Evaluation of the Corrosion at Early Age in Reinforced Concrete Exposed to Sulfates

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One of the mainly corrosion mechanisms in reinforced concrete structures (RCS) is the attack by sulfates, due to the cracking that cause this attack, is accelerates the penetration of the sulfate ion in the RCS’s, and causing depassivation of steel reinforced and generate the formation of electrochemical cells, triggering the corrosion of reinforcement steel. However, the present work shows the results of the electrochemical evaluation of reinforced concrete specimens expose in a 3 to 5% (Na2SO4) solutions during 120 days. The concrete was elaborated with water/cement ratio of 0.4, 0.5 and 0.6. The results obtained with the linear polarization resistance (LPR), shown that at early age the attack by sulfates is negligible and there is no difference between the different w/c, and the concentrations of sulfates for a well performance of the concrete under study.

Keywords: Concrete, Sulfates, W/C ratio, Corrosion Rate, Potential

1. INTRODUCTION

The corrosion in the subsoil is influenced mainly by the oxygen availability, the pH, the soil’s resistivity, the microbiology activity; however the water presence is a requirement to get a corrosion cell, so the minerals contains of the clays are a mainly cause of corrosion for the AISI 1018 steel. The
montmorillonite and illites clays retain more water than the kaolinite clay what is more effective for the deterioration of metals [1], also coupled with the fact of the presence of salts in nature commonly find in these kind of soils as are sodium sulfate (Na$_2$SO$_4$), potassium (K$_2$SO$_4$), calcium (CaSO$_4$) or magnesium (MgSO$_4$) or dissolved in water adjacent to the reinforced concrete structure (RCS), which can attack hardened concrete [2].

The sulfate ions incoming to the concrete and attack the cementitious materials accelerating the degradation of concrete which can allow the steel reinforced is exposed the environment originated in this way the corrosion. The sulfate ion is mainly in sea water, in industrial wastewater; in concrete cooling towers can also be a potential source of sulfate attack due to the evaporation of water replacement. In groundwater rarely appears free sulfate ion, normally is found on salts, namely, the sulfates. [3-5].

The presence of sulfate ions in water that is in contact with the hardened paste of cement can increase considerably the solubility of components of the paste and cause, one hand, the development of concrete degradation by leaching and on the other hand, the presence of sulfates can cause a reaction base change, during which the sulfate cation will be replaced by Ca$^{2+}$, originating the concrete degradation by ion exchange reaction. Under certain circumstances may occur that the presence of sulfates leads to a degradation by expansion due to the formation of other stables components in the hardened mass of cement [6].

The two effects of sulfates attack on concrete components best known are: the formation of ettringite (trisulphate calcium aluminate 32-hydrated, CAO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) and gypsum (hydrated calcium sulfate, CaSO$_4$·2H$_2$O). The formation of ettringite can generate an increase in solid volume exerting an expansive action in the pores of concrete (especially in the surface layers) up to 17.7%, causing expansion and cracking. If the solution of sulfates causes the attack contains magnesium sulfate, ettringite and gypsum in addition to, brucite (magnesium hydroxide Mg (OH)$_2$) occurs that produces a volume increase of approximately 19.9%. potentializing the deterioration of the structure[7].

Due to this cracking is accelerating the penetration of the sulfate ion in the RCS’s, and causing depassivation of steel reinforced and generate the formation of electrochemical cells, triggering the corrosion of reinforcement steel, can reach to the collapse of the structure. Concrete is usually attacked by sulfates has a characteristic whitish appearance. Going penetrating little by little giving a loss of stiffness and strength of concrete. These effects are shown as the most frequent problems in the preservation and conservation of RCS’s.

There are some studies where they have studied the corrosion of RCS’s on sulfates solutions [8-15], however there is not study about the development of corrosion at an early age, is for this reason the importance of generating knowledge in the behavior or reinforced concrete response to the presence of aggressive agents in this case sodium sulphate at an early age, allowing a clear idea of the shares to be used to predict damage to the structure, and thus meet de durability for which the structure was designed.
2. EXPERIMENTAL

2.1 Design of Concrete mixes and materials

The method used for the design of concrete mixtures was established by the method ACI 211.1 [16], and which is based primarily on the physical characteristics of materials and aggregates used in mixtures. These were determined according to Mexican standards of ONNCCE, in Table 1 shows the physical characteristics of aggregates.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Coarse Aggregate</th>
<th>Fine Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity (gr/cm³)</td>
<td>2.32</td>
<td>2.66</td>
</tr>
<tr>
<td>Dry-rodded weight (kg/cm³)</td>
<td>1380</td>
<td>- - -</td>
</tr>
<tr>
<td>Absortion (%)</td>
<td>4</td>
<td>3.8</td>
</tr>
<tr>
<td>Fineness Modulus</td>
<td>- - -</td>
<td>2.7</td>
</tr>
<tr>
<td>Maximum Aggregate Size (mm)</td>
<td>19</td>
<td>- - -</td>
</tr>
</tbody>
</table>

It was used a Portland cement CPC 30R type according to regulations NMX-C-414-ONNCCE-2004 [17], and the mixing water was obtained from the drinking water network, three different mixtures were prepared with water/cement ratio from 0.40, 0.50 and 0.60. Material quantities for each concrete mixture are shown in Table 2.

<table>
<thead>
<tr>
<th>Materials (kg)</th>
<th>Water/Cement Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>Water</td>
<td>209</td>
</tr>
<tr>
<td>Cement</td>
<td>513</td>
</tr>
<tr>
<td>Coarse Aggregate</td>
<td>1035</td>
</tr>
<tr>
<td>Fine Aggregate</td>
<td>606</td>
</tr>
</tbody>
</table>

2.2 Characterization of concrete in fresh and hardened state

Was performed the characterization of concrete in fresh and hardened state. In Table 3 are listed the tests performed and their corresponding standards.
Table 3. Physical and mechanics properties of concretes.

<table>
<thead>
<tr>
<th>Test</th>
<th>Water/Cement Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/Cement Ratio</td>
<td>0.40</td>
</tr>
<tr>
<td>Slump (NMX-C-156-1997-ONNCCE)</td>
<td>7 cm</td>
</tr>
<tr>
<td>Temperature (ASTM C 1064)</td>
<td>24 °C</td>
</tr>
<tr>
<td>Density (NMX-C-105-1987)</td>
<td>2254 kg/m³</td>
</tr>
<tr>
<td>Mechanical strength (NMX-C-083-ONNCCE-2002)</td>
<td>43.5 MPa</td>
</tr>
</tbody>
</table>

2.3 Specimens and Measurement Methods

Were performed cylindrical specimens of 15×30 cm (see figure 1) Two 3/8 in. (9.3-mm diameter) AISI 1018 steel bars, symmetrically embedded in the specimens, were used as working electrodes during the measurements, with one of the steel bars acting as working electrode (WE) and the other as counter electrode (CE). A copper-copper sulfate (Cu/CuSO4) electrode was used as reference (RE). An active area of 5 cm² was marked on the working electrodes with epoxy resin, thus isolating the triple mortar/steel/atmosphere interface to avoid possible localized corrosion attack due to differential aeration. The specimens were immersed in a 3 to 5% (Na₂SO₄) solutions for 120 days.

![Diagram of the prismatic specimen used.](image-url)
Electrochemical evaluation study of the specimens was carried out with electrochemical techniques of corrosion potential ($E_{corr}$) according to ASTM C 876-99 standard [18] and the corrosion rate with the technique of linear polarization resistance (LPR) according to the equation Stern-Geary [19], applying $\Delta E \pm 20$ mV at a polarization rate of rate $0.16$ mV s$^{-1}$; the constant $B$ was $26$ mV. Corrosion levels were defined according to the Durar Network Specifications (21). For $i_{corr} < 0.1$ µA cm$^{-2}$ passivity, for $0.1$ µA cm$^{-2} < i_{corr} < 0.5$ µA cm$^{-2}$ low corrosion, for $0.5$ µA cm$^{-2} < i_{corr} < 1.0$ µA cm$^{-2}$ high corrosion, and for $i_{corr} > 1.0$ µA cm$^{-2}$ very high corrosion. An ACM Instruments potentiostat/galvanostat/ZRA; with a Cu/CuSO$_4$ reference electrode.

The nomenclature used in this research is shown in Table 4.

**Table 4.** Nomenclature of specimens.

<table>
<thead>
<tr>
<th>Media Exposure</th>
<th>Water/Cement Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.40 0.50 0.60</td>
</tr>
<tr>
<td>Solution to 3% of Na$_2$SO$_4$</td>
<td>43S 53S 63S</td>
</tr>
<tr>
<td>Solution to 5% of Na$_2$SO$_4$</td>
<td>45S 55S 65S</td>
</tr>
</tbody>
</table>

3. RESULTS

![Figure 2: Corrosion potential ($E_{corr}$) versus time for steel bars embedded in concrete of water/cement ratio 0.40, (4B) exposed in H$_2$O, (43S) exposed in Na$_2$SO$_4$ to 3% and (45S) exposed in Na$_2$SO$_4$ to 5%](image-url)

Figure 2. Corrosion potential ($E_{corr}$) versus time for steel bars embedded in concrete of water/cement ratio 0.40, (4B) exposed in H$_2$O, (43S) exposed in Na$_2$SO$_4$ to 3% and (45S) exposed in Na$_2$SO$_4$ to 5%.
Figure 2 shows the behavior of $E_{\text{corr}}$ in a concrete of water/cement ratio 0.40 ($f'c=43.5$ MPa), exposed after four weeks of curing at different aggressive media, are perfectly identifies the effects of exposure to sodium sulfate attack in different concentrations in thermodynamic or probabilistic behavior, moreover is observed as the control specimen 4B from his immersion in curing stage shows a continuing trend towards more positive values, starting with a potential of -140 mV at week 1 and stabilized in week 15 with values close to -80 mV indicating a steel in passive state with 10% probability of corrosion according to the standard, however the two specimens immersed in sulphate solutions after the curing stage where they presented a noble or passive behavior, they present a tendency towards more negative values of corrosion, observing the effect of aggressive environment is also shown in the 43S specimen two periods of activation-passivation-activation the first of the week 10 to 15, this is related to the entry of sulfate ions and the reaction of them with products generated in the process of hydration. For specimen 45S is identified a single period of activation-passivation-activation that is generated from week 6 to 12, this effect is related to the absorption of sulphates.

Figure 3 shows the behavior of the corrosion potential ($E_{\text{corr}}$) of reinforcing steel embedded in concrete of water/cement ratio 0.50 ($f'c=33.4$ MPa), exposed in solutions to 3% and 5% in $\text{Na}_2\text{SO}_4$ and $\text{H}_2\text{O}$. Is observed that the specimen 5B from its immersion in curing stage, shows a continuing trend of noble values of corrosion potential of -180 mV at week 1, ending at week 15 with a value of -100 mV, indicating a steel in passive state with 10% probability of corrosion according to the standard ASTM C876-99. The two specimens: 53S y 55S immersed in solutions to 3% and 5% of $\text{Na}_2\text{SO}_4$ respectively, they present an almost identical behavior to week 13, with a trend towards more noble potential in curing stage with values from -190 mV to -150 mV, with a period of activation-passivation-activation from week 5 to 13, where the specimen 55S continues the trend to more negative values until week 15 and the specimen 53S presents more noble values to a steel passivation process.

**Figure 3.** Corrosion potential ($E_{\text{corr}}$) versus time for steel bars embedded of water/cement ratio 0.50, (5B) exposed in $\text{H}_2\text{O}$, (53S) exposed in $\text{Na}_2\text{SO}_4$ to 3% and (55S) exposed in $\text{Na}_2\text{SO}_4$ to 5%.
Figure 4 shows the corrosion potentials (E\text{corr}) obtained from the last group of specimens with water/cement ratio 0.60 (f'c=23.5 MPa), like the previous two groups (Figures 3 and 4), the three specimens shown a tendency to values more noble of potential corrosion (more positive) indicating a passivation of the steel for the specimen 6B along the period of continuous exposure to the trend of more positive values of E\text{corr}, reaching values of -100 mV at the end of the exposure period. In this group we can see the effect of the concentration of sulfate ions or aggressive environment and its relation to the quality of concrete, is more permeable than those analyzed in figures 3 and 4, so that the specimen 63S shows a tendency towards more negative values from the first week of exposure to 3% solution of Na\textsubscript{2}SO\textsubscript{4}, having values from -70 mV to reach -180 mV at the week 15, however, the most negative values are presented by the specimen 65S with a trend towards more negative values than those reported in the specimen 63S from its immersion to 5% solution in Na\textsubscript{2}SO\textsubscript{4}, with a potential of -72 mV at week 4 to reach a potential of -120 mV indicating a 50% probability of corrosion.

![Figure 4](image-url)

**Figure 4.** Corrosion potential (E\text{corr}) versus time for steel bars embedded of water/cement ratio a/c=0.60, (6B) exposed in H\textsubscript{2}O, (63S) exposed in Na\textsubscript{2}SO\textsubscript{4} to 3% and (65S) exposed in Na\textsubscript{2}SO\textsubscript{4} to 5%.

Figure 5 shows the behavior of corrosion rate (i\text{corr}) for a concrete of water/cement ratio 0.40 (f'c=43.5 MPa), exposed to different media, H\textsubscript{2}O as the control, solution to 3 and 5 % of Na\textsubscript{2}SO\textsubscript{4} as aggressive solutions. For specimen 4B (the control) are reported values for i\text{corr} of 0.22 µA/cm\textsuperscript{2} at week 1 to reach 0.10 µA/cm\textsuperscript{2} at week 4, to remain from week 5 to week 15 with i\text{corr} of 0.06 µA/cm\textsuperscript{2}; for specimen 43S have values of i\text{corr} of 0.14 µA/cm\textsuperscript{2}; at week 1 to remain in a passive state with i\text{corr} of 0.04 µA/cm\textsuperscript{2} during the entire period of exposure to 3% solution of Na\textsubscript{2}SO\textsubscript{4}. For specimen 45S exposed to 5% solution of Na\textsubscript{2}SO\textsubscript{4} presents in the curing stage values from i\text{corr} of 0.14 µA/cm\textsuperscript{2} to i\text{corr} of 0.05 µA/cm\textsuperscript{2}, value which is maintained throughout the period of exposure to aggressive media (week 5 to 15), having a passive state of steel reinforcement. Can be observed from this figure that all the specimens are in the passive state, but have small differences of i\text{corr} depending on types of media
that have, presenting the lowest values which were exposed to sulphates and related to the absorption of sulfate ions that contributed to the formation of a passive layer stronger than that formed in the specimens immersed in H$_2$O as control specimens.

![Figure 5](image5.png)

**Figure 5.** Corrosion rate ($i_{corr}$) of the specimens of water/cement ratio 0.40, (4B) exposed in H$_2$O, (43S) exposed in Na$_2$SO$_4$ to 3% and (45S) exposed in Na$_2$SO$_4$ to 5%.

![Figure 6](image6.png)

**Figure 6.** Corrosion rate ($i_{corr}$) of the specimens of water/cement ratio 0.50, (5B) exposed in H$_2$O, (53S) exposed in Na$_2$SO$_4$ to 3% and (55S) exposed in Na$_2$SO$_4$ to 5%.

In the Figure 6 can be observed the corrosion rate ($i_{corr}$) of the specimens of water/cement ratio 0.50 (f'c=33.4 MPa) exposed to different solutions, H$_2$O as the control, solution to 3 and 5% of Na$_2$SO$_4$ as aggressive environments. In the specimen 5B (or control) are reported values from $i_{corr}$ of
0.58 µA/cm² at week 1 to reach 0.27 µA/cm² at week 4 to be located in low corrosion with values of 0.16 and 0.12 µA/cm² at weeks 5 and 6 for maintain from week 7 in the passive estate with a value of \(i_{corr}\) to reach 0.08 µA/cm² at week 15. For specimen 53S were obtained values in the curing stage of \(i_{corr}\) ranging from 0.57 µA/cm² in week 1 to 0.09 µA/cm², to be located in a passive zone with values of \(i_{corr}\) from 0.06 to 0.05 µA/cm² during throughout the period of exposure to 3% solution of Na₂SO₄, the specimen 55S that was exposed to 5% solution of Na₂SO₄ presents in the curing stage values of \(i_{corr}\) from 0.63 to 0.06 µA/cm², to maintain \(i_{corr}\) of 0.05 µA/cm² during throughout the period of exposure to aggressive environment, is observed that all specimens are found after the curing stage in the passive state of steel reinforcement.

In the Figure 7 can be observed the corrosion rate (\(i_{corr}\)) of the specimens of water/cement ratio 0.60 (\(f’c=23.5\) MPa), and just like those shown in figures 6 and 7 exposed to different environments, H₂O as the control, solution to 3 and 5% of Na₂SO₄ as aggressive environments, can be observed how the specimen 6B (or control) reports values from \(i_{corr}\) of 0.59 to 0.19 µA/cm² in the curing stage from the week 1 to week 4 to show low corrosion even at weeks 5 and 6 with values \(i_{corr}\) of 0.13 µA/cm² and \(i_{corr}\) of 0.10 µA/cm² respectively. And from there placed with \(i_{corr}\) during throughout the period of exposure (weeks 7 to 15) from 0.09 µA/cm² to 0.08 µA/cm², with respect to the specimen 63S presents values of \(i_{corr}\) in the curing stage, ranging from 0.68 µA/cm² at week 1 to 0.08 µA/cm² at week 4, to locate in the passivity zone from week 5 to 15 with values of \(i_{corr}\) ranging from 0.08 µA/cm² to 0.07 µA/cm², for the specimen exposed to 5% in Na₂SO₄ presents in the curing stage values of \(i_{corr}\) ranging from 0.70 µA/cm² to 0.06 µA/cm², and remain there throughout the study period, indicating a passive state of steel reinforcement as the other two specimens, it seems that the lower quality of this concrete evidence of the ability of sulfate ion absorption by the concrete under study, and thus the formation of a more resistant layer related to the smaller value of corrosion kinetics reported for specimens exposed to a higher concentration of Na₂SO₄.

![Figure 7](image_url)

**Figure 7.** Corrosion rate (\(i_{corr}\)) of the specimens of water/cement ratio 0.60, (6B) exposed in H₂O, (63S) exposed in Na₂SO₄ to 3% and (65S) exposed in Na₂SO₄ to 5%.
4. DISCUSSION

In the Figure 8 compares $E_{\text{corr}}$ vs $i_{\text{corr}}$, is observed as in the curing stage are presented values of $i_{\text{corr}}$ indicating a low corrosion, for the three specimens under study and at the same corrosion potential values that indicate 10% probability of corrosion. As the specimen control remained immersed in H$_2$O presents a curve with tendency to decrease toward zeros on both axes: $E_{\text{corr}}$ vs $i_{\text{corr}}$, confirming the passive state of steel, agreeing well with the standard that interprets these values: ASTM C 876-99 in corrosion potential ($E_{\text{corr}}$) and the Durar Network Specifications [20], in the parts that corresponds to the corrosion rate ($i_{\text{corr}}$). For the specimens exposed to 3% and 5% in Na$_2$SO$_4$, they present a behavior between them, with $i_{\text{corr}}$ in the curing stage indicating low corrosion to decrease when exposed to aggressive environment toward more positive values (left) to move toward more negative values (right) to move toward the area of uncertainty, but indicating negligible corrosion values of $i_{\text{corr}}$. Described in the graphics for these two specimens a sort of “L”, where precisely the bottom (exposure time) can be associated to the period of initiation of useful life of Tuutti [21], where the level of corrosion is negligible.

![Figure 8](image_url)

**Figure 8.** Current density ($i_{\text{corr}}$ in µA/cm$^2$) versus corrosion potential ($E_{\text{corr}}$ in mV) of the specimens of water/cement ratio 0.40, (4B) exposed in H$_2$O, (43S) exposed in Na$_2$SO$_4$ to 3% and (45S) exposed in Na$_2$SO$_4$ to 5%.

In the case of lower-quality specimens, water/cement ratio 0.50 and 0.60, (Figures 9 and 10), are identified high and low corrosion values for both grades of concrete quality in the curing stage, related to the formation of the passive layer, giving the potential more negative than -200, which indicates according to the standard ASTM C-876-99 a 10% probability of corrosion, both concretes 0.50 and 0.60 when exposed to 3% and 5% solution in Na$_2$SO$_4$ and after decrease in the curing stage of its corrosion rate ($i_{\text{corr}}$), they present values that indicate passivity according to literature, but just
like noted in figure 9, tend in the first weeks of exposure to aggressive environment towards more positive values of \(E_{\text{corr}}\), but to go forward in time these values become more negative, again presents a sort of “L” where part of exposure as mentioned in the previous paragraph corresponds to the period of initiation of Tuutti useful life.

**Figure 9.** Current density \((i_{\text{corr}} \text{ in } \mu\text{A/cm}^2)\) versus corrosion potential \((E_{\text{corr}} \text{ in mV})\) of the specimens of water/cement ratio 0.50, (5B) exposed in \(H_2O\), (53S) exposed in \(Na_2SO_4\) to 3% and (55S) exposed in \(Na_2SO_4\) to 5%.

**Figure 10.** Current density \((i_{\text{corr}} \text{ in } \mu\text{A/cm}^2)\) versus corrosion potential \((E_{\text{corr}} \text{ in mV})\) of the specimens of water/cement ratio 0.60, (6B) exposed in \(H_2O\), (63S) exposed in \(Na_2SO_4\) to 3% and (65S) exposed in \(Na_2SO_4\) to 5%.
5. CONCLUSIONS

In concrete at early ages there is no a clear difference between the different relations in the water/cement ratio (0.40,0.50,0.60), when they are exposed to sulfates (solutions to 3 and 5% in Na$_2$SO$_4$).

The electrochemical behavior of specimens under study was favorable according to the results obtained of $E_{corr}$ vs $i_{corr}$ as brand the model of useful life of Tuutti and tests performed.

Was not observed a significant behavior in terms of corrosion rate according to the different relations of water/cement ratio. The concretes exposed to Na$_2$SO$_4$ always showed lower corrosion rates that the concretes in H$_2$O. The deterioration caused by corrosion at an early age in negligible according to the results obtained with technique of LPR.

Is associated with the formation of a passive layer more resistant in specimens exposed to sulfates, presenting values of icorr lower in magnitude over the specimens exposed in H$_2$O.

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References


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