International Journal of Advanced Scientific Research and Management, Volume 3 Issue 8, Aug 2018
www.ijasrm.com
ISSN 2455-6378

Surface Morphology of Protecive film formed on mild steel immersed in Simulated concrete pore solution in presence sodium tri poly phosphate

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Abstract

Corrosion inhibition of mild steel in simulated concrete pore solution (SCPS) Prepared in well water in the absence and presence of sodium tripoly phosphate (STPP) and Zn^{2+}has been evaluated by weight loss method. . It is observed that when STPP is added the corrosion inhibition efficiency (IE) increases. As the concentration of STPP increases, inhibition efficiency decreases 50 ppm of has 90 % IE . 100 ppm of STPP shows 93% IE. When 50 ppm of $Zn^{2+}$is added to the above system, both system shows 85% IE. The mechanistic aspects of corrosion inhibition have been investigated by polarization study and AC impedance spectra. The protective film formed on the metal surface is found to be SEM .

Keywords: *concrete corrosion, simulated concrete pore solution, mildsteel, sodium tripoly phosphate*.

1. Introduction

Corrosion is the destruction of metals and alloys by chemical and electro chemical reaction with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using appropriate techniques like metallic coating ,anodic protection, cathodic protection and using inhibitors etc. Inhibitors have very good role in the presence of corrosion inhibition. The organic inhibitors contain hetero atom like oxygen , nitrogen, sulphide and phosphorous. It shows better corrostion efficiency of the compounds containing hetero atom follows O<N<S<P (Thomas, 1981; Doneelly et al.,1997; Tadros & Abdel-Nab, 1998; Subramaniam et al.,1993). Application of polymers as corrosion inhibitors have been attracted several researchers (Umoren et al., 2008; Srimathi, et al., 2010, Umoren et al., 2010). Corrosion inhibition by conducting polymer has been studied (Gelling et al., 2001). It is common to use antiscalants like phosphates, poly phosphates (Rajan & Vankatath, 1997; Bahadur, 1996; Jefferies & Bucher, 1993; Beer & Ertel, 1991; Delavan & Mullins, 1984; Kuzenestsov, 2001), organophosphates (Sekine & Hirakawa, 1986; Veres et al., 1992; Galkin et al., 1995; Hirozawa, 1995, Galkin et al., 1996; Rajendran et al., 1995, 1996) etc .In industrial cooling water systems (Chaudhary, 2004). In the present work a study an antiscalant Trisodium phosphate (TSP) has been carried out to clealy understand its contribution towards corrosion control (Sastri, 1998; Bradford, 1992; Fontana & Staehle W, 1970; McCoy, 1974).

The use of polymers as corrosion inhibitors has attracted considerable attention. The inhibition efficiency of poly(vinyl alcohol) in controlling the corrosion of mild steel was investigated (Rajendran, et al., 2005; Umoren et al., 2006; Umoren et al., 2006) The inhibitors such as polyvinyl alcohol and polyethylene glycol were found to obey Temkin, Freundlich and Frumkin adsorption isotherm from the fit of the experimental data (Umoren et al., 2007). A saturated solution of calcium hydroxide is used as simulated concrete pore solution (Allaharam, et al., 2008; Mennucci , et al.,2009; Kitowsi & Wheat, 1997; Huriey & Scully, 2006; Li, 2004). The aim of the present study is to investigate the

IJASRM
International Journal of Advanced Scientific Research and Management, Volume 3 Issue 8, Aug 2018
www.ijasrm.com
ISSN 2455-6378

corrosion resistance of mild steel in simulated concrete pore solution in presence of polyvinyl alcohol and Zn^{2+}combination to carbon steel in well water. The physico-chemical parameters of the well water taken in preset study are given Table-1. The corrosion inhibition efficiency was collected using weight loss, polarization and AC impedance studies. The protective film formed on the metal surface characterized using morphological studies such as scanning electron microscopy (SEM) .

Table 1. Parameters of well water.

Parameters	Value
pH	8.38
Conductivity	1770µ_-1cm-1
Chloride	665 ppm
Sulphate	214 ppm
TDS	1100 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

2. Experimental Methods

2.1 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[26]) of the dimensions 1.0X4.0X0.2 cm were polished to a mirror finish and decreased with trichloroethylene and used for the weight loss method.

2.2 Simulated concrete pore solution (SCPS)

A saturated calcium hydroxide solution is used in the present study as SCP solution. The electrodes made of mild steel wire were immersed in the SCP solution Polarization study and AC impedance spectra was carried out.

2.3 Mass-loss method

Mild steel specimens in triplicate were immersed in 100 ml of simulated concrete pore solution (SCPS) containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY 210. The corrosion products were cleansed with Clarke's solution.[27].Thenthe inhibition efficiency (I.E.) was then calculated using the equation (1)

I.E = 100 [1-(W2/W1)] % ……………(1)

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively. The corrosion rate (CR)was calculated using the formula (2)

CR= [(Weight loss in mg)/(Area of the specimens in dm^2ximmersion period in days)mdd---(2)

2.4 Potentiodynamic Polarization

Polarization stud was carried out in Electrochemical impedenceAnalysermodel CHI 660 A using a three electrode cell assembly was used.Theworing electrode was used as a rectangular specimen of mild steel with the one face of the electrode of constant $1cm^2$ area exposed.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(E_{corr}) correction current(I_{corr}) and tafel slopes (anodic= ba and cathodic=bc)were calculated

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was the same. The real part (Z^1) and imaginary part (Z^{11}) of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

2.5 Surface Examination study

The mild steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of film formed on the surface of metal specimens was analysed by surface analysis technique, SEM .

2.6 Scanning Electron Microscopy

The mild steel specimens immersed in various test solutions for one day were taken out , rinsed with double distilled water , dried and subjected to the surface examination .The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy (SEM) using HITACHI –S-3000H SEM .

3. Results and Discussion

3.1 Analysis of weight loss study

The calculated inhibition efficiencies (IE) and corrosion rates (CR) STPP in controlling corrosion mild steel immersed in simulated concrete pore solution in the absence and presense of Zn^{2+} ion are given in Table 2.The calculated value indicates the ability of STPP to be a good corrosion inhibitor. 50 ppm STPP shows 90 % IE. As the concentration of CMCincreases, 100 ppm STPP shows 93 % IE . The inhibition efficiency decreases and the corrosion rate increases

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 8, Aug 2018
www.ijasrm.com
ISSN 2455-6378

Table 2 -Inhibition efficiencies (IE%) and corrosion rates (CR) obtained from STPP -Zn^{2+} system, when mild steel immersed in saturated concrete pore solution prepared in well water

System	*IE* %	*CR* mdd
50 ppm STPP	90	3.9
100 ppm STPP	93	2.7
50 ppm STPP +Zn^{2+} 50 ppm	85	5.8
100 ppm STPP +Zn^{2+}50 ppm	85	5.8

3.2 Analysis of polarization curves

The potentiodynamic polarization curves of mild steel immersed in simulated concrete pore solution prepared in well water in the absence and presence of inhibitor are shown in Figure-1. The corrosion parameters such potential(E_{corr}) ,Tafel slopes (b_c= cathodic ; b_a= anodic),Linear polarization resistance(LPR) and corrosion current (I_{corr}) are given in Table –3.When mild steel is immersed in SCPS the corrosion potential is -591 mV vs SCE (Saturated calomel electrode) When 100 ppm of STPP are added to the above system the corrosion potential shifted to the cathodic site -636 mV vs SCE . This indicates that the STPP system control the cathodic reaction predominantly. Further, the LPR value increase from 7965 ohmcm^{2}to 18362ohmcm^2 ,the corrosion current decreases from 4.187 x10^{-6}A/cm^2 to 1.884 x10^{-6}A/cm^2. Thus polarization study confirms the formatiom of a protective film on the metal surface.The anodic reaction is controlled by the formation of STPP confirms on the anodic sites. The cathodic reaction (generation of OH^-) is controlled by the formation of $Zn(OH)_2$on the cathodic sites the metal surface.Thus anodic reaction and cathodic reaction are controlled.

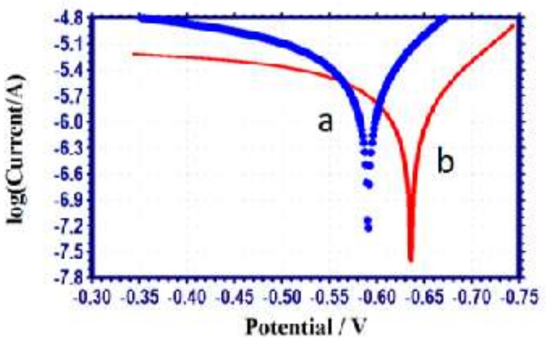

Figure 1. Polaraization curves of mild steel immersed in various test solution (a) SCPS(blank)
(b) SCPS + STPP 100 ppm

3.3 Analysis of AC impedance spectra

AC impedance spectra of mild steel immersed in simulated concrete pore solution prepared in well water in the absence and presence of inhibitor and Zn^{2+} are shown in the figs 2 to 4. Thenquist plots are shown in Fig 2. The Bode plots are shown in Fig 3 and 4 . The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values are derived from Nquist plots Impadancevalues , log (z / ohm) are derived from bode plots .The results are summarized in Table 3 .

When corrosion rate decreases .due to formation of protective film, the charge transfer resistance value increases and double layer capacitance value decreases, the impedance value log (z/ohm) increases . It is observed from Table 3 ,the $R_t$value 3045 ohm. cm^2, the C_{dl} Value is 6.305 x 10^{-9} Fcm^{-2} and the impedance value is 3.4 log (z/ ohm).

Table 3- Corrosion Parameters of mild steel immersed in SCPS prepared well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

System	Ecorr mV vs. SCE	b_c mV/decade	b_a mV/decade	LPR ohmcm^2	Icorr Acm^{-2}
SCPS (blank)	-591	107	269	7965	4.187 x10^{-6}
SCPS + 100 ppm STPP	-636	108	299	18362	1.884 x10^{-6}

Table 4. :Impadance parameters of metals immersed in simulated concrete pore solution prepared in well water, obtained by AC impedance spectra

System	Nquist plot		Bode plot log (z/ ohm)
	R_t ohm. cm^2	C_{dl} Fcm^{-2}	
SCPS (blank)	3045	6.305x 10^{-9}	3.4
SCPS + 100 ppm STPP	7919	2.4245 x 10^{-9}	3.8

When 50 ppm PVA and 50ppm $Zn^{2+}$are added to simulated concrete pore solution . The $R_t$value 7919 ohm. cm^{2}increases, the C_{dl} Value is 2.4245 x 10^{-9} Fcm^{-2} decreases and the impedance value is 3.8 log (z/ ohm) increases. The increases charge transfer resistance (R_t) value ,tha double layer capacitance (C_{dl}) value decreases and the impedance value (z) increases . This confirms the formation of protective film formed on the metal surface.

3.4 Scanning Electron Microscopy

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the

IJASRM
International Journal of Advanced Scientific Research and Management, Volume 3 Issue 8, Aug 2018
www.ijasrm.com
ISSN 2455-6378

extent of corrosion of mild steel, the SEM micrographs of the surface examined. The SEM micrograph (X 500, 1000) of a polished mild steel surface (control) in figure 5 (a & b) shows the smooth surface of the metal.

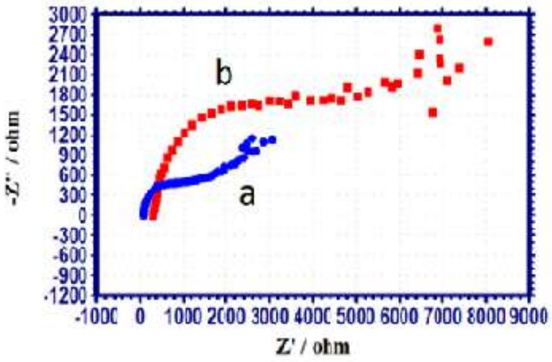

Figure 2. AC impedance spectrum of mild steel immersed in various test solution (a) SCPS (blank) (b) SCPS + STPP 100 ppm (Nquist plot)

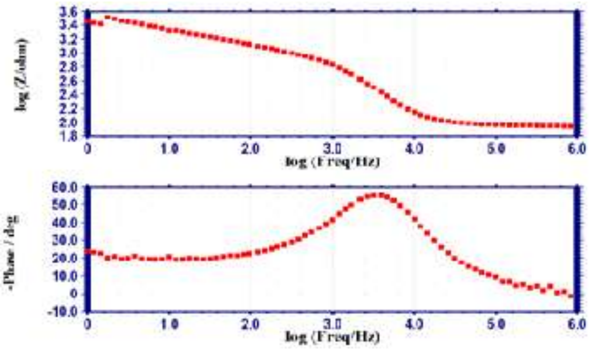

Figure 3.AC impedance spectrum of mild steel immersed in SCPS (Bode plot **)**

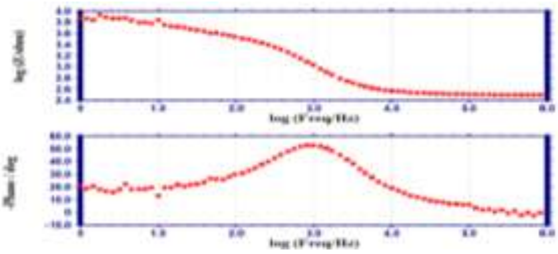

Figure 4. AC impedance spectrum of mild steel immersed in SCPS + STPP 100 ppm (Bode plot)

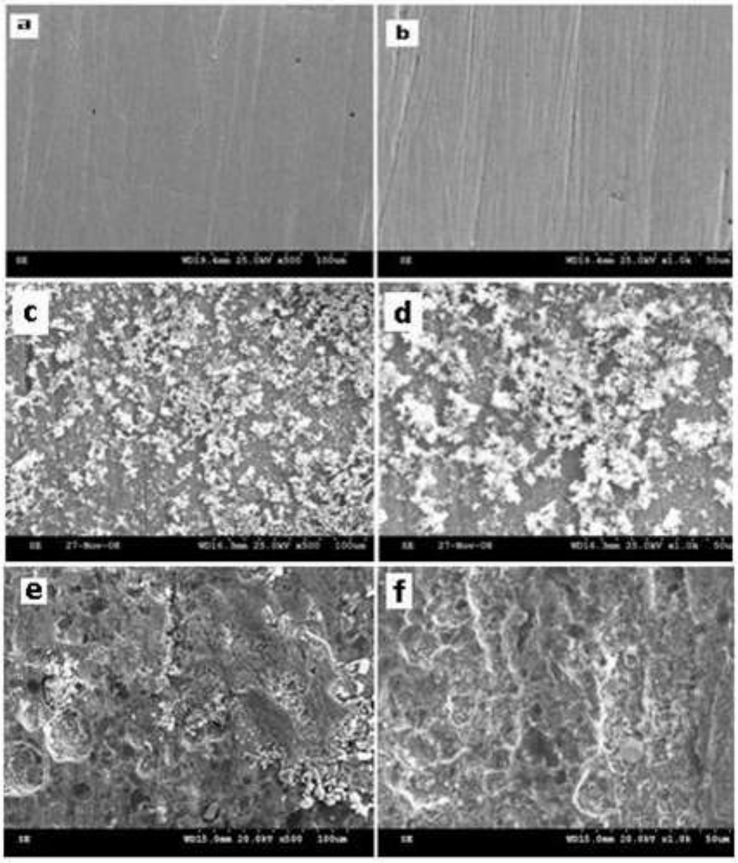

Figure 5 : SEM analysis of
a) Mild steel; Magnification X 500(control) b) Mild steel; Magnification X 1000(control)
c) Mild steel immersed in SCPS ; Magnification X 500(Blank)
d) Mild steel immersed in SCPS ; Magnification X 1000(Blank)
e) Mild steel immersed in SCPS + 100 ppm of STPP ; Magnification X 500
f) Mild steel immersed in SCPS + 100 ppm of STPP; Magnification X 1000

This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrographs (X 500 ,1000) of mild steel specimen immersed in the SCPS for one day is shown in figure 5(c & d) respectively .
The SEM micrographs of mild steel surface immersed in the SCPS is shown in figure 4 (b). This shows the roughness of the metal surface which indicates the corrosion of mild steel in SCPS. The figure 5 (e & f) indicates that in the presence of 100 ppm STPP and SCPS , the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface

4. Conclusion

The present study leads to the following conclusions:

1) The formulation consists of 100 ppm of STPP offers 93% IE to mild steel immersed in simulated concrete pore solution prepared in well water

2) Polarization study control the cathodic reaction predominantly.

3) AC impedance spectra reveal that the formation of protective film formed on the metal surface.

4) SEM study confirms the formation of protective film on the metal surface and hence the corrosion process is inhibited

Acknowledgement
The authors are thankful to their management and university grants commission, India, for the help and encouragement.

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