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EFFECT OF NITRITE ION ON CORROSION INHIBITION OF MILD STEEL IN SIMULATED COOLING WATER

Siragul Karim[1], C. M. Mustafa[1], Md. Assaduzzaman[1], Mayeedul Islam[*,2]

[1] *Dept. of Applied Chemistry and Chemical Technology, University of Rajshahi, Rajshahi-6205, Bangladesh*
[2] *Dept. of Chemistry, Rajshahi University of Engineering and Technology, Rajshahi-6204, Bangladesh*

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Abstract: Corrosion inhibition of mild steel by sodium nitrite in simulated cooling water (SCW) containing chloride ion was investigated. Electrochemical techniques such as corrosion potential (E_{corr}) measurement and potentiodynamic sweep experiments were used. The experimental parameters were concentration of the inhibitor, pH of the aqueous media and soaking time. Nitrite inhibited mild steel corrosion in near neutral and alkaline (pH 6 and above) SCW and accelerated corrosion in acidic media (pH 4 and below). Inhibition activity increased with the increase of nitrite concentration up to 500 ppm, and afterwards remained more or less constant at pH 6 and above. In stagnant SCW, maximum corrosion inhibition was observed at pH 8 for all concentration of $NaNO_2$. Inhibition action of $NaNO_2$ was found to increase with the increase of soaking time up to 24 hours, and afterwards it remained more or less constant at all nitrite concentrations at and above pH 6. Based on the experimental results, mechanisms of action of $NaNO_2$ on mild steel corrosion inhibition in SCW have been proposed.

Keywords: *Corrosion, Potentiodynamic sweep, Inhibitor*

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1. Introduction

Cooling water is an integral part of most of the chemical process and many other industries. This contains aggressive ions which cause corrosion problems in boilers, condensers, heat exchangers, pipe lines, economizers etc. Simulated Cooling Water (SCW) having composition 300 ppm Cl^-, 351 ppm SO_4^{2-}, 37 ppm CO_3^{2-}, and 123 ppm HCO_3^- represents cooling water in industry [1]. Use of inhibitors in controlling corrosion in cooling water systems is the most convenient and economic method compared to others [2]. Among numerous inorganic and organic inhibitors used in the last sixty years nitrite appears to be a promising oxidizing inhibitor for steel [3, 4]. It produces ferric oxide barrier on the surface of steel against corrosion. Tosun found nitrite as the best inhibitor in effectiveness among chromate, molybdate, benzoate, ascorbic acid and orthophosphate in neutral aqueous media containing 100 ppm NaCl [5]. Nitrite is also effectively used as inhibition admixture in concrete reinforcement [6–8]. Ramasubramanian reported the inhibition action of calcium nitrite on carbon steel in alkaline chloride containing media [9]. Synergistic inhibition action of nitrite in conjunction with chromate, molybdate, ascorbic acid, benzoate, ortho phosphate has been reported in the literature [9–12]. Most of the investigations on the inhibition effects of nitrite have been carried out in chloride free or in low chloride neutral or alkaline aqueous environment in ideal condition [9–12]. A systematic investigation on the corrosion inhibition of mild steel by nitrite in SCW in realistic condition can be found in the work of Mustafa et.al.[10, 12]. So, the present investigation is aimed to study the effectiveness of sodium nitrite on the corrosion inhibition of mild steel in realistic aqueous media like SCW in acidic and alkaline environment.

2. Experimentals

Commercial grade mild steel coupons (composition: 0.10 % C, 0.25 % Mn, 0.01 % Si, 0.01 % P, 0.018 % S) having dimension 4 cm × 2 cm × 0.1 cm were used in all experiments. The compositional analyses of the mild steel have been carried following the procedures described elsewhere[13]. The coupons were polished to mirror finish, degreased with acetone and rinsed in distilled water. The specimens were then insulated with synthetic paint leaving 1 cm × 1 cm area exposed for experiment. These were then dried in open air and stored in a desiccator over silica gel for subsequent use.

The base electrolyte, simulated cooling water (SCW), was prepared by dissolving 500 ppm NaCl, 520 ppm Na_2SO_4, 170 ppm anhydrous $NaHCO_3$, and 66 ppm Na_2CO_3 per liter of distilled water. Inhibitor solution was prepared by dissolving appropriate amount of sodium nitrite in the SCW. The pH of the solution was adjusted by using dilute solutions of NaOH or H_2SO_4. All reagents used in the study were analytical grade chemicals. Electrochemical cell was composed of platinum counter electrode, mild steel coupon as working electrode and saturated Ag/AgCl (SSE) as a reference electrode. The corrosion potential (E_{corr}) was measured against SSE using high impedance (1010 ohm) electrometer. The potentiodynamic experiment was made by using Hab-151 potentiostat at a scan rate of 40 mV/min.

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[*] Corresponding author, Email:mayeedul180@yahoo.com

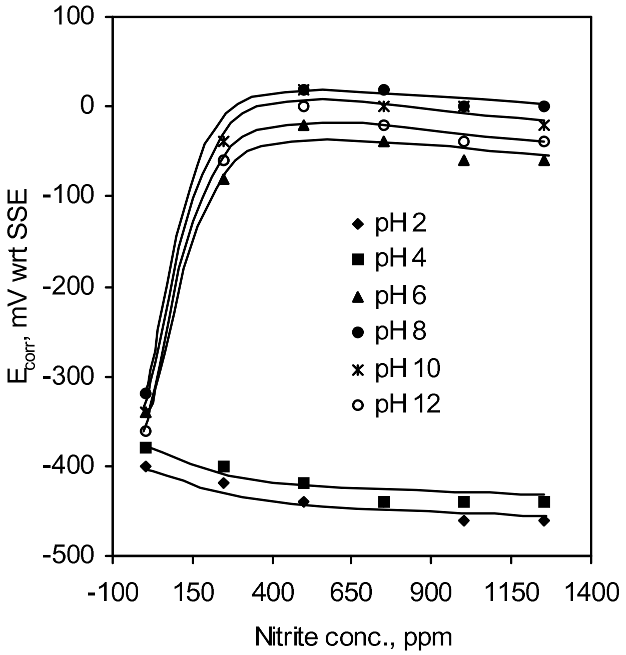

Figure 1: Effect of $NaNO_2$ conc. on the corrosion potential of mild steel. Base electrolyte SCW: soaking time 1 hr

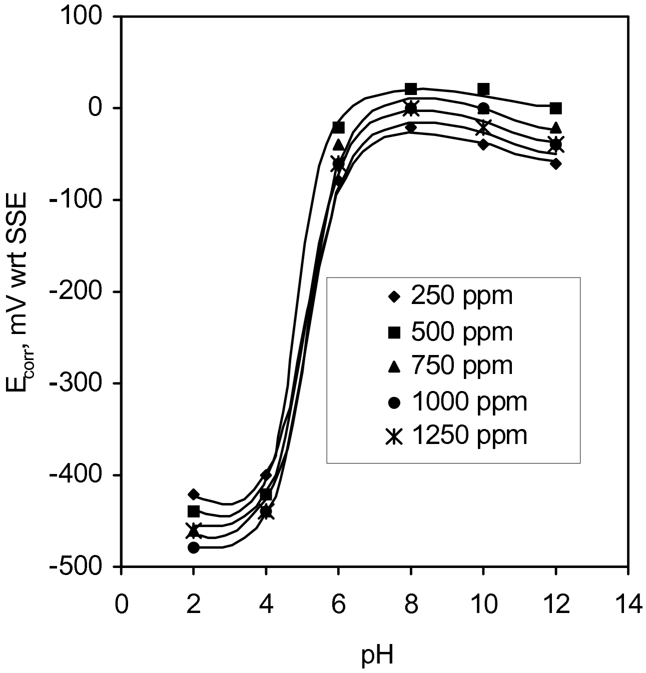

Figure 2: Effect of pH on the corrosion potential of mild steel. Base electrolyte SCW: soaking time 1 hr

3. Results and Discussion

Figure 1 shows the effect of $NaNO_2$ concentration on the corrosion potential after 1 hr. immersion. Corrosion potential (E_{corr}.) steeply increased with the increase of $NaNO_2$ concentration up to 500 ppm, and afterwards levelled off for pH 6 and above. At pH 2 and 4 corrosion potential slowly decreased with the increase of $NaNO_2$ concentration. Under identical concentration of $NaNO_2$ E_{corr} sharply increased with the increase of pH up to 8 and afterwards slowly decreased at all concentration of $NaNO_2$ as shown in Figure 2.

The effect of soaking time on the corrosion potential of mild steel in stagnant SCW containing $NaNO_2$ is shown in Figure 3. The corrosion potential increased slowly with the increase of soaking time up to 24 hours and then it remained constant up to 48 hours immersion (maximum immersion period) for pH 6 and above. No significant change in corrosion potential was found with the increase of immersion time for pH 2 and 4. As nitrite is known as an anodic corrosion inhibitor, therefore, increase of corrosion potential is an indication of corrosion inhibition. This indicates corrosion inhibition by $NaNO_2$ at pH 6 and above in stagnant SCW, and corrosion aggravation at or below pH 4. Maximum corrosion potental was found at pH 8 containing 500 ppm $NaNO_2$.

The potentiodymanic sweep on the mild steel in SCW containing $NaNO_2$ at pH 4 is shown in Figure 4. Absence of current arrest with the increase of potential is an indication of active corrosion. Early current rise at higher concentration of $NaNO_2$ shows its corrosion acceleration effect in SCW at pH 4.

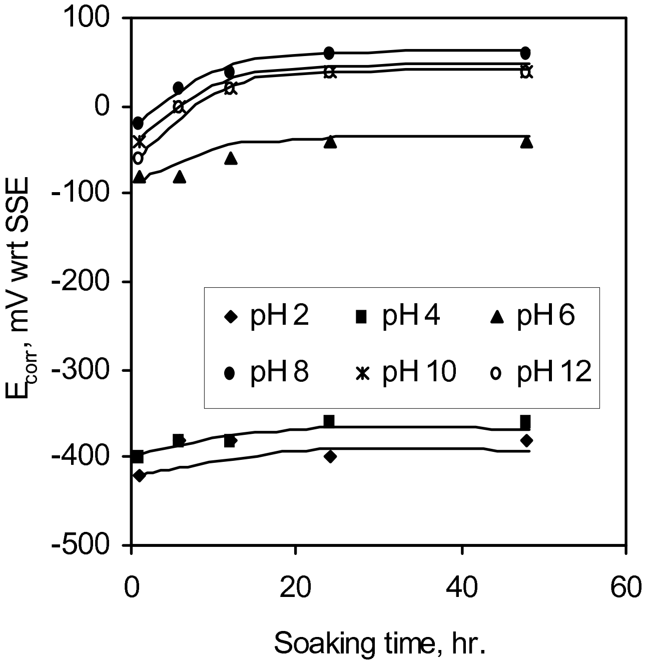

Figure 3: Effect of soaking time on the corrosion potential in SCW containing 250 ppm $NaNO_2$

Figure 5 shows the anodic potentiodynamic sweep on the mild steel in stagnant SCW containing $NaNO_2$ at pH 6. Current arrest with the increase of potential at all concentration of NaNO2 indicates passivation of mild steel. The extension of passive region was found up to 300 mV, 460 mV, 440 mV, 440 mV and 440 mV with respect to SSE in the presence of 250 ppm, 500 ppm, 750 ppm, 1000 ppm and 1250 ppm

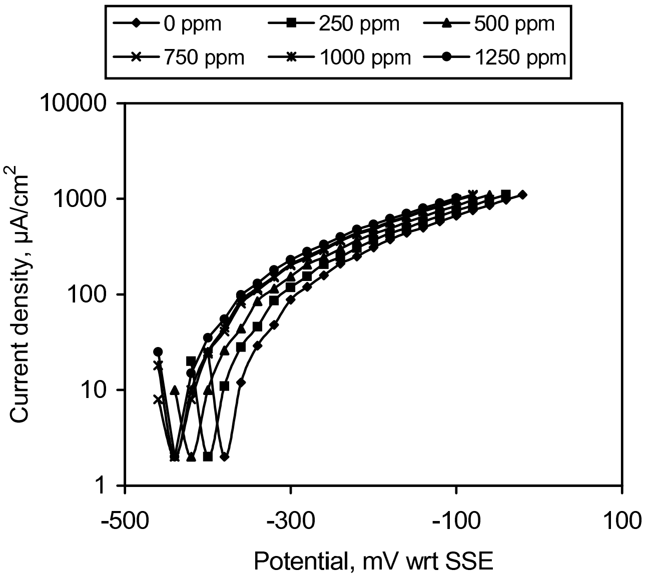

Figure 4: Potentiodynamic sweep on mild steel in SCW containing $NaNO_2$ at pH 4. Soaking time, 48hr

$NaNO_2$ respectively. The current density having magnitude below 1 $\mu A/cm^2$ in the passive region is an indication of good passivation. As this current density was observed even in the presence of as low as 250 ppm $NaNO_2$ in stagnant SCW it indicates effective corrosion inhibition by $NaNO_2$.

Figure 6 shows the effect of pH on the anodic potentiodynamic behaviour of mild steel in SCW containing 500 ppm $NaNO_2$. A more extensive passive range was observed at pH 8 compared to other pH values. At pH 2 and 4 no passion was observed. These results reveal that $NaNO_2$ is a corrosion inhibitor for mild steel in stagnant SCW at pH 6 and above and inhibition activity increases with the increase of $NaNO_2$ concentration up to 500 ppm.

Results for the effect of pH on the passivation breakdown potential of the mild steel in SCW containing $NaNO_2$ are shown in Figure 7 for 24 hour soaking. Passivation breakdown potentials were raised to more noble potentials with the increase of pH up to 8 and afterwards slowly decreased. The effect of $NaNO_2$ concentration on the passivation breakdown potential of the mild steel is shown in Figure 8. The passivation breakdown potential rapidly increased with the increase of $NaNO_2$ concectration up to 500 ppm, and then remained more or less constant.

In stagnant condition diffusion is the only process for ions to reach the surface of the mild steel and this is dependent on the size of the ions and time. In SCW chloride ion present is most harmful for mild steel as it forms highly soluble iron chloride with iron ion. Chloride ion also chemically reacts with the surface barrier oxide to form soluble iron oxy-chloride as $FeOOH + Cl^- \longrightarrow FeOCl + OH^-$ [14]. The Chloride ion attack on the surface usually takes place at the defects or weak sites of the oxide.

As there is always a competition between aggressive ion and nitrite to breakdown and repair the oxide of the surface; therefore, immersion time of the mild steel in stagnant SCW

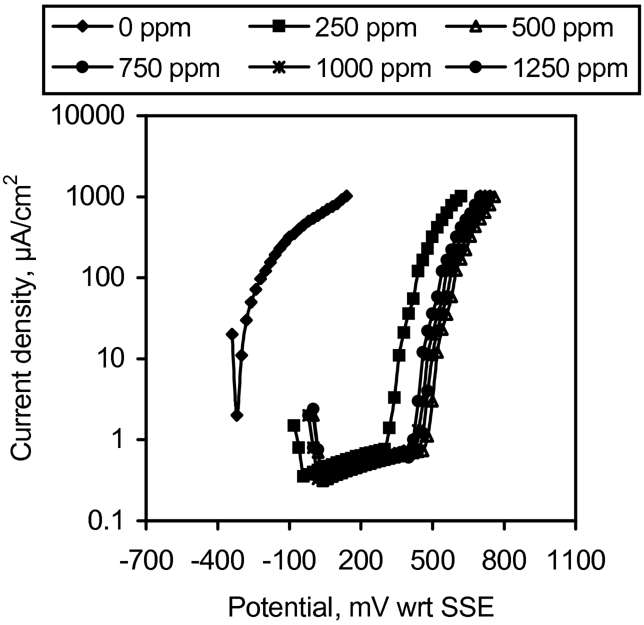

Figure 5: Potentiodynamic sweep on the mild steel in SCW containing $NaNO_2$ at pH 6. Soaking time, 24hr

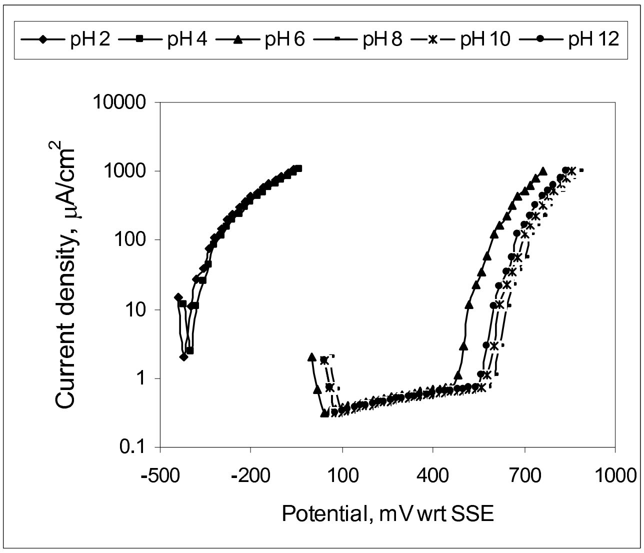

Figure 6: Effect of pH on the anodic potentiodynamic behaviour of mild steel in SCW containing 500 ppm $NaNO_2$

containing $NaNO_2$ can have an important role on the corrosion inhibition. The effect of soaking time on the passivation breakdown potential in stagnant SCW containing $NaNO_2$ at pH 6 is shown in Figure 9. The breakdown potential slowly increased with the increase of soaking time up to 24 hours and afterwards it remained more or less constant with the further increase of soaking time up to 48 hours for all $NaNO_2$ concentrations.

Prolonged exposure of mild steel in SCW results in the insertion of chloride ion and water molecule into the structure of $Fe(OH)_2$ leading to $3\,Fe(OH)_2 \cdot Fe(OH)Cl \cdot nH_2O$ (green rust, containing chloride) [15]. This also eventually leads to

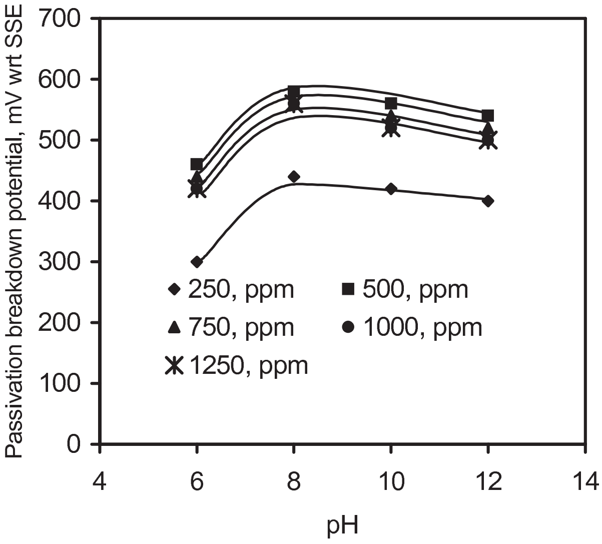

Figure 7: Effect of pH on passivation breakdown potential in SCW containing $NaNO_2$. Soaking time, 24 hr

corrosion.

Ferrous ions produced on the mild steel surface are converted to insoluble and stable ferric oxide in the oxide stability region (near neutral and alkaline region) according to the reaction [9].

$$2\,Fe^{2+} + 2\,OH + 2\,NO_2 \rightarrow 2\,NO + Fe_2O_3 + H_2O \qquad (1)$$

This Fe_2O_3 plugs the defects of the oxide layer. Thus the action of nitrite is two fold; firstly because of negative charge it repels Cl^- from the surface and secondly it repairs the oxide layer on the surface. These result in very effective corrosion inhibition of mild steel in SCW.

Oxide layer cannot exist on the steel surface below pH 4 [16]. In absence of oxide layer, iron surface becomes bare and freely corrodes as:

$$Fe + 2\,H^+ \rightarrow Fe^{2+} + H_2 \qquad (2)$$

When nitrite is added to the acidic SCW, FeOCl of very high solubility easily forms and there by accelerating corrosion.

4. Conclusion

- Nitrite inhibits mild steel corrosion in near neutral and alkaline media (at pH 6 and above) and accelerates in acid media (at pH 4 and below).
- Maximum inhibition activity was attained for 500 ppm sodium nitrite at pH 8.
- Inhibitive action of nitrite is assumed due to the oxidation of Fe_2^+ ion to form Fe_2O_3 on the surface in near neutral and alkaline region.

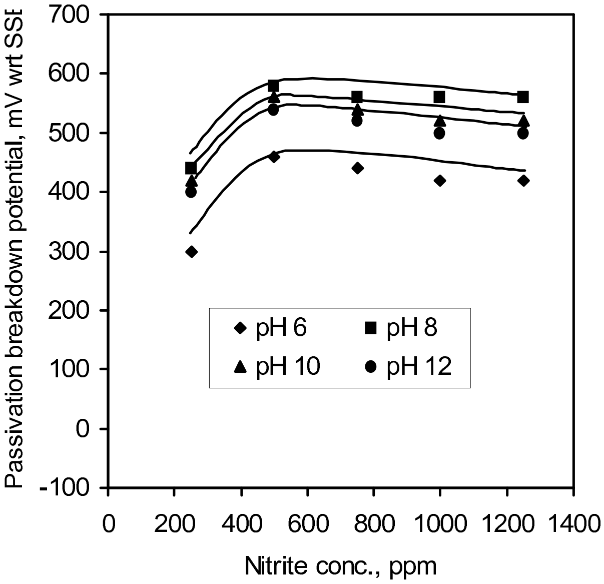

Figure 8: Effect of $NaNO_2$ conc. on the passivation breakdown potential in SCW, soaking time, 24 hr

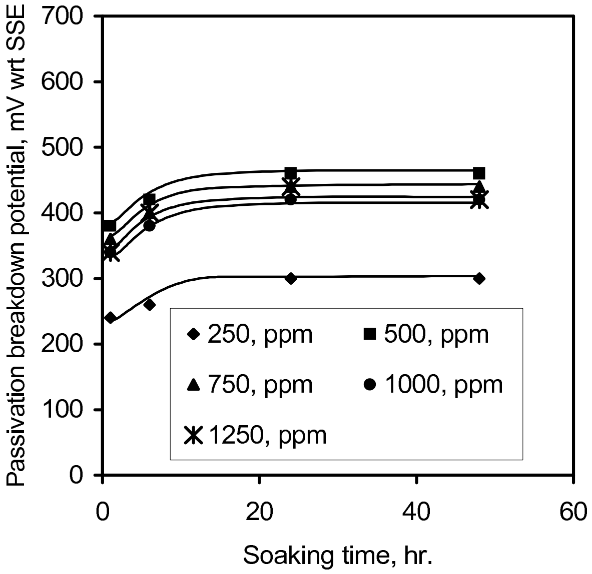

Figure 9: Effect of soaking time on the passivation breakdown potential in SCW containing $NaNO_2$ at pH 6

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