Influence of citric acid-Zn\textsuperscript{2+} System on Inhibition of Corrosion of Mild Steel in Simulated Concrete Pore Solution

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The inhibition efficiency (IE) of citric acid-Zn\textsuperscript{2+} system in controlling corrosion of mild steel in Simulated Concrete Pore Solution (SCPS) prepared in well water in the absence and presence of Zn\textsuperscript{2+} has been investigated by weight loss study. It can be seen from the data obtained that formulation consisting of 250 ppm of Citric acid and 50 ppm of Zn\textsuperscript{2+} provides 88\% of inhibition efficiency. Inhibition was found to increases with an increasing concentration of Zn\textsuperscript{2+}. Polarization study confirms the formation of a protective film on the metal surface. AC impedance spectra also revealed that a protective film formed on the metal surface. The inhibitor system controls the anodic reaction predominantly. The results obtained show that the Citric acid could serve as an effective inhibitor for the corrosion of mild steel in Simulated Concrete Pore Solution.

**Keywords:** Concrete Corrosion, Simulated Concrete Pore Solution, Mild Steel, Citric acid, Well water.

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1. **INTRODUCTION**

Design of concrete structures is currently focused especially on the effects of direct actions. Increasing the consequence of indirect accidental and environmental actions are manifesting. Long term exposure to environmental actions (chemical, biological and physical effects of the environment) causes deterioration of concrete and reinforcement. When considering the reliability of structures all type of actions should be taken into accounts. This holistic approach to the design and verification of structures shall be applied to all constructions especially civil engineering works, because of their larger ratio between the area exposed to the surrounding environment and cross-section dimensions as well as longer design life.[1].

Reinforced concrete is a versatile, economical and successful construction material. It is durable and strong, performing well throughout its service life. Conventional black steel reinforcements embedded in concrete are passive due to a protective, very thin oxide layer (about 10 nm) [2]that is formed on its surface in high alkaline media such as that the contained in the pores of the concrete (pH about 12.6) [3]. So, many authors have carried out the studies on steel corrosion in simulated concrete solution [4,5].Although the study is carried in the simulated solution, the results are still significant for the concrete. The simulated solution can not only reproduce the chemical environment in concrete but also shorten the experiment period. A saturated Ca(OH)\textsubscript{2} solution and a solution containing KOH, NaOH and Ca(OH)\textsubscript{2} are the most familiar solutions to simulate the alkalinity environment of the concrete pore solution [6].

In the present work, simulated concrete pore solution of Ca(OH)\textsubscript{2} is used. The study was conducted to examine the influence of citric acid and Zn2+ ions on the corrosion resistance of mild steel immersed in SCPS prepared in well water. Corrosion resistance was measured by Weight loss method, polarization study, AC impedance spectra. The protective film was analyses by FTIR spectra.

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2. EXPERIMENTAL

2.1 Preparation of simulated concrete pore solution (SCPS)

Simulated concrete pore solution is mainly consisted of Saturated Ca(OH)$_2$, KOH, NaOH with the pH-13.5 [7,8]. However in numerous studies of rebar corrosion saturated Ca(OH)$_2$ has been used a substitute for pore solution saturated calcium hydroxide solution is used in present study, as SCP solution with the pH-12.5.

2.2 Preparation of the specimens

Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2cm were polished to a mirror finish and degreased with acetone and used for the weight-loss method and surface examination studies. The environment chosen is well water and the physic-chemical parameter of well water is given in table 1.

Table–1
Physico-Chemical Parameters of Well Water

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.38</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1770μΩ·cm-1</td>
</tr>
<tr>
<td>Chloride</td>
<td>665 ppm</td>
</tr>
<tr>
<td>Sulphate</td>
<td>214 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>1100 ppm</td>
</tr>
<tr>
<td>Total hardness</td>
<td>402 ppm</td>
</tr>
<tr>
<td>Total Alkalinity</td>
<td>390 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>83 ppm</td>
</tr>
<tr>
<td>Potassium</td>
<td>55 ppm</td>
</tr>
<tr>
<td>Sodium</td>
<td>172 ppm</td>
</tr>
<tr>
<td>Calcium</td>
<td>88 ppm</td>
</tr>
</tbody>
</table>

2.3 Determination of Corrosion Rate:

The weighed specimens in triplicate were suspended by means of glass hooks in 100ml SCPS prepared in well water containing various concentration of citric acid in the presence and absence of Zn2+ for one day. The specimen were taken out, washed in running water, dried, and weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship:

\[
CR = \frac{[(Weight \ loss \ in \ mg) / (Area \ of \ the \ specimens \ in \ dm^2 \ \times \ Immersion \ periods \ in \ days)]}{mdd}.
\]  

Corrosion inhibition efficiency (IE, %) was then calculated using the equation:

\[
IE = 100\{1-(W/W_2)\} \%
\]

Where, \(W_1\) = corrosion rate in the absence of the inhibitor, and \(W_2\) = corrosion rate in the presence of the inhibitor.
2.4 Potentiodynamic Polarization:

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three electrode assembly is shown in Fig-1. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr) and Tafel slopes (anodic = ba and cathodic =bc) and Linear polarization resistance (LPR) were calculated. The scan rate (V/S) was 0.01.Hold time at (Efcs) was zero and quit time(s) was two.

![Figure-1 Circuit diagram of three-electrode cell assembly](image)

2.5 AC impedance spectra

AC impedance spectral studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. The real part (Z’) and imaginary part (Z”) of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (Rt) and the double layer capacitance (Cd) were calculated.

2.6 Fourier Transform Infrared Spectra

These spectra were recorded in a Perkin-Elmer -1600 spectrometer using KBr pellet. The spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

3. RESULTS AND DISCUSSION

3.1 Analysis of Weight loss Study

Corrosion rates (CR) of carbon steel immersed in SCPS prepared in well water the absence and presence of inhibitors (citric acid and Zn2+ system). The calculated corrosion inhibition efficiency (IE) and corrosion rates (CR) of citric acid in controlling corrosion of SCPS in well water, for a period of one day in absence and presence of zinc ion are given in Table 1. It is observed from the Table 2 that citric acid is a good inhibitor. The IE is found to be enhanced in the presence of Zn2+ ion. Citric acid alone shows some inhibition efficiencies.
The formulation consisting of 250 ppm of citric acid and 50 ppm of Zn2+ shows 88% of inhibition efficiency. Weight loss study reveals that citric acid and Zn2+ individually showed some IE, but exhibited better IE when applied in combination. This suggests that CA and Zn2+ exhibit synergistic behavior [9-15].

**Table 2**

Corrosion rates (CR) of mild steel immersed in Simulated Concrete Pore Solution (SCPS) prepared in well water in the presence and absence of citric acid Zn2+ in the inhibition efficiency (IE) obtained by weight loss method.

<table>
<thead>
<tr>
<th>Citric acid</th>
<th>Zn2⁺(0ppm)</th>
<th>Zn2⁺(25ppm)</th>
<th>Zn2⁺(50ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IE%</td>
<td>CR mdd</td>
<td>IE%</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>13.9</td>
<td>25</td>
</tr>
<tr>
<td>100</td>
<td>38</td>
<td>9.92</td>
<td>40</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>8.00</td>
<td>50</td>
</tr>
<tr>
<td>200</td>
<td>63</td>
<td>5.92</td>
<td>63</td>
</tr>
<tr>
<td>250</td>
<td>75</td>
<td>4.00</td>
<td>71</td>
</tr>
</tbody>
</table>

**Figure 2**: Effect of Citric acid+50ppm Zn2+ system
3.2 Analysis of Polarization Curves:

When mild steel is immersed in simulated concrete pore solution prepared in well water the corrosion potential was -842 mV vs SCE (saturated calomel electrode). When Citric acid (250 ppm) and Zn 2+(50 ppm) were added to the above system the corrosion potential shifted to the anodic side -822 mV vs SCE; that is noble side. This indicates that the CA- Zn2+ system controls anodic reaction predominantly. This indicates that the passive film is formed on the metal surface in presence of inhibitor. The shifting of corrosion potential towards anodic side in presence of inhibitors has been reported by several researchers [16-21].

![Polarization curve](image)

**Figure 3:** Polarization curves of mild steel immersed in various test solution

a) SCPS
b) Citric acid 250 ppm+ Zn2+ 50 ppm

**Table-3**

Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from Potentiodynamic Polarization Study.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ mV vs SCE</th>
<th>$b_c$ mV/decade</th>
<th>$b_a$ mV/decade</th>
<th>LPR Ohm cm$^2$</th>
<th>$I_{corr}$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCPS</td>
<td>-842</td>
<td>131</td>
<td>145</td>
<td>41473</td>
<td>7.237x10^{-7}</td>
</tr>
<tr>
<td>SCPS+citric acid 250ppm+zn2+50ppm</td>
<td>-822</td>
<td>140</td>
<td>157</td>
<td>46366</td>
<td>6.948x10^{-7}</td>
</tr>
</tbody>
</table>
Further, the LPR value increases from 41473 ohm cm\(^2\) to 46366 ohm cm\(^2\); the corrosion current decreases from 7.237x10\(^{-7}\) A/cm\(^2\) to 6.948x10\(^{-7}\) A/cm\(^2\). When a passive film formed on mild steel surface, in presence of inhibitor system the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

### 3.3 Analysis of AC Impedance spectra:

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance decreases and the impedance log (z/ohm) value increases [22-32]. The AC impedance spectra of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitors (CA- Zn\(^{2+}\)) are shown in Fig 4. (Nyquist plots) and Figures 4 and 5. (Bode plots). The AC impedance parameters namely charge transfer resistance (R\(_{t}\)) and double layer capacitance (C\(_{dl}\)) derived from Nyquist plots are given in table 4. The impedance log (z/ohm) values derived from Bode plots are also given in table 4.

#### Table-4

Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from AC impedance spectra.

<table>
<thead>
<tr>
<th>System</th>
<th>Nyquist plot</th>
<th>Bode plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rt, Ohm cm(^2)</td>
<td>C(_{dl}) F/cm(^2)</td>
</tr>
<tr>
<td>SCPS</td>
<td>566</td>
<td>9.013x10(^{-9})</td>
</tr>
<tr>
<td>SCPS+citric acid 250ppm+Zn(^{2+}) 50ppm</td>
<td>1291</td>
<td>3.9519x10(^{-9})</td>
</tr>
</tbody>
</table>

It is observed that when the inhibitors Citric acid (250ppm) + Zn\(^{2+}\) (50 ppm) are added to SCPS the charge transfer resistance (R\(_{t}\)) increases from 566 ohm cm\(^2\) to 1291 ohm cm\(^2\). The C\(_{dl}\) value decreases from 9.013x10\(^{-9}\) F/cm\(^2\) to 3.9519 x 10\(^{-9}\) F/cm\(^2\). The impedance values [log (z/ohm)] increases from 2.86 Z/ohm to 3.22 Z/ohm. These results lead to the conclusion that a protective film is formed on the metal surface.
Figure 4: AC Impedance curves of mild steel immersed in various test solution (Nyquist plots)

a) SCPS
b) SCPS + Citric acid 250 ppm + Zn2+ 50 ppm
Figure 5(a): AC impedance spectra of mild steel immersed in SCPS (Bode plots)
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3.4 Analysis of FTIR spectra:

The FTIR spectra were used to analyze the inhibitor film formed on mild steel.[33-38]. The FTIR spectrum of the pure citric acid (Fig 6 a) is compared with the FTIR spectrum of film formed on the metal surface after immersion in SCPS prepared in well water containing 250 ppm of citric acid and 50 ppm of Zn\textsuperscript{2+} (Fig6b). The results showed that the OH stretching frequency of pure citric acid appears at 3425 cm\textsuperscript{-1} where as in the SCPS containing 250 ppm of citric acid and 50 ppm of Zn\textsuperscript{2+} system, the stretching frequency has shifted from 3425 cm\textsuperscript{-1} to 3339 cm\textsuperscript{-1}. In case of C=O, the stretching frequency which appeared at 1733 cm\textsuperscript{-1} for citric acid has disappeared for the SCPS system containing 250 ppm of citric acid and 50 ppm of Zn\textsuperscript{2+} system. This confirms that the oxygen atom of carboxyl group has coordinated with Fe\textsuperscript{2+} resulting in the formation of Fe\textsuperscript{2+}-citric acid complex formed on the metal surface. And also, the peak appearing at 1589, 1023 and 599 cm\textsuperscript{-1} confirmed the presence of calcium carbonate, calcium oxide and calcium hydroxide formed on the metal surface [39-45].
Figure 6(a): FTIR spectrum of Pure Citric acid
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4. Conclusion

The present study leads to the following conclusions:

i. The formulation consisting of 250 ppm of citric acid and 50 ppm of Zn$^{2+}$ offers 88% IE to mild steel immersed in simulated concrete pore solution prepared in well water.

ii. Polarization study reveals that citric acid system controls the anodic reaction predominantly.

iii. AC impedance spectra reveal that the formation of protective film on the metal surface.

iv. FTIR spectra reveals that the inhibitive film consists of Fe$^{2+}$-citric acid complex, calcium carbonate, calcium oxide and calcium hydroxide.

5. ACKNOWLEDGEMENT

The authors are thankful to their respective managements.
6. Reference

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