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Corrosion behaviour of carbon steel in sodium nitrate solution

Corrosion behaviour of carbon steel in double distilled water, in the presence of various concentration of sodium nitrate (SN) have been evaluated by weight loss method, polarization study, AC impedance spectra, cyclic voltammetry, time vs current plots, and time vs potential plots. As the concentration of SN increases corrosion rate also increases. In the lower concentration regions (less than 500 ppm of SN) general corrosion takes place. Around 700 ppm of sodium nitrate (SN), SCC begins to start.

INTRODUCTION

Stress – corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium [1]. Many investigators have classified all cracking failures occurring in corrosive medium as stress-corrosion cracking including failures due hydrogen embrittlement. However, these two types of cracking failures respond differently to environmental variables.

The phenomena of SCC were generally observed in carbon steels and low alloy steels, especially in a series of high alloy steels, which contracted directly with nitrate solution in most equipments of chemical industries Besides, they also appeared often in steel structure of concrete for nitrogenous fertilizer factories [2], in underground pipe lines [3] and in hot blast stores [4, 5].

The influence of various factors on SCC of carbon steel and low alloy steel has mainly been investigated under constant load or constant strain is higher temperature, ranging from 90°C to boiling point [6-8]. In recent years it was found that at the ambient temperature and in the lower concentration of nitrate solution the carbon steels and low alloy steels suffered from SCC, although the mechanical stress was lower than the yield strength [2,3]. The carbon steel in nitrate solution could also give rise to non-classical SCC besides classical SCC. It had no critical potential for the anodic polarization [8,9].

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The association between sodium nitrate solution and SCC has been widely discussed in several websites [10–20]. SCC is observed in waste Heat recovery boilers [10,11], fasteners [14], aerospace applications [13] and high level radioactive waste tanks [14]. According to some authors sodium nitrate mitigate SCC [11,15] and some researchers report the SCC induced by sodium nitrate [16-18]. Zhao Keqing observed [21] that with decreasing solution temperature and/or nitrate concentration the corrosion morphology of the material (mild steel) has changed, i.e., from stress corrosion cracking into a general corrosion.

The present work is undertaken (i) to investigate whether sodium nitrate solution induces corrosion or not and (ii) to find out the optimum concentration of sodium nitrate at which SCC changes into general corrosion. Weight loss study and electrochemical studies like polarization, AC impedance, cyclic voltammetry, time vs potential curves and time vs current curves have been used in this study.

EXPERIMENTAL

Preparation of the specimen

Carbon steel (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest Fe) specimens were polished to a mirror finish and degreased with trichloroethylene. They were used for weight loss study. The surface area of the exposed metal surface was 0.5 cm², for electrochemical studies.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, model 660A. It was provided with iR compensation facility. A three-electrode cell assembly was used. The work electrode was carbon steel. A saturated calomel electrode (SCE) was the reference electrode; platinum

was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) Tafel slopes (anodic = b_a and cathodic = b_c) and linear polarization resistance (LPR) were calculated. During the polarization study, the scan rate (v/s) was 0.01; Hold time at Ef(s) was zero and quiet time (s) was 2.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated. AC impedance spectra were recorded with initial $E(v) = 0$; High Frequency (Hz) = 1×10^5 ; Low Frequency (Hz) = 1; Amplitude (V) = 0.005 and Quiet Time (s) = 2.

Cyclic voltammetry

Cyclic voltammograms were recorded in the same instrument used for polarization studies.

RESULTS AND DISCUSSION

Weight loss study

The corrosion rates (CR) of carbon steel immersed in test solutions containing various concentrations of sodium nitrate (SN) for one day are obtained by weight loss method shown in Fig.1. It is observed that when 50 ppm of SN is added, to double distilled water, the CR slowly decreased from 30.91 mdd to

24.55 mdd. However, when higher concentration of SN (100, 300, 500, 700 ppm) are added the corrosion rate increased. This suggests that SN accelerates corrosion.

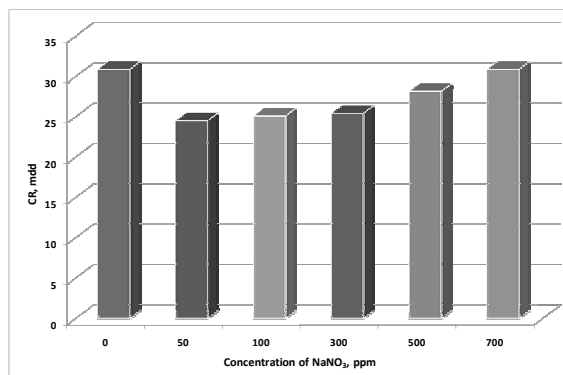


Fig.1: Corrosion rates of carbon steel in DD water in the absence and presence of various concentrations of sodium nitrate.

Polarization study

The polarization curves of carbon steel immersed in aqueous solution containing various concentrations of NaNO₃ are shown in Fig.2. The corrosion parameters such as corrosion potential (E_{corr}), cathodic Tafel slope (b_c = cathodic), anodic Tafel slope (b_a = anodic), linear polarization resistance (LPR), and corrosion current (I_{corr}) derived from these curves are given in Table 1.

Table 1 - Corrosion parameters of carbon steel immersed in aqueous solution containing various concentrations of sodium nitrate obtained by polarization study

NaNO ₃ ppm	E_{corr} mV vs SCE	b_c mV	b_a mV	LPR ohm cm ²	I_{corr} A/0.5 cm ²
0	-537	277	234	4.791×10^3	1.152×10^{-5}
50	-602	303	223	4.393×10^3	1.271×10^{-5}
100	-611	311	221	3.386×10^3	1.662×10^{-5}
300	-613	412	209	2.082×10^3	2.898×10^{-5}
500	-649	387	211	1.452×10^3	4.090×10^{-5}
700	-657	440	200	1.355×10^3	4.417×10^{-5}

It is observed that as the concentration of NaNO₃ increases the corrosion potential gradually shifts to the cathodic side. For 50 ppm of NaNO₃ the E_{corr} is -602 mV SCE and for 700 ppm of NaNO₃ the E_{corr} is 657mV vs SCE. This is reflected in the increase in the values of cathodic Tafel slopes also (from 303 mV to 490 mV). The anodic Tafel slopes slowly decreases.

It is also observed that the LPR value gradually decreases; but the corrosion current slowly increases. These observations suggest that in presence of NaNO₃ carbon steel undergoes corrosion. Protective films are not form. Even if formed they are repaired and broken.

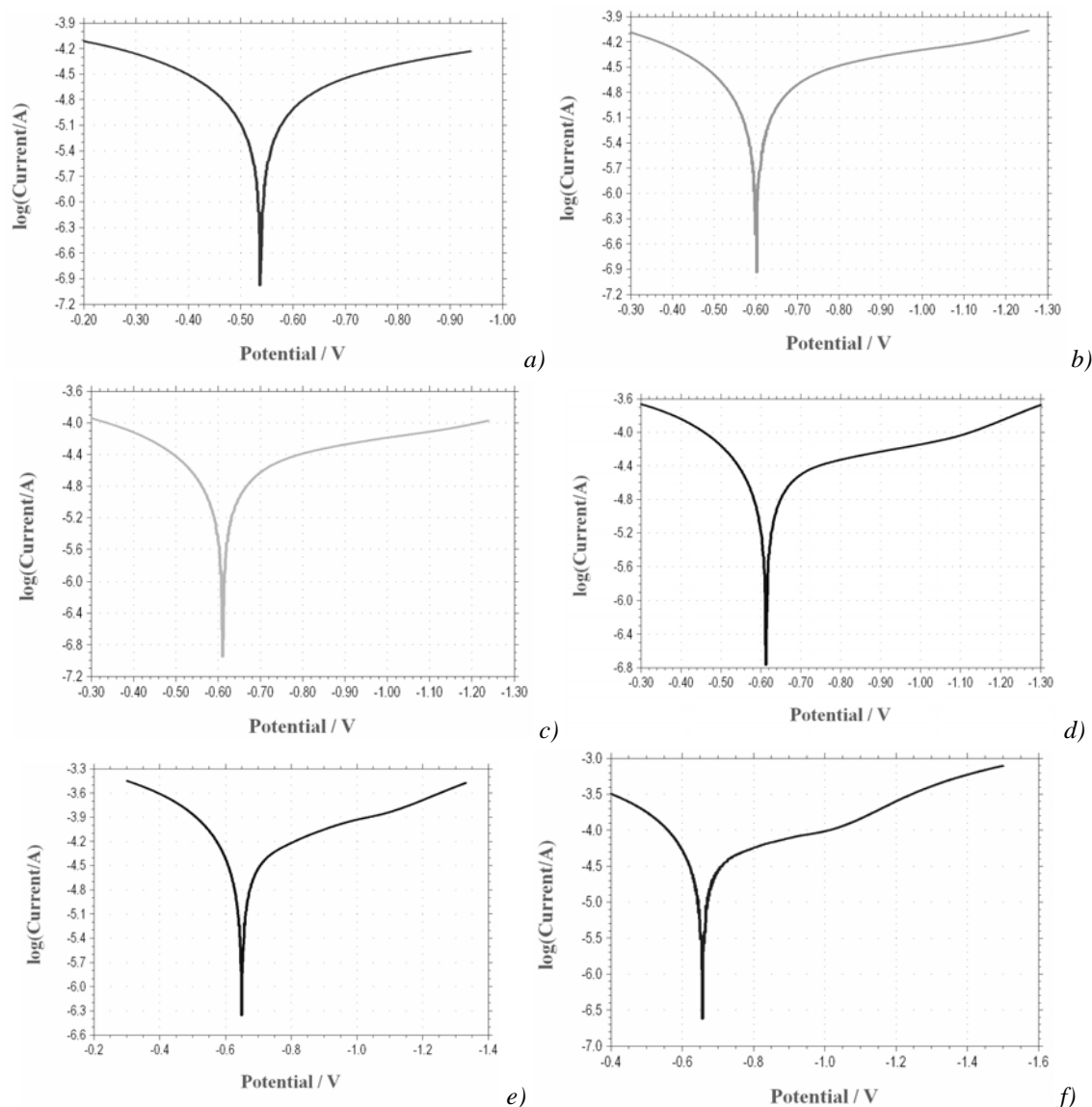


Fig.2. Polarization curves of carbon steel immersed in various test solutions: (a) DD water ($\text{NaNO}_3 = 0$ ppm), (b) 50 ppm of NaNO_3 , (c) 100 ppm of NaNO_3 , (d) 50 ppm of NaNO_3 , (e) 500 ppm of NaNO_3 , (f) 700 ppm of NaNO_3

AC impedance spectra

The AC impedance spectra of carbon steel immersed in various concentrations of NaNO_3 are shown in Fig.3. The various impedance spectra such as charge transfer resistance (R_t), and double layer capacitance (C_{dl}) derived from Nyquist plots and the impedance value [$\log(z/\text{ohm})$] derived from Bode plots are given in Table 2. It is observed that the charge transfer resistance values slowly decrease and the double layer capacitance values slowly increases. These observations suggest that protective film are not formed on the metal surface. This is in agreement with the conclusion derived from the polarization study. This view is further supported by the fact the impedance

values [$\log(z/\text{ohm})$] decrease as the concentration of NaNO_3 increases.

Table 2 - AC impedance parameters of carbon steel immersed in aqueous solution containing various concentrations of sodium nitrate

NaNO_3 ppm	R_t $\Omega \text{ cm}^2$	C_{dl} $\mu\text{F}/0.5\text{cm}^2$	Impedance $\log(z/\text{ohm})$
0	3100	2.992×10^{-9}	3.477
50	2378	3.810×10^{-9}	3.370
100	1673	5.415×10^{-9}	3.249
300	870	1.041×10^{-8}	2.973
500	699	1.296×10^{-8}	2.873
700	486	1.864×10^{-8}	2.693

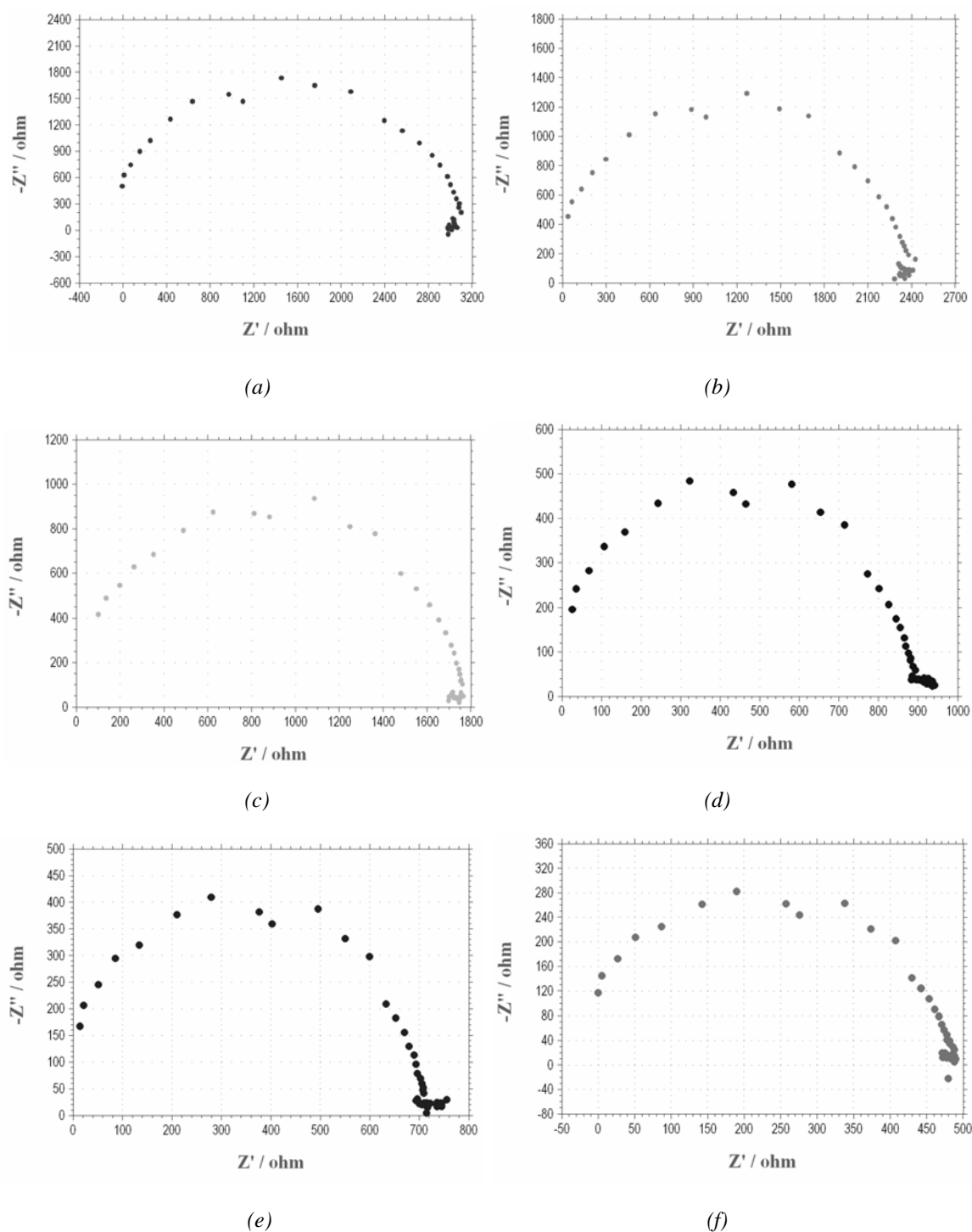


Fig. 3. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist Plot): (a) DD water ($\text{NaNO}_3 = 0$ ppm), (b) 50 ppm of NaNO_3 , (c) 100 ppm of NaNO_3 , (d) 500 ppm of NaNO_3 , (e) 500 ppm of NaNO_3 , (f) 700 ppm of NaNO_3

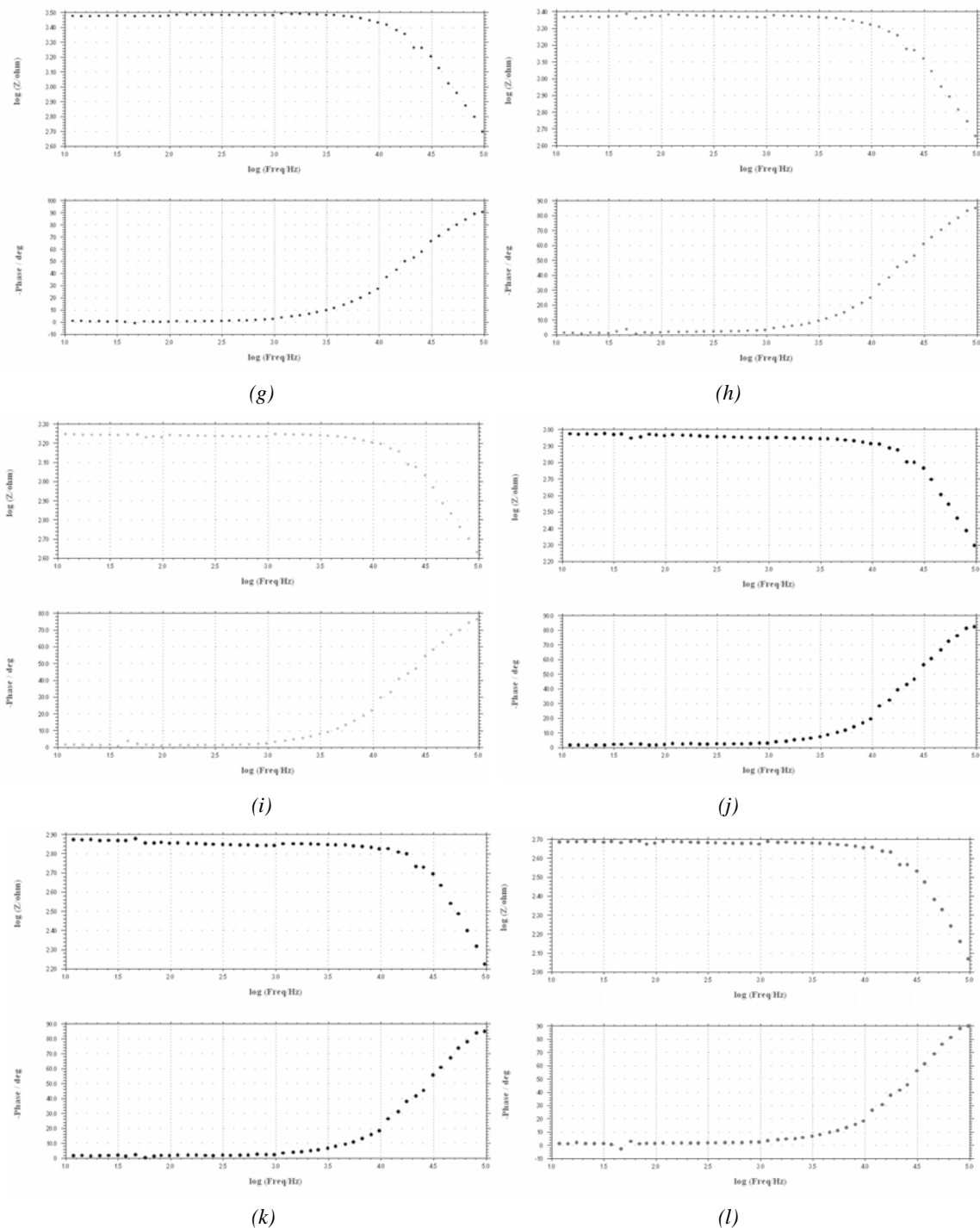


Fig. 3: AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot): (g) DD water ($\text{NaNO}_3 = 0$ ppm), (h) 50 ppm of NaNO_3 , (i) 100 ppm of NaNO_3 , (j) 300 ppm of NaNO_3 , (k) 500 ppm of NaNO_3 , (l) 700 ppm of NaNO_3

Cyclic voltammograms

The cyclic voltammograms of carbon steel immersed in various test solutions are shown in Fig.4. It

is observed that no redox couples and characteristic peaks are observed under the given set of experimental conditions.

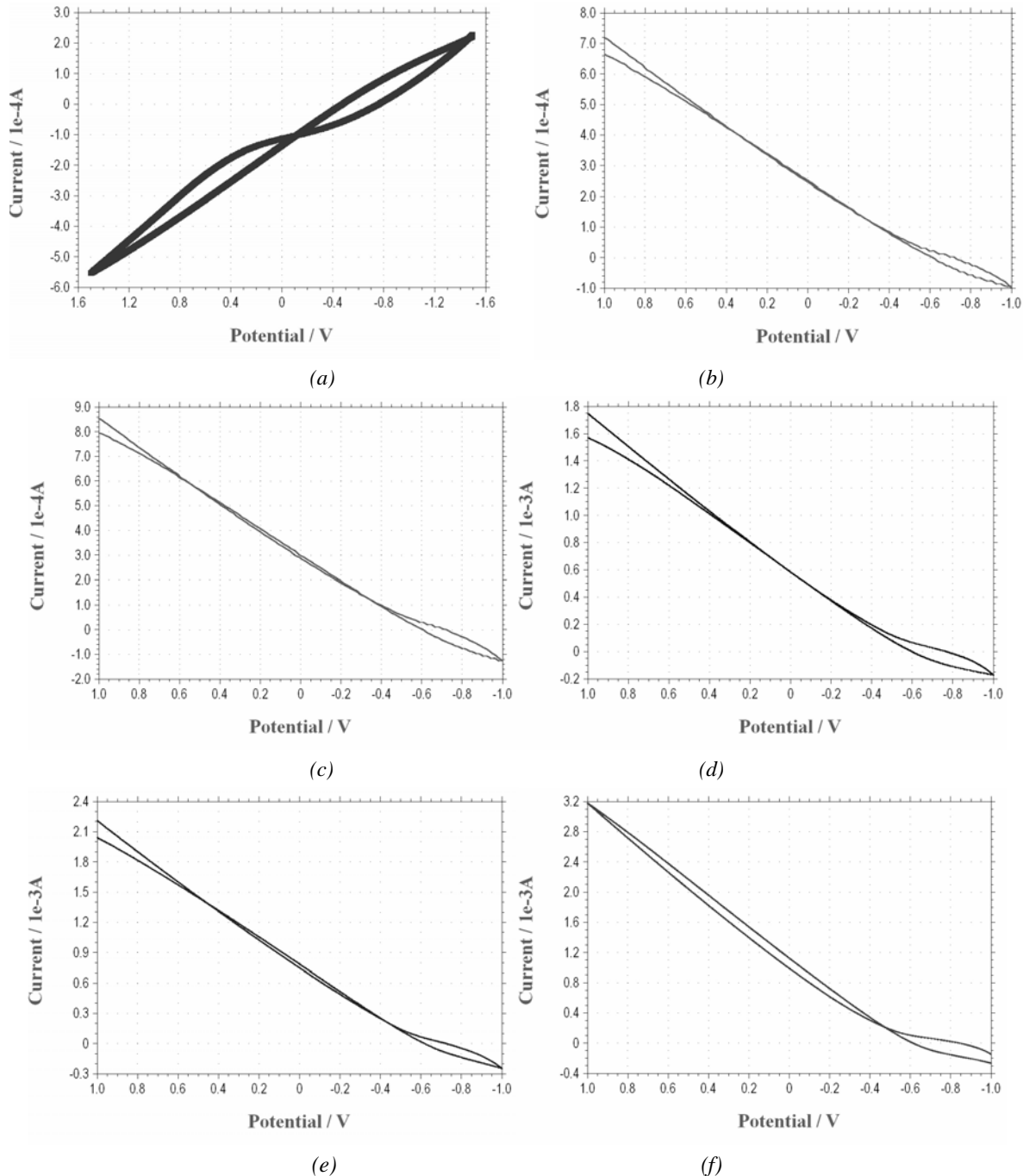


Fig.4: Cyclic voltammograms of carbon steel immersed in various test solutions:
 (a) DD water ($\text{NaNO}_3 = 0$ ppm), (b) 50 ppm of NaNO_3 , (c) 100 ppm of NaNO_3 , (d) 300 ppm of NaNO_3 ,
 (e) 500 ppm of NaNO_3 , (f) 700 ppm of NaNO_3

Time vs current plots

Time vs current plots for various time vs current plots for carbon steel immersed in various concentrations of NaNO_3 , for a period of sixty seconds are shown in Fig.5. The data are shown in Table 3. It

is observed that the current increases as the concentration of NaNO_3 increase at a given time. The rate of increase of current was high in the case of lower concentrations of NaNO_3 . At higher concentration, the rate was less. At 700 ppm of NaNO_3 , the rate was lesser. It almost remains constant.

Table 3- Variation of current ($A/0.5 \text{ cm}^2$) with Time (s)

NaNO ₃ ppm	Time, s							
	0	2	10	20	30	40	50	60
50	1.625×10^{-4}	1.444×10^{-4}	1.735×10^{-4}	1.935×10^{-4}	2.079×10^{-4}	2.185×10^{-4}	2.277×10^{-4}	2.354×10^{-4}
100	1.997×10^{-4}	1.698×10^{-4}	2.217×10^{-4}	2.512×10^{-4}	2.675×10^{-4}	2.785×10^{-4}	2.856×10^{-4}	
500	4.965×10^{-4}	4.412×10^{-4}	5.831×10^{-4}	6.485×10^{-4}	6.928×10^{-4}	7.250×10^{-4}	7.421×10^{-5}	
700	9.614×10^{-4}		10.47×10^{-4}	10.69×10^{-4}	10.78×10^{-4}	10.84×10^{-4}	10.90×10^{-4}	10.95×10^{-4}

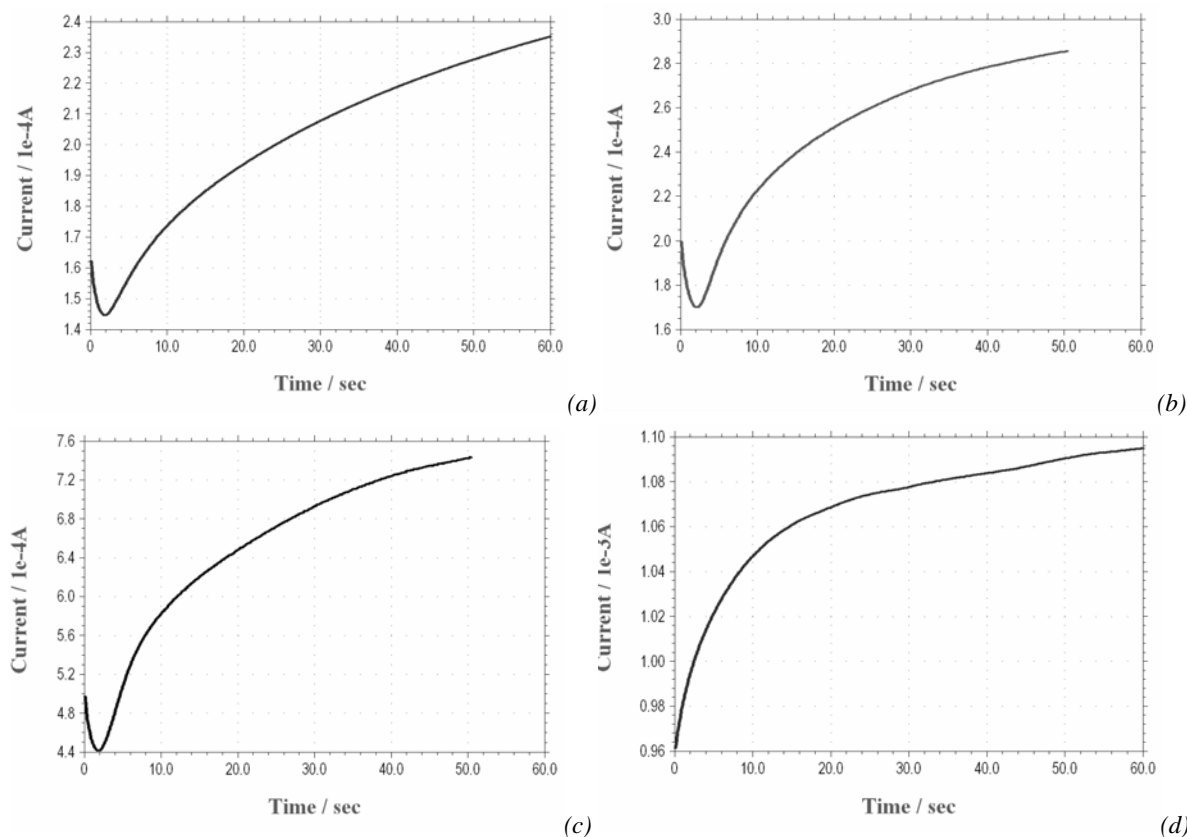


Fig. 5: Time vs Current curves of carbon steel immersed in various test solutions: (a) 50 ppm of NaNO₃, (b) 100 ppm of NaNO₃, (c) 500 ppm of NaNO₃, (d) 700 ppm of NaNO₃

Time vs potential curves

Time vs potential curves of carbon steel immersed in solutions contain various concentrations of NaNO₃ are shown in Fig.6. The data are given in Table 4. It is observed that as the period of immersion increases, the potential shifts to cathodic side. As the concentration of NaNO₃ increases the final potential (at 60 seconds) also increases. There is much difference between the initial potential ($t = 03$) and the final potential ($t = 60$ s). However it is interesting to note that when the concentration of NaNO₃ is 700 ppm the potential remains almost same. At 10th

second, the potential slightly increased and remained almost constant upto 40th sec. At 50th second there is a drop in potential. It seems that stress corrosion cracking starts to take place around 700 ppm of NaNO₃. At 10th second, SCC starts. It propagates upto 40th second. It is likely to complete by 50th second. The constant potential is an indication of SCC, after which the failure of the specimens take place. Similar observation has been made by Zhao Keqing with Type Q_{ST} 32-3 mild steel immersed in 1 mole NaNO₃ solution at 70°C, when the potential is referenced to Hg/Hg₂ Cl₂ solution [21]. This fact is further sup-

ported by the study of Trabanelli et al., regarding the intergranular stress corrosion cracking of sensitized AISI 304 by fluoride ions. They found that the corrosion potential remained the same till the rupture [22].

Table 4 - Variation of potential (mV) with Time (s)

NaNO ₄ ppm	Time, s						
	0	10	20	30	40	50	60
50	-581	-587	-591	-594	-597	-599	-600
100	-605	-609	-612	-613	-614	-614	-614
300	-598	-604	-609	-613	-616	-619	-620
500	-596	-603	-608	-613	-617	-620	-623
700	-628	-631.3	-631	-631	-630	-629	

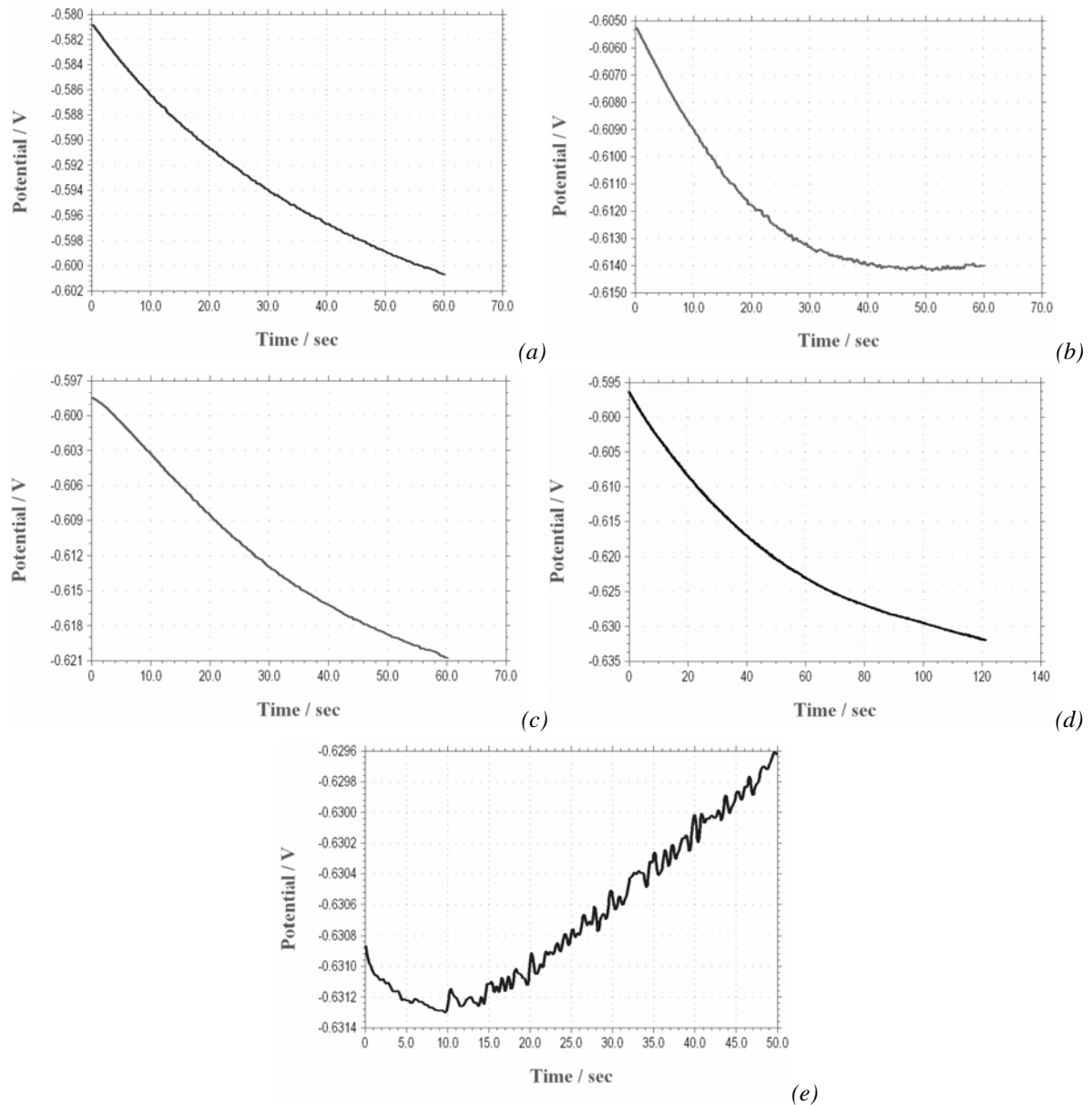


Fig.6: Time vs potential curves of carbon steel immersed in various test solutions: (a) 50 ppm of NaNO₃, (b) 100 ppm of NaNO₃, (c) 300 ppm of NaNO₃, (d) 500 ppm of NaNO₃, (e) 700 ppm of NaNO₃

Of all the electrochemical methods used, the time vs potential offers a due to know the concentration at which uniform corrosion changes into stress corrosion cracking.

This observation is in agreement with the report [21] that with decreasing solution temperature and/or nitration concentration the corrosion morphology of a materials has changed i.e., from stress corrosion cracking into a general corrosion.

The present study leads to the conclusion that at lower concentrations of NaNO_3 (less than 500 ppm) the corrosion is of general in nature; around 700 ppm of SCC begins to start.

CONCLUSION

Corrosion behaviour of carbon steel in double distilled water, in the presence of various concentration of sodium nitrate (SN) have been evaluated by weight loss method, polarization study, AC impedance spectra, cyclic voltammetry, time vs current plots, and time vs potential plots. The present study leads to the following conclusions :

- As the concentration of SN increases corrosion rate also increases.
- In the lower concentration regions (less than 500 ppm of SN) general corrosion takes place.
- Around 700 ppm of sodium nitrate, SCC begins to start.

Acknowledgement

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