The Effect of Environmental Conditions on Electrochemical Corrosion Behavior of AISI 1018 Low-carbon Steel in Concrete Pore Solution

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The effect of environmental conditions such as dissolved oxygen (DO) and temperature on electrochemical corrosion behavior of AISI 1018 low-carbon steel in concrete pore solution (CPS) were investigated. The corrosion behavior of low-carbon steel was determined using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods at temperatures ranging from 20 to 40 ºC and DOES concentration from 0.5 ppm to 4.5 ppm. The corrosion rate of steels increased with increasing ambient temperatures. The electrochemical corrosion resistance was observed to be higher in CPS with lower DO concentrations. The SEM analysis shows that the metal dissolution rate was more intense in CPS with higher DO levels.

Keywords: Dissolved oxygen; Electrochemical corrosion behavior; AISI 1018 low-carbon steel; Cement pore solution

1. INTRODUCTION

Corrosion resistance of reinforced concrete can be an important factor in its durability [1, 2]. Low-corrosion resistance may predictably cause significant and expensive repair work in the concrete [3, 4]. It is clear that the primarily protective environment that concrete structures provide for steel rebar is due to its alkaline nature [5, 6]. It usually happens in positive or passive corrosion potential for steel embedded in concrete [4, 7]. When corrosive ions for example chlorides penetrate into the concrete structure, the environment may become promising for corrosion of steel [8]. When corrosive ions reach dangerous amounts, the potential becomes more active, and hence a shift in values of corrosion potential is often related to the intrusion of corrosive ions [9]. It may result in an increase in the rate of corrosion. Consistent with classical corrosion theory [1, 10, 11], species existent in the environment can influence the anodic reaction, the cathodic reaction, or both through either preventing the reaction. Baek et al. [12] determined which dissolved oxygen (DO) into a NaCl medium plays an
important role for the creation of anodic oxide layer, as well as the kinetics of film growth on low carbon steels. Eyu et al. [13] reveals that an inferior DO content in coal-seam gas produced water increased with decreasing corrosion potential. With respect to the decrease of O₂ on carbon steels, Tachibana et al. [14] shows that the corrosion potential is primarily determined by cathodic polarization into oxygenated environments. In fact, the decrease of H₂O accompanied by H₂ production also shows a significant role in steel corrosion, particularly for the alkaline solution in low DO [15].These works considered the effect of DO on the corrosion behavior of steel at ambient temperature. However, some studies on the effect of DO on steel corrosion behavior have been conducted at a single temperature. Therefore, the temperature and DO influence on the corrosion resistance of carbon steel rebar in concrete pore solution (CPS) has not been studied systematically.

The aim of this study is to consider the effects of temperature and DO on the electrochemical corrosion behavior of the carbon steel in typical CPS and to experimentally evaluate the electrochemical parameters.

2. MATERIALS AND METHOD

To investigate the effects of temperature and DO on the electrochemical corrosion behavior of steel in cement pore solution, AISI 1018 low-carbon steels with 25cm long and 0.8cm diameter were used. The chemical composition of AISI 1018 steel is 0.17wt% C, 0.75wt% Mn, 0.03wt% P, 0.04wt% S and Fe (Balance). All steels were cleaned by acetone and washed in DI water and then air-dried. The ends of steel specimens are coated by an epoxy-resin.

To prepare concrete pore solution (CPS), a mixture of NaOH (0.2 mol/dm³), Ca(OH)₂ (0.3 mol/dm³) and KOH (0.5 mol/dm³) with pH-value 13 was used. The electrochemical tests were performed by a three-electrode system consisting of AISI 1018 steels (working electrode), a graphite rod (counter) and saturated calomel (reference electrode). The specimens were exposed to the CPS including 3wt% NaCl. The exposure temperatures were 20, 25, 30, 35 and 40°C as a seasonal change in temperature in a hot-CPS environment.

Electrochemical impedance spectroscopy (EIS) assessment was used in the range of frequencies from 1mHz to 10kHz at the open-circuit voltage with ±10mV perturbation. The potentiodynamic polarization experiment was done at a scanning rate of 0.5mV/s. A scanning electron microscope was used to examine the surface morphologies of low-carbon steel specimens.

The experiment solutions were bubbled through different O₂/N₂ gas mixes for 5 hours at ambient pressure and 75°C. The values of DO concentration for the solutions under various O₂ volume conditions were determined by polarographic technique (JSPS-605 F DO Analyzer) [16].

3. RESULTS AND DISCUSSION

Concentration of DO is reduced by nitrogen purging time (NPT). In this work, the NPT also led to a slight decrease in temperature. For example, at initial purging, the temperature of the test solution
was 20 °C, with 4 ppm DO. When DO concentration significantly decreased to 0.5 ppm after 12h, the temperature reduced to 19.4 °C which can be ignored. The temperature reduction with NPT was because of the nitrogen cooling effect.

**Figure 1.** Polarization plots of low-carbon steel in concrete pore solution in different concentrations of dissolved oxygen at 20 °C

**Table 1.** Polarization parameters of low-carbon steel in cement pore solution in different concentrations of dissolved oxygen

<table>
<thead>
<tr>
<th>DO concentration (ppm)</th>
<th>Corrosion current density (µA/cm²)</th>
<th>Corrosion potential (V)</th>
<th>βa (mV/des)</th>
<th>-βc (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.4</td>
<td>-0.654</td>
<td>174</td>
<td>311</td>
</tr>
<tr>
<td>1.5</td>
<td>4.8</td>
<td>-0.663</td>
<td>154</td>
<td>223</td>
</tr>
<tr>
<td>2.5</td>
<td>5.2</td>
<td>-0.617</td>
<td>185</td>
<td>228</td>
</tr>
<tr>
<td>3.5</td>
<td>5.7</td>
<td>-0.614</td>
<td>191</td>
<td>232</td>
</tr>
<tr>
<td>4.5</td>
<td>17.5</td>
<td>-0.528</td>
<td>213</td>
<td>242</td>
</tr>
</tbody>
</table>

Figure 1 indicates the polarization plots of low-carbon steel in CPS in different concentrations of DO. As shown, the anodic polarization was increased with no retardation at 3 ppm DO content, while one anodic peak was observed in solutions containing 0.5 ppm and 2.5 ppm DO. Furthermore, the current density rises with corrosion potential below -0.6 V_{SCE}, showing iron dissolution while at corrosion potentials higher than -0.6 V_{SCE}, the current density falls, revealing formation of passivation layers. The cause of this behavior could be the result of corrosion products. Such as, Fe(OH)₂ shaped on the steel surface, consistent with the following reaction [17]:
Fe + 2H₂O → Fe(OH)₂ + 2H⁺ + 2e⁻ \hspace{1cm} (1)

Fe(OH)₂ creates a defective hydrous layer between the solution and steel sample, and thus delays the anodic current densities [18]. As revealed in Table 1, the corrosion current densities are reduced by reducing DO concentrations from 17.5 µAcm⁻² to 3.4 µAcm⁻² at 4.5 ppm to 0.5 ppm, respectively. This shows that a more stable and compact oxide layer was formed at -0.6 V_sce at lower DO. The rise in anodic polarization current by falling DO content at a more positive potential can be related to solubility of corrosion products and negligible oxidation at the surface of steel to create oxide layer by the Kuch mechanism [19].

Figure 2 exhibits the Nyquist and Bode curves for different concentrations of DO in the CPS environment. As shown in figure 1a, the diameter of the semicircle rises with reducing DO content, which shows that reducing DO helps to form a more stable oxide film on the surface of low-carbon steel. A similar trend may be observed in the Bode plots (Fig. 2b), where the impedance rises with falling DO concentrations at low-frequencies. The phase angle indicates a greater peak as DO content reduces. A higher value of phase angle at low-frequency reveals a higher resistance of the steel surface.

The EIS data was fitted by an equivalent circuit model as indicated in Figure 3. Rₛ presents the solution resistance, R_f and C_f show resistance and capacitance of oxide film, respectively. They are used to simulate high-frequency loops. Furthermore, R_ct and C_dl indicate the charge-transfer resistance and double layer capacitance, respectively [20].

**Figure 2.** (a) Nyquist and (b) Bode curves of low-carbon steel for different concentrations of dissolved oxygen in concrete pore solution at 20 °C
Obtained data exhibited in Table 2 shows that by reducing DO content into the CPS, $R_c$ and $R_{ct}$ increase and $C_{dl}$ and $C_f$ reduce, which can be associated with the passive layer stability on low-carbon steel, improving the corrosion resistance. As shown in table 2, the film resistance ($R_f$) increases considerably with reducing DO content, indicating the corrosion product on the surface of low-carbon steel was more protective and dense at a relatively low concentration of DO as indicated in Figure 4.

<table>
<thead>
<tr>
<th>DO concentration (ppm)</th>
<th>$R_s$(Ω)</th>
<th>$R_f$(Ω)</th>
<th>$C_f$(mFcm$^{-2}$)</th>
<th>$R_{ct}$(Ω)</th>
<th>$C_{dl}$(mFcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>9.8</td>
<td>210</td>
<td>3.1</td>
<td>263</td>
<td>3.9</td>
</tr>
<tr>
<td>1.5</td>
<td>10.5</td>
<td>184</td>
<td>3.8</td>
<td>231</td>
<td>4.7</td>
</tr>
<tr>
<td>2.5</td>
<td>10.8</td>
<td>136</td>
<td>4.6</td>
<td>172</td>
<td>5.3</td>
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<tr>
<td>3.5</td>
<td>11.2</td>
<td>89</td>
<td>6.2</td>
<td>119</td>
<td>7.2</td>
</tr>
<tr>
<td>4.5</td>
<td>12.4</td>
<td>28</td>
<td>14.9</td>
<td>37</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Figure 5 demonstrates the polarization plots of low-carbon steel exposed to CPS at various ambient temperatures. As shown in Fig. 5, the polarization plots for the steels immersed in CPS at 40°C temperature shifted to anodic direction, indicating an improvement of the corrosion rate in comparison with other specimens exposed to CPS with lower temperatures. It may be associated with
the reaction rate of Cl ions with Fe which may be considerably affected by the kinetic of reaction by rising temperature, as stated in Eqs. (2) and (3).

\[ \text{Fe}^{2+} + 3\text{Cl}^- \rightarrow \text{FeCl}_3 + 3e^- \quad (2) \]

\[ \text{FeCl}_3 + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 + 3\text{Cl}^- \quad (3) \]

Corrosion products with the creation of Fe$_2$O$_3$ and Fe(OH)$_2$ as the intermediary product were formed, as shown in Equs (4) and (5).

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad (4) \]

\[ 4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3\text{H}_2\text{O} + 2\text{H}_2\text{O} \quad (5) \]

**Figure 5.** Polarization curves of low-carbon steel exposed to concrete pore solution at various ambient temperatures at 4.5 ppm of dissolved oxygen

**Table 3.** Polarization parameters of low-carbon steel in concrete pore solution in different temperature at 4.5 ppm of dissolved oxygen

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Corrosion current density (µA/cm$^2$)</th>
<th>Corrosion potential (V)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$-\beta_c$ (mV/dec)</th>
<th>CR (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>17.5</td>
<td>-0.528</td>
<td>213</td>
<td>242</td>
<td>4.38</td>
</tr>
<tr>
<td>25</td>
<td>23.7</td>
<td>-0.524</td>
<td>230</td>
<td>261</td>
<td>7.46</td>
</tr>
<tr>
<td>30</td>
<td>28.1</td>
<td>-0.518</td>
<td>245</td>
<td>276</td>
<td>10.25</td>
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<tr>
<td>35</td>
<td>33.9</td>
<td>-0.512</td>
<td>268</td>
<td>297</td>
<td>14.18</td>
</tr>
<tr>
<td>40</td>
<td>48.4</td>
<td>-0.531</td>
<td>298</td>
<td>329</td>
<td>18.63</td>
</tr>
</tbody>
</table>

The investigation of Tafel plots permits the consideration of electrochemical corrosion parameters. For example, the corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) are summarized in Table 3. The values of cathodic Tafel slope ($\beta_c$) were observed in the range 242–329 mV/decade, indicating activation control corrosion. The analysis of the Tafel plot enabled the calculation of $i_{corr}$, which was then used to calculate the corrosion rate (CR) [21]:

\[ \text{CR (mpy)} = [(1.95 \times 10^5)i_{corr}W]/(\rho A) \quad (6) \]
where A is the contact area between the solution working and electrode (cm$^2$), $\rho$ is metal density (g/cm$^3$) and W is equivalent mass of metal (g).

As shown in table 3, when the ambient temperature was increased from 20 to 40 °C, a significant rise in the CR was found. Consistent with NACE RP0775-2005, the corrosion rates are identified as high in the temperatures of 20 and 25°C (5-10 mpy) and severe in the temperatures of above 30 °C for the CR is greater than 10 mpy. The rise of metal dissolution by increasing temperature increases the oxidation-reduction reaction and current density which results in such behavior.

EIS measurements were done to further evaluate the electrochemical corrosion behavior of low-carbon steel in CPS at different temperatures at 4.5 ppm of DO, and to confirm the results achieved through Tafel plots. In this work, the standard EIS system was used in the range of frequencies from 1mHz to 10kHz at the open-circuit voltage with ±10mV perturbation.

![Figure 6. The Nyquist and Bode plots of AISI 1018 low-carbon steel in corrosive environment of concrete pore solution at different temperatures at 4.5 ppm of dissolved oxygen](image)

Figure 6 indicates the Nyquist and Bode plots of AISI 1018 low-carbon steel in the corrosive environment of CPS at different temperatures at 4.5 ppm of dissolved oxygen. The Nyquist plots show a semicircular loop whose diameter rises with reduced temperature, indicating a reduction in corrosion rate of low-carbon steel. Nyquist curves indicate the characteristic shape of semicircles showing that the corrosion procedure is in activation control. The greater diameter of the semicircles achieved by lower temperatures reveals high electrical-resistance at the interface solution-metal, which is due to the oxidation of Fe$^{+2}$ ions and...
iron in the CPS. The existence of a capacitive loop typically shows that the surface of steels is partially covered by corrosion products. The EIS plots at all temperatures were revealed to be the same in shape with a diameter of a capacitive loop which reduces with temperature. These results are compatible with those previously research done by other researchers [22].

The Echem Analyst program was used to analyze EIS data at various temperatures using the analogous circuit shown in Figure 3. $R_{ct}$ is the charge-transfer resistance; it is really the resistance of an electron to adjust phases, for example, from either the electrode into solution as well as, more precisely, to a species fixed in the solution. With the purpose of achieving a perfect fit, the double-layer capacitance is correlated with the modification of constant phase elements [23, 24].

### Table 4. EIS parameters of low-carbon steel in concrete pore solution in different temperature at 4.5 ppm of dissolved oxygen

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R_s$(Ω)</th>
<th>$R_f$(Ω)</th>
<th>$C_f$(mFcm$^{-2}$)</th>
<th>$R_{ct}$(Ω)</th>
<th>$C_{dl}$(mFcm$^{-2}$)</th>
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<td>7.8</td>
<td>22</td>
<td>21.4</td>
<td>27</td>
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<tr>
<td>35</td>
<td>9.2</td>
<td>19</td>
<td>23.6</td>
<td>24</td>
<td>28.7</td>
</tr>
<tr>
<td>40</td>
<td>8.4</td>
<td>15</td>
<td>26.2</td>
<td>21</td>
<td>31.3</td>
</tr>
</tbody>
</table>

The circuit's fitting values indicate that both $R_{ct}$ and $R_s$ fall with increasing temperature, with the lowest values achieved at the highest temperature (40 °C), indicating an increased corrosion rate with increasing temperature. [25, 26]. The results of the EIS analyses agree with the results gained from the polarization curves. Table 4 summarizes the simulated circuit parameters of low-carbon steel corrosion in CPS.

### 4. CONCLUSIONS

The effect of environmental conditions such as DO and temperature on electrochemical corrosion behavior of AISI 1018 low-carbon steel in CPS was investigated. The corrosion behavior of low-carbon steel was determined using EIS and potentiodynamic polarization methods at temperatures ranging from 20 to 40 °C and DOS concentration from 0.5 ppm to 4.5 ppm. The corrosion rate of steels increased with increasing ambient temperatures. The electrochemical corrosion resistance was observed to be higher in CPS with lower DO concentrations. The SEM analysis shows that the metal dissolution rate was more intense in CPS with higher DO levels.

### References


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