located very close to the shoreline, on a roof. Significant influence of airborne salinity. Coastal site.</td>
</tr>
<tr>
<td>MINVEC</td>
<td>360</td>
<td>On the roof of a parking area of a 12th floor building located in front to the shoreline. The parking area is located in the back of the building. The direct influence of airborne salinity on the samples is very difficult. Urban coastal site</td>
</tr>
<tr>
<td>CEADEN</td>
<td>615</td>
<td>Located on a roof very close to a main road in Havana. A group of trees is located previous to the roof, in such a way that the influence of airborne salinity could be diminished. Urban site relatively close to the shoreline.</td>
</tr>
<tr>
<td>Casa Blanca</td>
<td>1500</td>
<td>On the floor, at about 200 m of the inside shore of Havana Bay. Urban-coastal site.</td>
</tr>
<tr>
<td>GECEN</td>
<td>1600</td>
<td>On the floor, near to a small group of trees. Urban site</td>
</tr>
<tr>
<td>MINAL</td>
<td>2678</td>
<td>On a roof, close to a main road. Urban site</td>
</tr>
<tr>
<td>TICONS</td>
<td>4500</td>
<td>On a roof, close to a main road. Relatively far from the shoreline. Urban</td>
</tr>
</tbody>
</table>
Samples exposed at Yucatan sites. The experiment was carried out previously to the one performed in Havana. Although samples were not prepared in the same manner as in Havana, we consider important to analyze the differences in order to obtain more general conclusions. Cylindrical specimens of 75 mm diameter x 150 mm length were elaborated using Portland cement (ASTM Type I) with a w/c ratio of 0.46 (considered approximately 0.5 for comparison with Cuban samples) and 0.6. One batch of samples prepared using crushing calcareous aggregates, but only w/c ratio 0.5, was exposed at Puerto Progreso, Yucatan, from August 1993 to August 1994. Samples of w/c ratio 0.5 and 0.6 were exposed at Campeche (PCGM) during February 1995 to January 1996. River stone was used as aggregates. River aggregates present a lower contact area because their surface is less roughness.

Table 2. Characteristics of exposure sites in Yucatan Peninsula.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Distance to the Mexican Gulf shoreline (m)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puerto Progreso</td>
<td>50</td>
<td>In front to the open sea. Coastal site.</td>
</tr>
<tr>
<td>Campeche PCGM</td>
<td>150</td>
<td>On a roof. Some buildings are located closer to the shoreline, but none of them should have appreciable screening effect respecting the samples. Urban site.</td>
</tr>
</tbody>
</table>

It is important to note that compression resistance of samples prepared in Havana is significantly higher than those prepared at Yucatan. At the same time, slump is significantly lower for Yucatan.
samples. Although capillarity absorption coefficient and effective porosity were not measured, a higher capillary and porosity should correspond to these samples respecting those prepared in Havana.

Atmospheric deposition rate of Chlorides. Deposition rate of atmospheric Chloride in Havana was determined using the dry plate method, consisting in the employment of a dry cotton fabric of known area exposed under a shed. This method has some differences respecting the wet candle method because in the last one, the surface is more wet and more sensible to get Chloride aerosol. The results, in general\textsuperscript{1}, are comparable, but usually data corresponding to dry plate are lower than for wet candle. Perhaps dry plate method could represent a better approximation to porous material systems.

The magnitude of Chloride deposition is extremely high at Arandia site (20 m to the shoreline). These conditions cause an extreme steel corrosion rate that is over the higher classification of ISO 9923 standard. At the other six sites, Casa Blanca site presents a C4 atmospheric corrosivity level, MINVEC and CEADEN show Chloride deposition rate classification S1 and the other three sites So. C4-C3 corrosivity level should correspond to MINVEC and CEADEN and C3 to GECEN, MINAL and TICONS, according to the magnitude of Chloride deposition and climatic data.

Sulphur compounds deposition rate. The origin of sulphur compounds deposition could be natural or product of man behavior. The higher sulphur compounds deposition rate corresponds to the exposure site located closer to the shoreline (Arandia). The main source of sulphur compounds in this case should be marine aerosol.

Chloride penetration profiles. Havana exposure sites. Chloride penetration was determined at the surface and 1 cm depth, considering that it is the region where Chloride penetration occurs due to capillary sorption that is, depending on the Capillarity coefficient of concrete. The influence of the atmospheric environment is more significant in this part of the concrete cover.

A very clear difference in Chloride penetration is observed between the three w/c ratios tested. It means that corrosion of steel reinforcement will start before in samples having higher w/c ratio and consequently, higher capillarity absorption coefficient and effective porosity. In the site where an extreme corrosion rate of carbon steel is very probable (Arandia), due to a very high atmospheric Chloride deposition rate, the higher Chloride penetration is reported, particularly for the higher w/c ratio.

It is important to note that samples exposed at Yucatan Peninsula (Campeche and Puerto Progreso) show a significant higher Chloride penetration. It is undoubtedly caused by a higher porosity and capillarity, as it is suggested by a significant lower Compression Resistance. It means that w/c ratio is not the only parameter to take into account concerning Chloride penetration facilities because in the case of Yucatan samples, slump is significantly lower and it is an index of higher porosity instead to a similar w/c ratio respecting Havana.

A multilinear regression carried out between average Chloride deposited on the surface or at 1 cm penetration versus average atmospheric deposition determined by dry plate method and water/cement ratio gave the following results:

For Chloride in the surface of concrete:

\[
\text{Cl}^-_{\text{(surface)}} = -0.034 + 0.000072 \text{Cl}^-_{\text{(dry plate)}} + 0.11 \text{ w/c}, \quad r^2 = 52.39, \quad P<0.01
\]
Cl\(^-\) (1 cm) = -0.103 + 0.00012 Cl\(^-\) (dry plate) + 0.27 w/c, \(r^2 = 55.43, P<0.01\)

An overall behaviour obtained by multilinear regression, show that w/c ratio and atmospheric Chloride deposition are two very important variables in determining Chloride deposition in the surface of concrete samples and at 1 cm of penetration, but only less than 60% changes in Chloride in the surface or at 1 cm penetration are explained by the obtained equation. The above regression equations could be used as an orientation respecting the prediction of Chloride penetration at 1 year of exposure for tropical coastal zones.

A similar dependence is obtained if instead of w/c ratio, capillarity absorption coefficient is included:

Chloride in the surface of concrete:

\[ Cl^- (surface) = -0.0052 + 0.00007 Cl^- (dry plate) + 867.3 \text{[Capillarity]}, \quad r^2 = 52.16, \quad P<0.01 \]

Penetration of Chloride at 1 cm depth:

\[ Cl^- (1 \text{ cm}) = -0.037 + 0.00012 Cl^- (dry plate) + 2276.1 \text{[Capillarity]}, \quad r^2 = 57.93, \quad P<0.01 \]

In case of effective porosity the results are the followings:

Chloride in the surface of concrete:

\[ Cl^- (surface) = -0.02 + 0.000072 Cl^- (dry plate) + 137.05 \text{[Effective Porosity]}, \quad r^2 = 52.39, \quad P<0.01 \]

Penetration of Chloride at 1 cm depth:

\[ Cl^- (1 \text{ cm}) = -0.07 + 0.00012 Cl^- (dry plate) + 334.2 \text{[Effective porosity]}, \quad r^2 = 55.43, \quad P<0.01 \]

Reinforcement steel corrosion potential. Corrosion potential (mV) of reinforcement steel embedded in concrete samples of three different w/c ratios was determined after one and two years of exposure.

An acceptable potential curve fitness of corrosion potential versus distance to the north shoreline is obtained for one and two years of exposure at a thickness cover of 2 cm, as in the case of Chloride deposition versus distance to the shoreline:

\[
\begin{align*}
\text{w/c = 0.6} & \quad \text{E = -274.6 + 31.6 d} & \quad r^2 = 0.68 & \quad \text{1 year} & \quad \text{E = -372.1 + 23.6 d} & \quad r^2 = 0.56 & \quad \text{2 year} \\
\text{w/c = 0.5} & \quad \text{E = -266.9 + 34.4 d} & \quad r^2 = 0.81 & \quad \text{1 year} & \quad \text{E = -333.7 + 16.4 d} & \quad r^2 = 0.16 & \quad \text{2 year} \\
\text{w/c = 0.4} & \quad \text{E = -208.9 + 28.79d} & \quad r^2 = 0.84 & \quad \text{1 year} & \quad \text{E = -438.1 + 39.1 d} & \quad r^2 = 0.84 & \quad \text{2 years}
\end{align*}
\]
Only fitness corresponding to w/c=0.5 and two years of exposure is not good. In the other cases acceptable fitness levels are obtained. It means that corrosion potential changes are directly link to distance to the shoreline. A similar behavior should occur for corrosion rate of rebars. Corrosion probability calculated according to ASTM 876-91 [8] standard for different w/c ratios at one and two years vs distance to the north shoreline in Havana are represented of figure 1. Significant changes are only obtained between Arandia site at two years of exposure and CEADEN at two years of exposure and w/c=0.6. However, a tendency to increase corrosion with diminishing distance to the shoreline is clearly observed.

![Corrosion probability according to ASTM standard](image)

Corrosion current. Values of current determined using polarization resistance are very low (< 0.1 µA/cm²) after the first year of exposure. After two years of exposure, corrosion current significantly increased for samples of w/c=0.6 and 0.5. It can be observed that, in the case of w/c=0.4, corrosion current is always lower than reference samples (not exposed). Changes of corrosion current vs distance to the shoreline shows that, as expected, higher corrosion current values are determined in sites closer to the shoreline, particularly at distances lower than 615 m. A qualitative evaluation shows that two main corrosion aggressivity levels could be defined respecting distance to the shoreline, lower than 600 m and higher than 600 m.

It is important to note that in polarization resistance technique, corrosion current is calculated based on geometrical surface of the uncovered rebars. In this calculation, a completed uniform corrosion is supposed and in reality, localized corrosion is the main phenomenon occurring. A higher dispersion of the results concerning corrosion current vs distance is obtained respecting corrosion potential vs distance.

A linear fitness relatively acceptable between log corrosion current and corrosion potential is obtained when plotted data corresponding to one and two years of exposure. It is a Tafel like behaviour, but including passive and active potentials and currents. According to the results
obtained, corrosion potential is a better variable to consider in order to determine corrosivity after two years of exposure.

CONCLUSIONS
1.- Corrosion potential is suggested as an important factor to consider for determining atmospheric corrosivity respecting reinforced steel at two years of exposure. Taking into account the localized nature of corrosion phenomena in reinforced steel, corrosion current is not recommended as a parameter to consider respecting corrosivity of atmospheric evaluation.
2.- Two main corrosivity levels have been observed at two years of exposure in Havana sites:
   - High corrosivity: Areas close to the shoreline (open atmosphere) at a distance lower than 600 m.
   - Moderate corrosivity: Areas close to the shoreline (open atmosphere) but at distance higher than 600 m.
3. Changes in slump caused by the use of plasticizer additives and differences in aggregates properties, influence on Chloride penetration at the same w/c ratio.

REFERENCES