Corrosion resistance of mild steel in simulated concrete pore solution in presence of chloride ion

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\textbf{ABSTRACT}
Corrosion resistance of mild steel in simulated concrete pore solution in the presence and absence of 4000 ppm of chloride ion has been evaluated by weight loss method. The experiments have been carried out in presence of corrosion inhibitor such as Tri sodium citrate (TSC). It is observed that when 200 ppm of TSC is added 81\% inhibition efficiency is obtained for the 4000 ppm chloride system. In the absence of chloride system, the corrosion inhibition efficiency is 99\%. VIBGYOR coloured film were observed on the metal surface. The mechanistic aspects of corrosion inhibition have been investigated by Electrochemical studies such as polarization study and AC impedance spectra. It is observed that in the presence of inhibitor LPR value increases, corrosion current decreases, charge transfer resistance increases, Impedance value increases.
Double layer capacitance value decreases. It is concluded that addition of TSC increases corrosion resistance of mild steel in simulated concrete pore solution which is nothing but a saturated solution of Ca(OH)$_2$.

**Keywords:** Simulated concrete pore solution, mild steel, corrosion inhibition, TSC(Tri sodium citrate), Electrochemical studies.

**INTRODUCTION**

Reinforced concrete is widely used for building materials. It plays a significant role in economic development. However, the premature degradation of reinforced concrete structures due to the reinforcing steel corrosion has become a serious problem in modern society, which results in a huge economic loss[1-5]. Under normal conditions, reinforcing steel in concrete can be protected from corrosion by forming a compact passive film on its surface in concrete pore solution with high alkalinity (pH 12.5-13.5). However, the passive film can be locally damaged and the localized corrosion of reinforcing steel takes place when pH and/or the chloride concentration at the steel/concrete interface reach the critical values for corrosion[6-9]. The pH of concrete pore solution decreased during concrete carbonation due to the neutralization of Ca(OH)$_2$ in the interstitial solution with the acidic gases (CO$_2$, SO$_2$, etc.) which diffuse into the steel/concrete interface from the air[10]. The pH value of concrete pore solution is one of the most important parameters affecting the corrosion behaviour of reinforcing steel in concrete.

In spite of the extensive studies of corrosion behaviours of reinforcing steel[11-14], exact mechanism of its depassivation is still unclear. Even though the effect of pH on the corrosion of reinforcing steel was discovered decades ago, there were only a few studies focusing on the depassivation of the steel caused by decreasing pH of concrete pore solution during the carbonation process[15-19]. In the urban and industrial areas, the acidic gases (CO$_2$, SO$_2$,NO$_2$, etc.) can make the local atmosphere acidic, and attack the hydrated concrete. The reactions of neutralization in concrete may decrease the pH value of concrete pore solution, induce the steel surface depassivation, and consequently cause the steel corrosion.

Several research papers have investigated the corrosion behaviour of metals in presence of simulated concrete pore (SCP) solutions[20-24].Pandiyarajan et al[25-29] and Shanthy et
Suriyaprabha et al. have studied the corrosion behaviour of metals in SCPS. Usually steel rebars have been used in such studies.

The Present Study is undertaken to investigate the corrosion of mild steel in SCPS prepared in double distilled water in presence of TSC. A saturated solution of calcium hydroxide is used as SCP solution[34-40]. Polarization study has been used to evaluate the corrosion resistance of mild steel.

MATERIALS AND METHODS

Metal specimens Preparation of 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)

Preparation of the specimens

Carbon steel specimens (0.026%P, 0.4%Mn, 0.1%C and rest iron) of the dimensions 1.0 x 4.0x 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and used for the weight-loss method.

Simulated Concrete Pore (SCP) Solution

A saturated calcium hydroxide solution is used in the present study, as SCP solution. The electrodes made of mildsteel wire were immersed in the SCP solution, polarization study and AC impedance was carried out.

Weight-loss method

Carbon steel specimens were immersed in 100mL of a solution containing 60 ppm of Cl- and various concentrations of the inhibitor in the presence and absence of Zn²⁺ for a period of 1 day. The weight of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The inhibition efficiency (IE) was then calculated using the equation

\[
IE=100\left[1-\left(\frac{w_2}{w_1}\right)\right]\%
\]

where \(w_1\)=corrosion rate in absence of the inhibitor ; \(w_2\)= corrosion rate in presence of the inhibitor

Potentiodynamic polarization study

Polarization 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. From the polarization study, corrosion parameters such as corrosion
potential (Ecorr), corrosion current (Icorr) and Tafel slopes (anodic = ba and cathodic = bc) were calculated.

**AC impedance measurements**

A CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. The real part (Z’) and imaginary (z”) of the cell impedance were measured in ohms for various frequencies. The Rt (charge transfer resistance) and Cdl (double layer capacitance) values were calculated.

**RESULTS AND DISCUSSION**

**Analysis of results of weight loss method**

The inhibition efficiency of SCPS in the absence and presence of NaCl are given in Table 1 (Fig 1). The influence of Trisodium citrate on the inhibition efficiency is also given in the table.

**Table 1. Corrosion rate (CR) of mild steel immersed in SCPS prepared in DD water, in the absence and presence of inhibitors, and the inhibition efficiency (IE%) obtained by weight loss method**

<table>
<thead>
<tr>
<th>System</th>
<th>CR(mdd)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD Water</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>SCPS</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>SCPS+ 4000 ppm NaCl</td>
<td>3.8</td>
<td>81</td>
</tr>
<tr>
<td>SCPS+ TSC(200 ppm)</td>
<td>0.4</td>
<td>98</td>
</tr>
<tr>
<td>SCPS+ TSC(200 ppm)+NaCl(4000 ppm)</td>
<td>2</td>
<td>91%</td>
</tr>
</tbody>
</table>

Immersion period: one day, CR=Corrosion Rate; IE=Inhibition Efficiency, mdd=milligram per square decimeter per day.
It is observed from the table that in presence of SCPS the corrosion inhibition efficiency is 90%. When 4000 ppm of NaCl is added to the system, the inhibition efficiency decreases to 81%. This is due to the fact that chloride ion penetrates through the pores of the protective film and attack the metal surface. When 200ppm of TSC is added to the SCPS the inhibitor efficiency increases to 98%. However when 4000ppm of NaCl is added to the system, the inhibition efficiency decreases from 98% to 91%. This is due to the attack of chloride ion penetrates through the pores of the protective film and attack the metal surface.

Thus weight loss study leads to the conclusion that in presence of chloride ion the inhibition efficiency decreases. In presence of TSC the inhibition efficiency increases.

**Analysis of polarization curves**

Electrochemical studies such as polarization study have been used to detect the formation of protective film on the metal surface [41-43]. When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current (I$_{corr}$) decreases. The potentiodynamic polarization curves of carbon steel immersed in TSC is shown in Fig2. The corrosion parameters namely corrosion potential(E$_{corr}$), Tafel slopes (b$_c$=cathodic ; b$_a$=anodic), linear polarization resistance (LPR) and corrosion current
Suriyaprabha et al.,

are given in Table 1, when carbon steel is immersed in an SCPS; the corrosion potential is -930 mV vs SCE. The formulation consisting of 200 ppm of TSC shifts the corrosion potential to -831 mV vs SCE. This suggests that the reaction is predominantly controlled. The LPR value anodically increases from 6947.0 ohm cm$^2$ to 14218.1 ohm cm$^2$. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 5.366$x10^{-6}$ A/cm$^2$ to 2.924$x10^{-6}$ A/cm$^2$.

**Table 2.** Corrosion parameters of mild steel immersed in simulated concrete (saturated calcium hydroxide solution) pore solution obtained by 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 (blank)</td>
<td>-930</td>
<td>122</td>
<td>288</td>
<td>6947.0</td>
<td>5.366$x10^{-6}$</td>
</tr>
<tr>
<td>SCPS + TSC (200 ppm)</td>
<td>-831</td>
<td>127</td>
<td>388</td>
<td>14218.1</td>
<td>2.924$x10^{-6}$</td>
</tr>
</tbody>
</table>

**Figure 2.** Polarization curves of mild steel immersed in various test solution (a) SCPS (blank), (b) SCPS + TSC 200 ppm
Analysis of AC Impedance spectra

Electrochemical studies such as AC impedance spectra have been used to detect the formation of protective film on the metal surface. If a protective film is formed, the charge transfer resistance increases and the double layer capacitance value decreases, the AC impedance value increases\[44-49]. The AC impedance spectra of carbon steel immersed in TSC is shown in fig.3(Nyquist plot) and figures 4 and 5(Bode plots). The AC impedance parameters namely charge transfer resistance ($R_t$) and double layer capacitance ($C_{dl}$) are given in Table 3.

Table 3. Corrosion parameters of carbon steel immersed in various test solutions, obtained from AC impedance spectral study

<table>
<thead>
<tr>
<th>System</th>
<th>Nyquist plot</th>
<th>Bode plot</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_t$ ohm cm$^2$</td>
<td>$C_{dl}$ F/cm$^2$</td>
<td>Log ($Z$/ohm)</td>
</tr>
<tr>
<td>SCPS(blank)</td>
<td>1477.1</td>
<td>3.3850x10$^{-9}$</td>
<td>3.35</td>
</tr>
<tr>
<td>SCPS+TSC(200ppm)</td>
<td>2512.6</td>
<td>1.9899x10$^{-9}$</td>
<td>3.6</td>
</tr>
</tbody>
</table>

When carbon steel is immersed in SCPS $R_t$ value is 1477.1 ohm cm$^2$, $C_{dl}$ value is 3.3850x10$^{-9}$ F/cm$^2$ and the impedance value log ($Z$/ohm) is 3.35. When 200 ppm of TSC is added $R_t$ value increases from 1477.1 ohm cm$^2$ to 2512.6 ohm cm$^2$, $C_{dl}$ value decreases from 3.3850x10$^{-9}$ F/cm$^2$ to 1.9899x10$^{-9}$ F/cm$^2$ and the impedance value increases from 3.35. These results suggest that in presence of TSC (in the absence of chloride) corrosion resistance of carbon steel in SCPS increases. The shape of the curves in Nyquisit plot indicates the process is a diffusion controlled process.

Mass Transport mechanisms may be explained as follows. The faradaic current that flows at any time is a direct measure of the rate of the electrochemical reaction taking place at the electrode. Further, the current itself is dependent upon two things: 1) the rate at which material gets from the bulk of solution to the electrode, known as mass transport, and 2) the rate at which electrons can transfer across the interface, or charge transfer kinetics. These two processes are inexorably intertwined in the flow of current. There are three basic mechanisms of mass transport:
Diffusion: The random movement of molecules from a region of high concentration to regions of lower concentration, is called diffusion. The rate at which a molecule diffuses is dependent upon the difference in concentration between two points in solution, called the concentration gradient, and on the diffusion coefficient, D, which has a characteristic value for a specific solution species at fixed temperature.

Migration: The movement of charged particles in response to a local electric field is called migration. The contribution of migration to the total flux is proportional to the charge of the ion, the ion concentration, the diffusion coefficient, and the magnitude of the electric field gradient experienced by the ion. A change in the applied potential to a solid electrode in a solution containing ions affects charge migration.

Convection: The movement of fluids is described by hydrodynamics. Convection as it applies to electrochemistry is forced movement of solution species by mechanical (stirring) or other means. In the present study the movement of charged species such as citrate ion towards the metal surface is a diffusion controlled process combined with migration of ions.

Figure 3. AC impedance spectrum of mild steel immersed in various test solution (a) SCPS(blank) , (b) SCPS + TSC 200 ppm (Nyquist plot)
The inhibition efficiency of Trisodium citrate (TSC) in controlling corrosion of mild steel immersed in simulated concrete pore solution prepared in distilled water in the presence and absence of chloride has been evaluated by weight loss method.

The present study leads to the following conclusions.

- The formulation consisting of 2 mL TSC has 98% corrosion inhibition efficiency.
- Polarization study reveals that TSC system controls the cathodic reaction predominantly.
- AC impedance spectra reveal that the formation of protective film on the metal surface.

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REFERENCES


