Original Article

Electrochemical investigation on effect of sodium thiosulfate (Na$_2$S$_2$O$_3$) and ammonium chloride (NH$_4$Cl) on carbon steel corrosion

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ABSTRACT

The effect of sodium thiosulfate (Na$_2$S$_2$O$_3$) concentrations (0.01, 0.1 and 1 M) on carbon steel corrosion behavior in 3.75 M ammonium chloride (NH$_4$Cl) solution was investigated. The potentiodynamic polarization results show that the $i_{corr}$ increases from $8.7 \times 10^{-6}$ A cm$^{-2}$ to $7.2 \times 10^{-4}$ A cm$^{-2}$ when thiosulfate (S$_2$O$_3^{2-}$) concentration increases from 0 to 1 M. Electrochemical impedance spectroscopy measurements also mimic the same trend. However, it is also observed that the $i_{corr}$ value starts decreasing when S$_2$O$_3^{2-}$ concentration equals or exceeds the NH$_4$Cl concentration (Cl$^{-}$:S$_2$O$_3^{2-}$ ≥ 1:1) in the electrolyte solution. The polarization behavior and field-emission scanning electron microscopy images reveal that the carbon steel undergoes general corrosion at lower concentrations (0.01 M S$_2$O$_3^{2-}$ and 0.1 M S$_2$O$_3^{2-}$) and, both pitting and general corrosion at higher concentration (1 M S$_2$O$_3^{2-}$). Based on the experimental results, the mechanistic reaction pathway, which involves two dissolution paths for carbon steel dissolution is suggested.

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1. Introduction

In oil refinery industries, ammonium chloride (NH$_4$Cl) corrosion has been reported to be one of the main causes of equipment and piping failures [1–3]. Severe corrosion failures result from aggressive species such as chlorides, sulfur, amines, salts, carbon dioxide and acids present in crude oil [1–9]. Among them, polythionates, especially thiosulfates (S$_2$O$_3^{2-}$) has been reported to be a well identified problem in oil refinery units, particularly in the sulfurous processing streams [4–6], in addition to pulp and paper industry [10,11] and nuclear power industry [12]. Of all the sulfur species, S$_2$O$_3^{2-}$ is found to be one of the most intriguing, metastable polysulfur oxyanions, which can undergo both oxidation and reduction or disproportionation and decomposition [5,13,14] depending upon the corresponding electrochemical/chemical environment. Marcus et al. [15] developed potential-pH diagram for Fe in water containing various sulfur species including S$_2$O$_3^{2-}$ at 25 °C and 300 °C.

Besides, S$_2$O$_3^{2-}$ renders a thermodynamic basis for use as a substitute of noxious hydrogen sulfide (H$_2$S) in laboratory
scale corrosion studies of sour gas conditions [5,6]. This was basically proposed based on the following reactions, where the elemental sulfur generated via both electrochemical (Reaction 1) and chemical (Reaction 2) reactions, may further undergo disproportionation (Reaction 3)/reduction (Reaction 4) to produce H₂S:

\[ \text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 4e^- \rightarrow 2\text{S}+3\text{H}_2\text{O} \]  
\[ \text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{S}^0 + \text{HSO}_3^- \]  
\[ 4\text{S}^0 + 4\text{H}_2\text{O} + \text{H}^+ \rightarrow 3\text{H}_2\text{S} + \text{SO}_4^{2-} + 3\text{H}^+ \]  
\[ \text{S} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{S} \]

Thus, investigating the combined effect of S₂O₃²⁻ and chloride (Cl⁻) ions on corrosion of various metal alloys has been of great interest. The corrosive effect of S₂O₃²⁻–Cl⁻ ions [10–12,16–23] on various metal alloys have been reported. Wensley et al. [10] reported that polysulfides and S₂O₃²⁻ present in white liquor caused a detrimental effect on mild steel by degrading the passivating ability of the steel. It was observed that the sulfur adsorbed on the surface prevented the repassivation process in Cl⁻ solutions. X-ray photoelectron spectroscopy (XPS) studies [22] showed that sulfite ions are reduced on the metal electrode (M) surface as per the following reactions:

\[ \text{M} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{M-S}_{\text{ad}} + \text{SO}_2^{2-} + 2\text{H}^+ + 2e^- \]  
\[ \text{xM-S}_{\text{ad}} + (y-x)\text{S} \rightarrow \text{M}_x\text{S}_y \text{(sulfide)} \]

It was reported that Cl⁻:S₂O₃²⁻ ratio is one of the most significant factors in enhancing pitting corrosion of steels in Cl⁻ media. Also, it was found that S₂O₃²⁻ ions are not corrosive enough when present alone, as it does not initiate the breakdown of the passive film formed on the steel surface [16,17,19,24]. However, these studies were conducted for other steel alloys and hence, understanding the corrosion mechanism of carbon steel in Cl⁻–S₂O₃²⁻ system will be of interest in the present work.

Similarly, in the studies reported in the literature, NaCl solutions were mainly considered and to the best of author’s knowledge, the effect of S₂O₃²⁻ ions in the presence of NH₄Cl solution for carbon steel was not investigated yet. Although, cations will not participate in the electrochemical reactions directly, it may alter the anionic activity and, thereby affect the corrosion rate and mechanism. Many parameters such as pH of the electrolyte solution, hydrolysis of cations, hardness of cations, corrosion inhibitory effect of cations, formation and solubility of corrosion products in the presence of given cation will influence the corrosion rate as well as the mechanism [25–28]. Hence, the investigation of effect of sodium thiosulfate (Na₂S₂O₃) on the corrosion behavior of carbon steel in NH₄Cl solution is of particular interest in the present work.

The electrochemical techniques such as linear polarization, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed to analyze the corrosion mechanism of carbon steel in NH₄Cl solution containing S₂O₃²⁻ ions. In addition, other techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) were employed to support our research findings.

## 2. Experimental

### 2.1. Materials

All the measurements were carried out with carbon steel of following composition (wt.%): C (0.22–0.26 %); Si (0.11–0.14 %); Mn (1.03–1.06 %); P (0.04% maximum); S (0.03% maximum); Cr (0.03% maximum); and rest Fe. The electrolytes were prepared utilizing chemicals of analytical reagent grade (NH₄Cl from Himedia, India; Na₂S₂O₃ from Loba Chemie, India) and distilled water. The experiments were performed at natural pH of the solution: 4.22 for pure 3.75 M (20 wt.%) NH₄Cl solution; 4.54, 5.32 and 6.16 respectively for 3.75 M NH₄Cl solution containing 0.01 M, 0.1 M and 1 M Na₂S₂O₃ respectively. The pH values of pure 0.01 M, 0.1 M and 1 M Na₂S₂O₃ solutions are 6.5, 7.57 and 8.99 respectively. The microscopy image of carbon steel sample was obtained using an optical microscope (Leica DM2500 M, Germany), which reveals the presence of ferrite, bainite and pearlite phases (Figure S1).

### 2.2. Electrochemical measurements

The electrochemical measurements were performed using a potentiostat (PGSTAT 204, Switzerland), and a conventional three electrode system. Ag/AgCl (3 M KCl) was used as the reference electrode and a Pt wire as the counter electrode. The working electrode was cylindrical carbon steel of 8 mm diameter with exposed surface area of 0.5 cm² to the electrolyte solution. The solution temperature was controlled at (25.5 ± 1) °C. During the experiments, the corrosion cell was housed inside a faraday cage to minimize the external noises. Prior to each experiment, the surface of the working electrode was pretreated by grounding sequentially with 220, 320, 600 and 1000 grades of silicon carbide (SiC) paper, followed by polishing with 1.0 μm and 0.3 μm alumina powder. Then, the electrode was rinsed with distilled water, and ultrasonicated to remove any particle adhered on the specimen surface. The electrode was finally rinsed and dried using tissue paper. The sample was pretreated to ensure that the results obtained are repeatable and reproducible. All the experiments were performed at least thrice to check the repeatability and reproducibility of the results. On the whole, all the experiments were carried out in naturally aerated stagnant electrolyte solutions.

#### 2.2.1. Polarization measurements

The polarization measurements were performed once the open circuit potential (OCP) reached a stable value after 1 h (refer Figure S2). Potentiodynamic polarization was employed by sweeping the potential from −250 mV (vs. Ag/AgCl) to +500 mV (vs. Ag/AgCl) w.r.t OCP, at a scan rate of 1 mV s⁻¹. Potentiostatic polarization measurements were also performed at various overpotentials in order to understand the pitting behavior of carbon steel.
2.2.2. Cyclic voltammetry
The cyclic voltammogram of carbon steel in different concentrations of corrosive media were obtained by sweeping the potential linearly from starting potential, \(-1.20\) V (vs. Ag/AgCl) to \(-0.20\) V (vs. Ag/AgCl) and then reversed back to the starting potential at a potential scan rate of 50 mV s\(^{-1}\). Scanning was also performed from \(-0.20\) V (vs. Ag/AgCl) to \(-1.20\) V (vs. Ag/AgCl) and vice versa, and no significant change in peak position and intensity was observed.

2.2.3. Electrochemical impedance spectroscopy
Before each experiment, the working electrode (specimen) surface was exposed to open circuit for a period of 1 h. The impedance responses were obtained by employing an amplitude signal of 10 mV (rms) at the corresponding OCP value, within the frequency range of 10 kHz to 10 mHz, with 7 frequencies per decade. The impedance results were further analyzed with electrical equivalent circuit (EEC) model using Nova software (Metrohm Autolab, Switzerland). The EIS data obtained was validated with Kramers Kronig transform in order to ensure the stability, linearity and causality of the system.

2.3. Surface analysis using immersion tests
The surface morphology of carbon steel was inspected via field emission scanning electron microscope (FESEM) [Zeiss, Sigma, Germany], in order to confirm the type of corrosion attack. The steel specimen was immersed in nitric acid (70%, as received), and rinsed with distilled water. Further, the specimen was polished with SiC paper and abrasive alumina powder. Subsequently, the sample was rinsed with distilled water, ultrasonicated, dried and then introduced in the respective corrosive media for 12 h. At the end of 12 h, the specimen was taken out of the system, washed with distilled water and dipped in nitric acid to remove the corrosion layer formed on the surface. The steel specimen was then rinsed with distilled water, air dried and finally, the micrograph images were taken.

Energy dispersive X-ray spectroscopy (EDS) was performed to elucidate the elemental composition of the corrosion products using FESEM [Zeiss, Sigma, Germany]. The steel specimen was polished in a similar fashion as above, and then submerged in the system of interest for 72 h.

2.4. X-ray diffraction measurement
X-ray diffraction (XRD) was used to characterize the corrosion product formed on the carbon steel surface submerged in solutions containing NH\(_4\)Cl and Na\(_2\)S\(_2\)O\(_3\). XRD patterns were obtained using TTRAX-III (Rigaku) diffractometer (Japan), with Cu K\(_\alpha\) (\(\lambda = 1.5406\) Å) radiation (50 kV, 100 mA). The steel specimen was exposed to the respective solution of interest for a period of 72 h, so that sufficient corrosion product is obtained for XRD detection. The corrosion product formed were scrubbed out of the specimen, dried, and placed on a quartz plate to provide a planar surface in the diffractometer. The XRD pattern was acquired over a range of 10°–70°, with a scan rate of 4° per minute.

![Fig. 1 – Potentiodynamic polarization curves of carbon steel corroded in 3.75 M NH\(_4\)Cl solution containing various concentrations of S\(_2\)O\(_3^{2-}\). Scan rate = 1 mV s\(^{-1}\).](image)

3. Results and discussion

3.1. Potentiodynamic polarization

In the current investigation, the NH\(_4\)Cl concentration was fixed at 3.75 M and the concentration of Na\(_2\)S\(_2\)O\(_3\) was varied from 0.01 M to 1 M, to understand the combined effect on carbon steel corrosion. The concentrations used in the study are usually encountered in the refineries, as reported in the literatures [1–3,16,17,19,22,23]. Fig. 1 shows the potentiodynamic polarization behavior of carbon steel in NH\(_4\)Cl solution containing various concentrations of S\(_2\)O\(_3^{2-}\) ions. It is to be noted here that the molar ratio of Na\(_2\)S\(_2\)O\(_3\) to NH\(_4\)Cl is less than one for all the cases. Table 1 shows \(E_{corr}\) and \(i_{corr}\) values, which were obtained from these polarization curves by means of corrosion fit analysis, using Nova 1.10.4 software. In some cases, where the polarization curves do not possess linear range long enough for extrapolation, estimating Tafel slopes were difficult and the reported values might not be accurate. However, the overall trend will not be changed. The polarization curves clearly depict a considerable effect of S\(_2\)O\(_3^{2-}\) on the electrochemical behavior of carbon steel in NH\(_4\)Cl solution. One of the main observations from these polarization curves is that \(E_{corr}\) value shifts toward negative potential with the addition of 0.01 M S\(_2\)O\(_3^{2-}\) to the NH\(_4\)Cl solution. However, the value of \(E_{corr}\) keeps increasing to a more positive potential with further increase in S\(_2\)O\(_3^{2-}\) concentration. Similar kind of behavior is also reported for carbon steel in caustic soda–thiosulfate system [10], and other systems as well [29,30]. On the other hand, the \(i_{corr}\) value is increasing from \(8.7 \times 10^{-6}\) A cm\(^{-2}\) to \(7.2 \times 10^{-4}\) A cm\(^{-2}\) when the S\(_2\)O\(_3^{2-}\) concentration increases from 0 M to 1 M. It implies that the addition of S\(_2\)O\(_3^{2-}\) ions to the NH\(_4\)Cl solution accelerates the corrosion rate of carbon steel.

The substantial increase in the cathodic corrosion current density could also be observed because of the presence of S\(_2\)O\(_3^{2-}\) ions in the NH\(_4\)Cl solution. It would be attributed to the role of these species in either of the reduction reaction (1) or (4) as mentioned in the introductory section. The solution
The pH [31,32], electrochemical potential [14] and nature of the surface being corroded (passivated/non-passivated) [12,23,33,34] determines the typical cathodic reactions occurring on metal surface. Besides, the elemental sulfur produced may further react with Fe$^{2+}$ to form FeS film, thereby accelerating the corrosion process [23]. Similar effect is also reported for NaCl solution [23], i.e. the addition of Na$_2$S$_2$O$_3$ to NaCl solution influences both the anodic and cathodic reactions.

It is also interesting to see that the polarization curves (Fig. 1) show non-linear behavior, which is more evident especially at 0.1 M and 1 M Na$_2$S$_2$O$_3$ concentrations. In particular, 1 M Na$_2$S$_2$O$_3$ solution shows constant current regime, for a potential range from −0.58 V to −0.45 V (vs. Ag/AgCl), which indicates the formation of pseudo-passive layer (the current remains more or less constant at 1.1 mA cm$^{-2}$) on the carbon steel surface. This layer then finally breaks down at a breakdown potential ($E_b$) of −0.449 V (vs. Ag/AgCl), as evident by the increase of current. The pseudo-passive layer comprises of a mixture of sulfides and oxides. However, the major constituent could be sulfides as the formation of the same is thermodynamically more feasible than the formation of oxides [34].

The reduction of S$_2$O$_3^{2−}$ to sulfur is more likely to happen on non-passivated surfaces [12,22,34]. In HN$_4$Cl solutions, the surface is not completely covered with an oxide film, which triggers the formation of sulfur and thereby FeS layer on the carbon steel surface. The formation rate of FeS will probably be increasing with S$_2$O$_3^{2−}$ concentration, which results in the formation of pseudo-passive layer as evident by the constant current regime in polarization curve. At higher anodic potential, the pseudo-passive layer breaks down indicating the susceptibility of carbon steel to localized corrosion. In general, the sulfide film is more porous and non-protective compared to that of oxide film [34]. Thus, this pseudo-passive layer could not completely protect the underlying metal, and as a result, general corrosion also occurs simultaneously at higher Na$_2$S$_2$O$_3$ concentration. Simultaneous occurrence of general and pitting corrosion in acidic and neutral solution is also reported for other metals [35,36]. However, at lower Na$_2$S$_2$O$_3$ concentrations, the corrosion is of only general type as observed in the case of pure HN$_4$Cl solutions [37].

As the Na$_2$S$_2$O$_3$ concentration varies from 0.01 M to 1 M, the pH value increases from 4.54 to 6.16. According to Pourbaix diagram, the passivation due to Fe$_{1+x}$S/FeS is thermodynamically feasible in this pH range of 4−8 [15,38,39]. However, the pseudo-passive layer is formed only at higher concentration of Na$_2$S$_2$O$_3$. Thus, these results clearly depict that concentration of Na$_2$S$_2$O$_3$ plays a significant role in determining the nature of the corrosion process.

### Table 1 – $E_{corr}$ and $i_{corr}$ values attained from potentiodynamic polarization curves.

<table>
<thead>
<tr>
<th>Electrolyte concentration</th>
<th>$\beta_+$(mV dec$^{-1}$)</th>
<th>$-\beta_-$ (mV dec$^{-1}$)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure 3.75 M NH$_4$Cl</td>
<td>137.9</td>
<td>62.9</td>
<td>−0.683</td>
<td>8.7 × 10$^{-6}$</td>
</tr>
<tr>
<td>3.75 M NH$_4$Cl + 0.01 M S$_2$O$_3^{2−}$</td>
<td>142.7</td>
<td>362.9</td>
<td>−0.743</td>
<td>1.3 × 10$^{-4}$</td>
</tr>
<tr>
<td>3.75 M NH$_4$Cl + 0.1 M S$_2$O$_3^{2−}$</td>
<td>148.1</td>
<td>375.2</td>
<td>−0.719</td>
<td>3.8 × 10$^{-4}$</td>
</tr>
<tr>
<td>3.75 M NH$_4$Cl + 1 M S$_2$O$_3^{2−}$</td>
<td>160.4</td>
<td>326.4</td>
<td>−0.655</td>
<td>7.2 × 10$^{-4}$</td>
</tr>
<tr>
<td>Pure 0.01 M S$_2$O$_3^{2−}$</td>
<td>190.6</td>
<td>159.8</td>
<td>−0.665</td>
<td>2.4 × 10$^{-5}$</td>
</tr>
<tr>
<td>Pure 0.1 M S$_2$O$_3^{2−}$</td>
<td>146.5</td>
<td>315.6</td>
<td>−0.743</td>
<td>4.1 × 10$^{-5}$</td>
</tr>
<tr>
<td>Pure 1 M S$_2$O$_3^{2−}$</td>
<td>132.2</td>
<td>328.3</td>
<td>−0.789</td>
<td>7.1 × 10$^{-5}$</td>
</tr>
</tbody>
</table>

*Fig. 2 – Potentiodynamic polarization curves of carbon steel corroded in various concentrations of pure S$_2$O$_3^{2−}$ solutions. Scan rate = 1 mV s$^{-1}$.*

In order to understand further, whether the observed behavior at higher Na$_2$S$_2$O$_3$ concentrations is due to the presence of S$_2$O$_3^{2−}$ ions alone or because of the combined effect of S$_2$O$_3^{2−}$ and Cl$^−$ ions, the polarization experiments were carried out in pure Na$_2$S$_2$O$_3$ solutions (0.01 M−1 M) and the results are shown in Fig. 2. For an increase in Na$_2$S$_2$O$_3$ concentration, the curves indicate a marked increase in the current density from $2.4 \times 10^{-5}$ A cm$^{-2}$ to $7.1 \times 10^{-5}$ A cm$^{-2}$ with decrease in $E_{corr}$ value from −0.665 V to −0.789 V (vs. Ag/AgCl). The higher current density in pure S$_2$O$_3^{2−}$ solutions ($2.4 \times 10^{-5}$ A cm$^{-2}$ at 0.01 M Na$_2$S$_2$O$_3$ vs. $8.7 \times 10^{-6}$ A cm$^{-2}$ at 3.75 M NH$_4$Cl) indicates that S$_2$O$_3^{2−}$ ions are more aggressive compared to that of Cl$^−$ ions in corroding carbon steel surface. Besides, it does not show constant current regime for long potential range as observed in case of 1 M S$_2$O$_3^{2−}$ in 3.75 M NH$_4$Cl solution (Fig. 1). However, a non-linear behavior is observed in the curve at 1 M S$_2$O$_3^{2−}$ concentration, which may be due to the formation of a porous and non-protective sulfide layer on the surface. This implies that susceptibility to pitting enhances only in presence of both Cl$^−$ and S$_2$O$_3^{2−}$ species. Thus, when the solution contains only NH$_4$Cl or Na$_2$S$_2$O$_3$, carbon steel undergoes general corrosion, whereas when the solution contains both the species, then carbon steel undergoes either general or pitting corrosion depending on the concentration of both the species.

The polarization experiments were further carried out at different molar ratios of Na$_2$S$_2$O$_3$ to NH$_4$Cl: <1, 1 and >1 and the results are shown in Fig. 3. The pH of the corresponding solutions varied from 6.17 to 7.13. It is to be noted that the concentration of NH$_4$Cl is fixed at 0.93 M (5 wt.%) instead of 3.75 M,
and the concentration of Na₂S₂O₃ is varied to get these desired ratios. At 3.75 M NH₄Cl, achieving ratio 1 and >1 is difficult as the solution is saturated. It appears from these results that initially the corrosion rate of the carbon steel in NH₄Cl solution increases markedly to a maximum on addition of Na₂S₂O₃ (as observed in 3.75 M NH₄Cl solution, Fig. 1) and then starts decreasing when the ratio of Cl⁻ and S₂O₃²⁻ species becomes 1:1 or higher than 1 as shown in Fig. 4.

The reason for icorr showing a maxima at particular S₂O₃²⁻ concentration could be explained as follows: In pure NH₄Cl solution, the surface coverage of oxide layer is very low [37]. Na₂S₂O₃, being an oxidizer, increases the oxidation state of the carbon steel when added to NH₄Cl solution and thereby increases the dissolution rate at lower concentrations. However, higher concentrations of S₂O₃²⁻ leads to the formation of thick layer of Fe₅ on the carbon steel surface, which restricts the Cl⁻ ions or O₂ molecules to diffuse through it, and thereby finally lowers the dissolution rate. Thus, both Cl⁻ and S₂O₃²⁻ has a pronounced effect on the corrosion mechanism.

3.2. Potentiostatic experiments

The potentiostatic experiments were also carried out for carbon steel in the electrolyte solution containing 3.75 M NH₄Cl and 1 M Na₂S₂O₃ in order to understand the pitting behavior at two different overpotentials: (a) 50 mV below Ep, and (b) 50 mV above Ep. The results obtained are shown in Fig. 5. When the overpotential is below the pitting potential, the current is constant (1.2 × 10⁻⁴ A cm⁻²) with time, which implies that there is no formation of passive layer on the electrode surface. However, when the overpotential is above the pitting potential, the current decreases and then increases sharply to 9 × 10⁻³ A cm⁻² indicating the growth of pit with time. After 1600 s, the current value does not increase significantly (saturates at 9.3 × 10⁻³ A cm⁻²), which implies that the growth of pit is impeded by the deposition of corrosion products inside the pit.

3.3. Cyclic voltammetry

Fig. 6(a)–(d) shows the cyclic voltammograms obtained for carbon steel in NH₄Cl media containing S₂O₃²⁻ of varied concentrations. The voltammograms are interpreted in terms of Fe as the content of other elements in carbon steel is very low. In pure 3.75 M NH₄Cl solution, two anodic peaks A1 and A2 appeared at −0.581 V and −0.393 V (vs. Ag/AgCl) respectively. The peak A1 corresponds to oxidation of Fe to Fe²⁺ and the peak A2 corresponds to oxidation of Fe²⁺ to Fe³⁺. Besides, the high anodic current (A4) is observed at higher

![Fig. 3 - Potentiodynamic polarization curves of carbon steel corrosion in various Cl⁻ to S₂O₃²⁻ concentration. Scan rate = 1 mV s⁻¹.](image)

![Fig. 4 - Ecorr and icorr values acquired for various ratio of Cl⁻:S₂O₃²⁻.](image)

![Fig. 5 - Potentiostatic measurements of carbon steel in 3.75 M NH₄Cl solution containing 1 M S₂O₃²⁻ at overpotentials: (a) 50 mV below pitting potential (Ep): −0.499 V (vs. Ag/AgCl), and (b) 50 mV above pitting potential (Ep): −0.399 V (vs. Ag/AgCl).](image)
anodic potentials for all the cases, which is due to the combined effect of transpassive dissolution and oxygen evolution. In the cathodic side, one peak C1 appears at −0.991 V (vs. Ag/AgCl) which is more likely to be the conjugate peak of A1. The peak intensity of C1 for all the cases comes out to be slightly more than its counter peak A1, which suggests that most of the species being oxidized are completely reduced.

On addition of 0.01 M Na$_2$S$_2$O$_3$ to the NH$_4$Cl solution, the peak A1 shifts toward more negative potential to −0.644 V (vs. Ag/AgCl) and one more peak A3 appears close to A1 peak at −0.586 V (vs. Ag/AgCl), which may be due to competitive diffusion/adsorption of both Cl$^-$ and S$_2$O$_3^{2-}$ ions on the surface. The peak A3 is more likely to be the oxidation of Fe to form FeS on the electrode surface along with Fe oxide/chloride layer. Thus, both reactions occur simultaneously on the electrode surface. In the cathodic region, in addition to C1, one more peak C2 appears at −0.759 V (vs. Ag/AgCl), which is more likely to be the conjugate peak of A3, i.e. the reduction of FeS. Thus, the electrode surface might be covered with mixture of oxide and sulfide layers. When the concentration of S$_2$O$_3^{2-}$ in NH$_4$Cl solution is increased to 0.1 M, the two peaks A1 and A3 merge together, and form as one broad peak A1 that appears at −0.653 V (vs. Ag/AgCl). It is indicating the increase in aggressiveness of the system due to the S$_2$O$_3^{2-}$ ions. The peak A2 is not observed for these two cases, which may be due to the reason that, the generation of Fe$^{3+}$ is overshadowed by transpassive and oxygen evolution reactions.

However, in NH$_4$Cl solution containing 1 M S$_2$O$_3^{2-}$, there appears a region of lower and constant current density from −0.83 V to −0.65 V (vs. Ag/AgCl), with the disappearance of A1 peak. The peak A2, which is arising at a comparatively higher overpotential, −0.466 V (vs. Ag/AgCl) corresponds to oxidation of both oxides and sulfides. This suggests that a pseudo-passive layer is formed on the entire surface. This also corroborates with the results obtained from the polarization measurements (Fig. 1) where formation (insignificant increase in current density) and breakdown of passive layer (significant increase in current density) is observed on the steel surface. The occurrence of positive hysteresis in the CV also indicates the possibility of pitting corrosion on carbon steel surface.

### 3.4. Electrochemical impedance spectroscopy

The impedance spectra obtained for various concentration of S$_2$O$_3^{2-}$ in NH$_4$Cl solution are shown in Fig. 7(a)−(c). Although two time constants (capacitance loops) were observed for all the cases, the two time constants were not clearly distinguishable in some cases, as it is merged together. The electrical equivalent circuit (EEC) showed in Fig. 7(d) is employed to analyze the impedance data quantitatively. Here, $R_s$ represents the solution resistance, $Q_1$ and $R_1$ corresponds to constant phase element (CPE) associated with electrical double layer and charge transfer resistance respectively. The other parameters $Q_2$ and $R_2$ corresponds to capacitance and resistance associated with reduction reactions respectively, while $Q_3$ and
R3 is associated with diffusion phenomenon and chemical reactions occurring in bulk solution respectively. The EEC parameters obtained are shown in Table 2. It is clearly evident that Q3 is increasing and R1 is decreasing with increase in the S2O3^{2−} concentration. Thus, the total impedance associated with Faradaic reaction decreases as the Na2S2O3 concentration increases. Instead of capacitor, CPE is employed in EEC model to quantify the non-idealities observed in the capacitor behavior [40–44]. The electrical double layer capacitance is calculated from the CPE element using the following Brug's equation and the values are shown in the same Table 2.

\[ C_{dl} = \left[ Y_0 \left( \frac{1}{R_s} + \frac{1}{R_C} \right) \right]^{1/n} \] (7)
where $C_{dl}$ is the double layer capacitance, $Y_0$ and $n$ are the CPE parameters, $R_s$ and $R_{ct}$ are the solution resistance and charge transfer resistance respectively. The values of $C_{dl}$ obtained for the present system are high. However, similar values were reported for carbon steel in H$_2$S environment [44,45] and for other systems as well [46-48]. The other capacitive element $Q_2$ is increasing, while the resistance $R_2$ is decreasing with increase in S$_2$O$_3^{2-}$ concentration. It indicates the fact that the cathodic reaction rate increases with S$_2$O$_3^{2-}$ concentration. The capacitance values are higher compared to $C_{dl}$. It might be attributed to the adsorption of various corrosion products on the carbon steel surface [44]. The exponent value of $Q_2$ is nearly 0.5 in all these cases, which signifies the diffusion effect. The total impedance arising from these parameters is decreasing with S$_2$O$_3^{2-}$ concentration. This indicates that the corrosion rate increases with S$_2$O$_3^{2-}$ concentration as observed in the polarization measurements.

3.5. **FESEM and EDS**

The surface morphology of carbon steel after immersion in NH$_4$Cl solution containing S$_2$O$_3^{2-}$ of various concentrations are shown in Fig. 8(a)-(c). As expected from the polarization behavior, uniform corrosion is observed at lower S$_2$O$_3^{2-}$ concentrations (0.01 M and 0.1 M), as observed in pure NH$_4$Cl solution [37]. While pits are clearly observed at higher S$_2$O$_3^{2-}$ concentration (1 M). It supports our observation from polarization measurements that a pseudo-passive layer is formed when the concentration of Cl$^-$ and S$_2$O$_3^{2-}$ ions in solution are higher, which is attacked further by Cl$^-$ ions resulting in localized corrosion.

Fig. 9(a)–(d) shows the results obtained from EDS analysis, carried out on corrosion products formed on carbon steel surface, at different concentrations of S$_2$O$_3^{2-}$ in 3.75 M NH$_4$Cl solution. In pure NH$_4$Cl solutions, the corrosion film is mainly oxides and chlorides of Fe. When Na$_2$S$_2$O$_3$ is added to the NH$_4$Cl solution, the sulfur peak appears indicating the formation of sulfide layer on the surface. Thus, the corrosion products are oxides and chlorides of Fe in Cl$^-$ only solution and a mixture of oxides, chlorides and sulfides in Cl$^-$–S$_2$O$_3^{2-}$ solutions. EDS analysis were also carried out on the corrosion product formed inside the pit. The result confirms the presence of both sulfur and chlorine in the pit (Figure S3). EDS mapping of carbon steel after reaction with 3.75 M NH$_4$Cl–1 M Na$_2$S$_2$O$_3$ is also presented in Fig. 10(a)–(d). The result shows that the species S, Cl and O are present on the carbon steel surface as well as on the pit. These results imply that both sulfur and chlorine species took part in the formation of stable pits as reported by other researchers [12,34]. Also, the species S and O are more concentrated inside the pit. It indicates that the pits are covered with corrosion products as observed in the potentiostatic measurements.

3.6. **XRD**

The crystalline phases of corrosion film formed on carbon steel surface in NH$_4$Cl–Na$_2$S$_2$O$_3$ solutions were identified by XRD spectra and the results are presented in Fig. 11. The peaks were identified using JCPDS software. XRD spectra
Fig. 9 – EDS analysis of corrosion products formed on the surface of carbon steel after immersion in: (a) pure 3.75 M NH₄Cl, (b) 3.75 M NH₄Cl + 0.01 M S₂O₃²⁻ solution, (c) 3.75 M NH₄Cl + 0.1 M S₂O₃²⁻ solution, and (d) 3.75 M NH₄Cl + 1 M S₂O₃²⁻ solution, for a period of 72 h.

exhibits various crystalline phases including α-FeOOH, FeCl₃, FeS, Fe₂O₃ depending upon the concentration of S₂O₃²⁻ in NH₄Cl solution. The peaks corresponding to FeS did not appear in pure NH₄Cl solution as expected and the corrosion film comprises of only FeOOH, FeCl₃ and Fe₂O₃. Although, the dissolution of carbon steel in NH₄Cl solution occurs via Fe²⁺, the oxidation of these products to Fe³⁺ is more common in non-deaerated solution containing dissolved oxygen or during its exposure to atmospheric air. The appearance of FeS peaks in the recorded XRD spectra for NH₄Cl–S₂O₃²⁻ solutions clearly depicts the formation of FeS layer on the carbon steel surface. This is also corroborating our results obtained from other techniques employed in the present investigation.
Fig. 10 – EDS mapping of carbon steel exposed to 3.75 M NH₄Cl + 1 M S₂O₃²⁻ solutions for a period of 72 h.

Fig. 11 – XRD pattern of corrosion products obtained after carbon steel corroded in 3.75 M NH₄Cl solution containing S₂O₃²⁻ of varied concentrations. Peak label indicates: +, (FeOOH); −, (FeCl₃); *, (FeS); &*, (Fe₂O₃).

3.7. Dissolution mechanism of carbon steel in S₂O₃²⁻–Cl⁻ solutions

The pitting corrosion is reported for various metal alloys in Cl⁻ only solutions [12,49–51] and Cl⁻–S₂O₃²⁻ solutions [12,16,52].

Point defect model (PDM) is widely employed to explain the pitting corrosion of metal alloys [53,54]. As PDM could be applied only when strong passive film is present on the carbon steel surface, the following mechanistic reaction pathway is suggested to explain the features observed in electrochemical and non-electrochemical experiments.

The following anodic reaction occurs in NH₄Cl solution (corresponds to peak A1 in CV).

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (8)
\]

Besides, the following chemical reactions also occur in NH₄Cl solution.

\[
\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \quad (9)
\]

\[
\text{Fe}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{FeCl}_2 \quad (10)
\]

\[
\text{FeCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{FeO} + \text{HCl} \quad (11)
\]

The dissolution–precipitation reactions in presence of S₂O₃²⁻ ions (corresponds to peak A3 in CV) are given by the following anodic reaction.

\[
2\text{Fe} + 2\text{H}_2\text{S} \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{S} + 4e^- \quad (12)
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{S} \rightleftharpoons \text{FeS} + 2\text{H}^+ \quad (13)
\]

In the above dissolution reaction, H₂S is regenerated and further reacts with Fe²⁺ to form FeS.

The possible cathodic reactions occurring in the system are,

\[
\frac{1}{2}\text{S}_2\text{O}_3^{2-} + 3\text{H}^+ + 2e^- \rightleftharpoons \text{S} + \frac{3}{2}\text{H}_2\text{O} \quad (14)
\]

\[
4\text{H}^+ + 2\text{S} + 2e^- \rightleftharpoons 2\text{H}_2\text{S} \quad (15)
\]
The peaks corresponding to the above cathodic reactions were not observed in CV. It is probably because these reactions were buried under the other major reduction process of iron oxides and sulfides. The overall reaction network is presented in Fig. 12.

In case of carbon steel in NH₄Cl solution, the corrosion layer does not completely block the carbon steel surface as observed from polarization measurement. Consequently, general corrosion occurs as reported in our earlier studies [37]. Thus, based upon these results, it could be envisaged that in Cl⁻ only solutions, an oxide-chloride layer could be formed on the carbon steel surface but not as a continuous layer as shown in Fig. 13a.

With the addition of lower concentrations of S₂O₃²⁻, FeS could be precipitated on the carbon steel surface without blocking the surface layer completely as shown in Fig. 13b. As the S₂O₃²⁻ addition enhances the dissolution rate also, the formation of FeS would enhance the anodic reaction rate by acting as a reduction site [23,34]. Further, the pseudo-passive layer forms on the carbon steel surface only in the presence of both S₂O₃²⁻ and Cl⁻ ions, especially at higher concentrations. This implies that the pseudo-passive layer formed on the carbon steel surface is a mixture of oxides, chlorides and sulfides as evident from EDS and XRD results. Also, CV results confirm that the redox reactions due to both S₂O₃²⁻ and Cl⁻ ions are occurring on the carbon steel surface, unlike in pure NH₄Cl solutions.

The FeS/FeO/FeCl₂ could also undergo partial oxidation (corresponds to peak A2 in CV) as per the following equation [32,34].

\[
\text{FeS} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + S^{2-} + \text{3H}^+ + \text{e}^-
\]

(17)

\[
2\text{FeS} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{S}^{2-} + 6\text{H}^+ + 2\text{e}^-
\]

(18)

\[
2\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^-
\]

(19)

\[
\text{FeCl}_2 + \text{Cl}^- \rightarrow \text{FeCl}_3 + \text{e}^-
\]

(20)

Further, these iron oxides dissolved in the solution via transpassive reaction along with oxygen evolution (corresponds to peak A4 in CV).

Thus, the dissolution of Fe in Cl⁻–S₂O₃²⁻ solution occurs via two paths as shown in Fig. 12. As observed from polarization measurements, the corrosion rate in pure Na₂S₂O₃ is...
more comparing to the corrosion rate in pure NH₄Cl solutions. Thus, the dissolution rate via path B would be higher. Besides, the concentration of these individual ions would also play a critical role in determining the nature and the rate of the process occurring at metal-electrolyte solution interface. For example, when the concentration of the S₂O₃²⁻ is increased to 1 M (the ratio of S₂O₃²⁻ to Cl⁻ is still less than one), the rate of dissolution via reaction path B would enhance further and form a complete layer consisting of both oxides and sulfides on the surface as shown in Fig. 13c. Subsequently, Cl⁻ ions penetrate into this layer and causes pitting corrosion as explained before. Due to the pseudo-passivity of film formed on the carbon steel surface, general corrosion also occurs together. When S₂O₃²⁻ concentration equals or exceeds the Cl⁻ ion concentration, the decrease in current density is observed from polarization measurements. It is probably due to the formation of thicker sulfide layer formed on the electrode surface, which limits the diffusion of active species.

4. Conclusion

The following conclusions are drawn from this present study:

1. The corrosion rate increases first with the increase in S₂O₃²⁻ concentration in NH₄Cl solution. However, further increase in S₂O₃²⁻ concentration decreases the corrosion rate. It would be attributed to formation of thicker film on carbon steel surface when the Na₂S₂O₃ concentration is higher.

2. The nature of corrosion (uniform or pitting corrosion) is determined by the concentration of S₂O₃²⁻ ions in Cl⁻ solution. At lower concentrations, general corrosion is observed, while at higher concentrations, simultaneous occurrence of pitting and general corrosion is observed.

3. EDS and XRD results reveals that the corrosion products are mainly FeCl₃, Fe₂O₃ and FeO(OH) in NH₄Cl solution, while FeS was formed in addition to oxides and chlorides of Fe with the addition of Na₂S₂O₃.

4. The dissolution of Fe occurs via two different paths, and both involves electrochemical and chemical steps. The concentration of both NH₄Cl and Na₂S₂O₃ determines the rate of these steps.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmrt.2018.05.029.

References

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