Effect of Ammonium Molybdate Inhibition on Corrosion Behaviour of Mild Steel in Chloride and Sulphide Media

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Abstract
The corrosion inhibition of mild steel in 3.0 M sodium chloride and 0.5 M sodium sulphide using various concentrations of ammonium molybdate was investigated in this work. The inhibition effect of this reagent in these media was monitored by weight loss and pH measurements. The analyses of the weight loss results showed that the corrosion susceptibility of mild steel in 3.0 M sodium chloride was more pronounced than in 0.5 M of sodium sulphide due to the aggressive chloride ions in the former and the weak nature of the latter. Ammonium molybdate produced a better inhibition performance of mild steel in 0.5 M sodium sulphide than in 3.0 M sodium chloride medium and the higher the concentration of ammonium molybdate the more the inhibition performance on mild steel in the media studied. Optimum inhibition was obtained at 2.5 M ammonium molybdate in both media. The pH values in chloride medium remained acidic throughout the exposure period while those of sulphide medium shifted to alkaline region with exposure time; an effect that was traceable to higher inhibition obtained in the latter medium.

Keywords: Chloride; Corrosion; Inhibition; Mild steel; Sulphide

1. Introduction
Corrosion has always been a menace to engineering and structural materials and has continued to attract a lot of investigations for many years [1–3]. Mild steel is one of the most commonly used structural materials and is being used in various forms such as beams, plates, bars, and pipes used in seawater which contains chlorides and for conveying petroleum products that sometimes contains sulphides that are detrimental to the steel. Since corrosion is always a function of the environmental conditions, control in some cases may be more concerned with preventing contact of the surrounding with these structural materials.

Mild steel is employed widely in most industries due to its low cost and availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines etc. [4–5]. Steel equipment undergoes corrosion because of the corrosive nature of the
constituents such as chloride and sulphide they are in contact within a particular application [6–7]. Mild steel which is used to manufacture many essential parts and components in the petroleum industry has always been at risk of corrosion from sulphide-containing solutions because these oil environments usually contain sulphides [8–10]. Sulphide contamination often occurs in seawater from industrial waste discharge, biological and bacteriological process, such as seaweeds, marine organisms or microorganisms and sulphide reducing bacteria, in seawater which promotes aqueous corrosion of steel materials [11].

The National Association of Corrosion Engineers (NACE) editor described corrosion inhibitors as substances that when added to an environment decrease or slow down the rate of attack on the metallic material [12] and they function in one or more of the following mechanisms: by adsorption of a thin film onto the surface of a corroding material, by inducing the formation of a thick corrosion product, or by changing the characteristic of the environment resulting in reduced aggressiveness [13]. These substances have been of great practical importance in minimizing the menace of corrosion in engineering materials. Several authors have investigated the working phenomenon of inhibitors [14–16] and their synergism [17–21] in various media.

The first use of molybdate as a corrosion inhibitor can be traced to 1939, when two patents were issued claiming the use of molybdate for corrosion protection in alcohol-water antifreeze for automotive cooling systems [22]. Investigation of molybdate as a corrosion inhibitor continued in the 1940’s leading to the publication of the first fundamental study of corrosion inhibition by molybdate in 1951 [23]. Molybdate is regarded as anodic inhibitor which works in the presence of oxygen to form a protective layer on ferrous metals [24]. Mild steel corrode with the formation ferrous ions at the anode (FeO → Fe²⁺ + 2e⁻), soluble molybdate ions react with the ferrous ions to form a non-protective ferrous-molybdate complex. This complex is then oxidized by dissolved oxygen to form an insoluble and protective ferric molybdate complex in combination with ferric oxide [25]. Furthermore, molybdate is believed to strengthen the outermost hydrated iron oxide layer by hydrogen bonding to hydroxide groups on the surface, thus imparting a negative surface charge, which impede aggressive chloride and sulphide ions from depassivating the metal surface and ferrous ions from leaving the surface [26]. Pitting corrosion may also occur from the presence of high concentration of chlorides but molybdate can retard the growth of these pits. When chlorides should have caused a break in protective film, absorbed molybdate will be released (since molybdate inhibits by adsorption) and concentrate inside the pits and precipitate as either FeMoO₄ [27] or as a condensed molybdate species [28].

Among many inhibitors available, molybdate has been proved to be an effective inhibitor to mitigate the corrosion of many engineering systems such as automobile cooling systems, paints, cooling towers, metal forming fluids [29], lubricants, boilers, metallic glasses, acids and concrete [30]. However, little work has been done on the use of molybdate in chloride and sulphide media. Therefore this work is set to study the inhibiting effect of ammonium molybdate on mild steel in chloride and sulphide media.

<table>
<thead>
<tr>
<th>Table1. Chemical composition (wt %) of the mild steel sample</th>
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<tr>
<td>Element</td>
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<tr>
<td>Composition</td>
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</table>
2. Experimental

The mild steel used in this work was obtained from Continental Shipyard Limited in Lagos, Nigeria. Its chemical composition as supplied by the manufacturer is shown in Table 1.

Sixteen corrosion test samples were made in 20 mm X 20 mm X 8 mm and were totally immersed in 3.0 M sodium chloride and 0.5 M sodium sulphide containing different concentrations of ammonium molybdate inhibitor as shown in Table 2. Weight loss measurements were conducted every three days for all the samples in the media using a sensitive electronic weighing machine for twenty–seven days following the procedures and precautions described by Bastidas et al., [31], Kolman et al., [32] and Ashassi-Sorkhabi et al., [33]. The pH values of these media were also recorded every three days.

3. Results and discussion

Fig. 1 shows the comparative corrosion behaviour of the mild steel sample in 3.0 M sodium chloride and 0.5 M sodium sulphide media. The two curves indicate increase in weight loss throughout the exposure period studied. However, the chloride medium shows a higher weight loss than the sulphide medium, which indicates higher corrosion susceptibility in the former than the latter. The behaviour is attributed to the aggressive chloride ions and possibly higher concentration of this medium than the sulphide medium. Chloride ions are known to be depassivating agent which usually breaks down any protective corrosion product on the steel.

Mild steel corrodes in the presence of air by forming iron oxide. This product is very porous and non protective in most media particularly chloride and hence allows further dissolution of this metal to occur. Chloride ions aid in the continued dissolution of this product which is evident in the progressive weight loss with exposure time observed in the chloride medium as shown in Fig. 1. Sulphide ion on the other hand, could not passivate the surface of this metal even though the corrosion susceptibility in this medium is less than that in the chloride medium as indicated by the lower values of weight losses recorded in the sulphide medium.

Table 2. Concentrations of corrosion media and/or ammonium molybdate inhibitor

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Concentration of Medium and/or Inhibitor</th>
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<tbody>
<tr>
<td>A</td>
<td>3.0 M Sodium Chloride</td>
</tr>
<tr>
<td>B</td>
<td>0.5 M Sodium Sulphide</td>
</tr>
<tr>
<td>C</td>
<td>3.0 M Sodium Chloride and 0.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>D</td>
<td>0.5 M Sodium Sulphide and 0.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>E</td>
<td>3.0 M Sodium Chloride and 1.0 M Ammonium Molybdate</td>
</tr>
<tr>
<td>F</td>
<td>0.5 M Sodium Sulphide and 1.0 M Ammonium Molybdate</td>
</tr>
<tr>
<td>G</td>
<td>3.0 M Sodium Chloride and 1.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>H</td>
<td>0.5 M Sodium Sulphide and 1.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>I</td>
<td>3.0 M Sodium Chloride and 2.0 M Ammonium Molybdate</td>
</tr>
<tr>
<td>J</td>
<td>0.5 M Sodium Sulphide and 2.0 M Ammonium Molybdate</td>
</tr>
<tr>
<td>K</td>
<td>3.0 M Sodium Chloride and 2.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>L</td>
<td>0.5 M Sodium Sulphide and 2.5 M Ammonium Molybdate</td>
</tr>
<tr>
<td>M</td>
<td>3.0 M Sodium Chloride and 3.0 M Ammonium Molybdate</td>
</tr>
<tr>
<td>N</td>
<td>0.5 M Sodium Sulphide and 3.0 M Ammonium Molybdate</td>
</tr>
</tbody>
</table>

Fig. 1. Corrosion of mild steel in 3.0 M NaCl and 0.5 M Na₂S.
Fig. 2 shows the inhibition effect of various concentrations of ammonium molybdate on corrosion of mild steel in 3.0 M sodium chloride. It is observed from this Figure that the uninhibited sample shows the highest weight loss during the exposure period studied. The corrosion susceptibility of this steel reduces gradually with increasing in the concentration of the ammonium molybdate, while the lowest weight loss of this material is observed at 2.5 and 3.0 M concentrations of this inhibitor. This indicates that the maximum inhibition that could be obtained from this reagent in 3.0 M concentration of sodium chloride medium is 2.5 M; above this concentration no inhibition effect is observed. Hence this value seems to be the optimum concentration of ammonium molybdenum that should be applied to effect the inhibition of mild steel in 3.0 M chloride medium. The effect of different concentrations of ammonium molybdate on mild steel immersed in 0.5 M sodium sulphide is presented in Fig. 3. This Figure shows similar trend as Fig. 2 in which increase in concentration of ammonium molybdate produces enhanced inhibition effect of this medium. This effect seems to reduce at the last two highest concentrations of this inhibitor.

The effect of various concentrations of ammonium molybdate inhibitor on the pH of the chloride medium during the exposure time is shown in Fig. 4. It is observed from this Figure that all the pH values stayed within the acidic medium throughout the exposure period and at lower concentrations of this inhibitor, the pH increased slightly towards the basic region. This could be explained by the fact that the porous corrosion products formed into the medium is alkaline in nature and therefore reduced the acidic concentration of this environment. At high concentrations of this inhibitor, the pH values fluctuate until the last few days of the exposure period when stability was achieved. This behaviour can be attributed to the passivation achieved due to the inhibition effect of the ammonium molybdate on the steel. This indicates that during passivation the pH of the corrosion medium was constant because there was no change in the composition of the medium. The effect of pH on the inhibition performance of ammonium molybdate on mild steel immersed in 0.5 M sodium sulphate is shown in Fig. 5. The pH values of all the samples tend to the alkaline region with exposure time while only the pH of the uninhibited sample remains within the alkaline medium throughout the exposure period. A closer look at the Figure indicates that the samples with increasing concentration of inhibitor remain in the alkaline region which
is traceable to inhibition effect of ammonium molybdate in this medium.

4. Conclusions

The following conclusions can be drawn from the investigation of the effect of inhibition performance of ammonium molybdate on mild steel in chloride and sulphide media.

(i) Mild steel was susceptible to corrosion in both 3.0 M sodium chloride and 0.5 M sodium sulphide media but this material was more susceptible to corrosion in 3.0 M sodium chloride than in 0.5 M sodium sulphide medium. This was as a result of aggressive chloride ions in the former and the weak nature of the latter.

(ii) Ammonium molybdate produced a better inhibition performance of mild steel in 0.5 M sodium sulphide than in 3.0 M sodium chloride medium.

(iii) The higher the concentration of ammonium molybdate the more the inhibition performance on mild steel and an optimum inhibition was achieved at 2.5 M concentration of ammonium molybdate in the media studied.

(iv) The pH values in chloride medium remained acidic throughout the exposure period while those in sulphide medium shifted to alkaline region with exposure time; an effect that was traceable to higher inhibition obtained in the latter medium.

References
