Corrosion Behaviour of Mild Steel in 0.5 M Sulphuric Acid
Media in the Presence of Potassium Chromate

1Olugbenga Adeshola Omotosho, 1Joshua Olusegun Okenyi, 1Jacob Olumuyiwa IKOTUN,
2Cleophas Akintoye Loto and 2Abimbola Patricia Idowu Popoola
1Department of Mechanical Engineering, Covenant University, 112001 Ota, Nigeria
2Department of Chemical and Metallurgical Engineering,
Tswane University of Technology, 0001 Pretoria, South Africa
3Department of Civil Engineering and Building, Vaal University of Technology, Vanderbijlpark
1900, South Africa

Abstract: This research investigates the behaviour of K2CrO4 on mild steel corrosion in 0.5 M H2SO4 at ambient temperature of 30°C. The study was conducted using weight loss and potentiodynamic polarization measurements. Data were recorded from the weight loss tests while the readout from the potentiostat was documented. Adsorption studies were also carried out. Furthermore, an investigation was conducted using surface coverage against concentration plot to determine when the best surface would be obtained during the experiment. Results from the study revealed that inhibitor efficiency increased as inhibitor concentration increased. The potentiodynamic polarization plot also identified the inhibition mechanism of action as mixed but predominantly anodic type inhibition with maximum Ecorr displacement of 68 mV. The adsorption of the inhibitor agrees with the Langmuir adsorption isotherm while the separation factor which is a component of the Langmuir expression showed a favourable adsorption. The Gibbs free energy of adsorption showed negative value (-9.8 kJ/mol) depicting a spontaneous process with a prevalence of physical adsorption. The first day curve showed the best surface coverage values across all inhibitor concentrations utilized.

Key words: Corrosion, weight loss, potentiodynamic polarization, Tafel slope, adsorption isotherm, physical adsorption

INTRODUCTION

The problems associated with corrosion is often considered to be economical because of consequences like loss of man-hours, facility replacement costs, compensation litigation by polluted communities, implied costs resulting from corrosion monitoring, maintenance and rehabilitation (Okenyi et al., 2012, 2014a, b; Omotosho et al., 2012, 2014). However, this is not the only concern because the effect of corrosion has a substantial influence on environmental safety. For example, the corrosion of sulphuric acid storage tanks and pipelines in the Motiva petrol refining facility in the US in 2001 led to the failure of the storage tanks and resulted in the death of one worker and injury to eight others. The surrounding water body was also contaminated leading to the loss of marine life. The report of the ultrasonic test revealed that continuous corrosion of the sulphuric acid tank was the reason for the failure because 50% of the corrosion allowance was lost in a sizeable portion of the exposed area of the tank.

The use of corrosion inhibitors has been identified as an effective corrosion control system (Finsgar and Jackson, 2014; Rani and Basu, 2012). However, it begins with understanding the mechanisms by which inhibitors are introduced into an aggressive acidic environment to stifle the reaction between the material and the environment (Onuchukwu, 1988). Normally, inhibition process is triggered by either the chemisorptions or physisorption route. In the physisorption route inhibitor molecules become bonded to the cathodic sites of the metal surface, essentially suppressing the metallic dissolution process. On the other hand the chemisorbed route ensures the anodic site is sheltered to decrease the characteristic ionization of the metal (Oguzie et al., 2005). It would seem that chemisorbed molecules of efficient inhibitors are overtly biased towards the anodic sites as they find greater expression in the region by protecting it (Debbery et al., 1984).

Chromate inhibitors are known to have the tendency to stifle reaction at the anode (Okonji et al., 2015a-c). However, since, inhibitors are environment specific it is
imported to gain more insight into the behaviour of potassium chromate in the sulphuric acid media. The adsorption layer of chromates is primarily made up of chromate oxide and it functions as a barrier separating the metal from the aggressive acidic media. The extent to which the process proceeds will depend on the metal involved, inhibitor structure, concentration and environmental temperature. Therefore, this study deals with the corrosion inhibition behaviour of mild steel in 0.5 M H$_2$SO$_4$ solution in the absence and presence of potassium chromate. The investigation will be conducted by monitoring of the corrosion process with gravimetric (weight loss) and electrochemical techniques.

**MATERIALS AND METHODS**

**Preparation of mild steel specimen and test solutions:** Mild steel sheet was cut into coupons measuring 2x2=0.3 cm for gravimetric measurements. For the linear sweep voltammetry tests, the electrode size had an exposure area 1 cm$^2$ with a long electrical wire connection for electrochemical contact to the Digi-Ivy potentiostat. The mild steel specimen utilized in this study was analyzed for its chemical composition in the Department of Metallurgical Engineering, University of Lagos, Nigeria and the metal was found to have the following composition (in wt%): 0.2654% Mn, 0.1203% C, 0.008% P, 0.034% S, 0.2212% Ni and the rest Fe. The aggressive media was 0.5 M H$_2$SO$_4$. The stock concentration of the acid with a purity and density of 94% and 1.84 g/cm$^3$, respectively was obtained from Sigma Aldrich, USA. The 0.5 M acid concentration was obtained by diluting a stock concentration of the H$_2$SO$_4$ (18.1 M) with distilled water in a fume chamber until the desired concentration was attained. K$_2$CrO$_4$ with 99% purity was obtained from Burgoine Burdick and Co, (India). The potassium chromate inhibitor concentration was prepared by making up the diluted concentration of the chromate inhibitor and the acid to 1 liter in a flat bottom flask. The concentration of the inhibitor for both test technique was varied from 2-10 g/L, with increments of 2 g/L.

**Gravimetric (weight loss) measurements:** The test coupons were chemically treated before the test according to ASTM D2688-94 R99 (2005) procedures. The coupon weights were recorded before the experiment. At the end of the tests, the samples were subject to post-experimental cleaning. This procedure was conducted in accordance with ASTM (2005). To obtain the weight loss data, the readings after the experiment were subtracted from the reading before the experiment. The specimens were then immersed in 0.5 M H$_2$SO$_4$ with and without the varying inhibitor concentrations for 60 days at ambient temperature of 30°C. The weight loss readings were taken every 4 days but the reading for the 1st day of the experiment was also taken. Before taking measurements every 4 days, the coupons were removed from the test solution, rinsed, dried well and weighed.

**Electrochemical tests:** The electrochemical technique of potentiodynamic polarization (Tafel) was conducted using Digi-Ivy potentiostat instrument (Model DY 2312) purchased from the U.S. The test solution was introduced into a three-electrode electrochemical cell kit model K47 manufactured by Princeton Applied Research in the U.S. The exposed surface area of 1 cm$^2$ for mild steel sample was embedded in a resin epoxy system with wire connection linking it from the test solution in the corrosion cell kit to the instrument. Prior to commencement of the tests the working electrode was treated with chemicals according to procedures earlier stated. The working electrode was polished before use. Other electrodes in the corrosion cell kit were a Ag/AgCl electrode as the reference electrode and graphite rod as the counter electrode. A steady-state reading of open circuit potential by metal sample was reached by the working electrode before commencement of the experiment. Potentiodynamic polarization monitoring at a scan rate of 100 mV/sec was conducted from anodic potential and cathodic potential of +0.5 V and -1.0 V, respectively (Omotosho et al., 2017a, b, 2016a-c).

**Corrosion rate analyses:** The weight loss data from the gravimetric tests were used to calculate the corrosion rate, CR$_{w}$ using the expression in Eq. 1 (Omotosho et al., 2011; Eddy et al., 2015; Umore et al., 2007; Karthik and Sundaravadivelu, 2013):

$$CR_{w} (\text{mmpy}) = \frac{87.6W}{A \times T \times D}$$  (1)

Where:
- $A$ = The Area (cm$^2$)
- $W$ = Mass change (g)
- $T$ = The Time of immersion (hr)
- $D$ = The Density of mild steel (g/cm$^3$)

Also, the corrosion rate (CR$_{p}$) from potentiodynamic polarization tests were obtained from machine readout using Eq. 2 (Omotosho et al., 2017a, b, 2016a-c; Carnet, 2008):

$$CR_{p} = \frac{3.27 \times 10^{-3} \times i_{corr} \times EW}{D}$$  (2)

Where:
- $EW$ = The Equivalent Weight (g)
- $i_{corr}$ = Corrosion current density ($\mu$A/cm$^2$)
- $D$ = Density (g/cm$^3$)
Inhibitor efficiency: Corrosion rate values from the gravimetric experiment is then used for estimating the Inhibition Efficiency (IE%) of the K₂CrO₄ inhibitor using Eq. 3 (Okenyi et al., 2014a-d, 2015a-c, 2016a-d, 2017a-c; Yadav et al., 2010):

\[
\text{IE\%} = \frac{CR_{\text{inhibited-sample}} - CR_{\text{inhibited-sample}}}{CR_{\text{inhibited-sample}}} \times 100
\]

Similarly, the surface coverage (\(\theta\)) was estimated using in Eq. 4 (Okenyi et al., 2015a-d 2017a-c; Karthikaiselvi and Subhashini, 2014):

\[
\text{IE\%} = \frac{CR_{\text{inhibited-sample}} - CR_{\text{inhibited-sample}}}{CR_{\text{inhibited-sample}}} \times 100
\]

**RESULTS AND DISCUSSION**

Figure 1 shows the graph of Corrosion Rate (\(CR_{\text{ep}}\)) against time for the mild steel sample immersed in H₂SO₄ in the presence of K₂CrO₄ at ambient temperature of 30°C. The control sample displayed very high CR values at the beginning of the experiment (first 24 h). This value, however, kept reducing as the experiment progressed but the very high initial value of the control sample CR ensured that the average of the CR ep values of the control was the highest. Figure 1b is a rescaled plot to view the disparity in CR ep values from 20 days to the end of the experiment, since, the curves on the plot (Fig. 1a) for the entire experiment is not delineated. As the experiment progressed at some point the CR ep of the inhibited samples were higher than that of the control. The 2 g/L inhibitor concentration displayed higher CR ep values than the control on the 28 and 36th day of the experiment. Generally, the CR ep values of the inhibited samples were lower than the control throughout the test period. This implies that the inhibitor was effective in retarding corrosion of mild steel sample in the acid solution.

![Graph of corrosion rate against time for the immersion of mild steel samples in 0.5 M H₂SO₄ solution at ambient temperature of 30°C](image)

**Fig. 1:** Graph of corrosion rate against time for the immersion of mild steel samples in 0.5 M H₂SO₄ solution at ambient temperature of 30°C: a) Normal scale for 60 days and b) Rescaled to view 0.0010-0.0110 mmipy for 20-60 days

Figure 2 shows the inhibition efficiency of potassium chromate on the corrosion of mild steel in 0.5 M H₂SO₄ solutions at ambient temperature of 30°C.

![Inhibition efficiency of potassium chromate on the corrosion of mild steel in 0.5 M H₂SO₄ solutions at ambient temperature of 30°C](image)

**Fig. 2:** Inhibition efficiency of potassium chromate on the corrosion of mild steel in 0.5 M H₂SO₄ solutions at ambient temperature of 30°C

Figure 3 is a plot of the curves of surface coverage (\(\theta\)) against inhibitor concentration as the experiment progressed. It is obvious from the graph that the curve for the first day produced the best surface coverage, possibly because no activity had really started to hamper the film.

![Variation of surface coverage (\(\theta\)) with potassium chromate concentration (g/L) at a temperature of 30°C for different time intervals for mild steel immersed in 0.5 M H₂SO₄](image)

**Fig. 3:** Variation of surface coverage (\(\theta\)) with potassium chromate concentration (g/L) at a temperature of 30°C for different time intervals for mild steel immersed in 0.5 M H₂SO₄
Fig. 4: Plots of kinetic parameters from electrochemical experiments: a) Potentio-dynamic polarization plots from LSV monitoring and b) Plots of corrosion potential and Tafel slopes against concentration of K$_2$CrO$_4$ from LSV experiments at ambient temperature of 30°C

Acting by stifling reactions at the anodic sites. Therefore, the inhibitor acted by reducing the anodic metal dissolution. Figure 4b is a plot of the Tafel constants and corrosion potential against concentration. The anodic and cathodic slope curves are clearly separated in the graph. The anodic curve displays an up trend as the inhibitor concentration increases up till 6 g/L and thereafter decreases at 8 g/L and then increases again at 10 g/L concentration. This behaviour is similar to the behaviour of the surface coverage curves in Fig. 3 where the $\theta$ values also decreased and increased at same concentration. Thus, this shows an agreement in the relationship between these two graphs (Fig. 3 and 4b).

Also, the value of $E_{corr}$ drifts from the cathode region at the beginning when concentration is zero (control) into the anodic region of the graph and stays in the anodic region at the high concentration of 10g/L. It is also noted from Fig. 4b, that all inhibited samples displayed $E_{corr}$ values in the anodic region. This behaviour clearly agrees with the $E_{corr}$ displacements values that inferred an anodic inhibition mode.

Table 1: R-values of different adsorption isotherms employed for metal-K$_2$CrO$_4$ interaction mechanism in 0.5 M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>R-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frankin</td>
<td>0.504</td>
</tr>
<tr>
<td>Flory-Huggins</td>
<td>0.766</td>
</tr>
<tr>
<td>Boris-Swinkel</td>
<td>0.840</td>
</tr>
<tr>
<td>Temkin</td>
<td>0.912</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>0.920</td>
</tr>
<tr>
<td>El-Awady</td>
<td>0.920</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.930</td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.969</td>
</tr>
</tbody>
</table>

Adsortion studies: Adsorption isotherms are normally deployed to describe the interaction mechanisms by the fitting of the test data to any of the adsorption isotherms identified for use. This experimental data fit was conducted using Frankin, Flory-Huggins, Boris-Swinkel, Temkin, Dubinin-Radushkevich, El-Awady, Freundlich and Langmuir isotherms. The results of the linear regression of the isotherms are shown in Table 1.

In Table 1, the R-values of each of the isotherms are the highest R-value. The expression shown in Eq. 5 (Fco and Hameed, 2010), represents the Langmuir adsorption equation, i.e.

$$ C = \frac{1}{K_{eq}Q_K} + \frac{C}{Q_K} $$

$K_{eq}$ and $Q_K$ is the Langmuir isotherm constant and maximum monolayer capacity (mg/g). $K_{eq}$ in the Langmuir
Table 2: Parameters of the linear regression of Langmuir isotherm plot and separation factor

<table>
<thead>
<tr>
<th>Slope</th>
<th>Intercept</th>
<th>( Q_a )</th>
<th>( K_{lg} )</th>
<th>( R_{lg} )</th>
<th>Favourability condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.607</td>
<td>0.689</td>
<td>1.647</td>
<td>0.881</td>
<td>0.362</td>
<td>Favourable</td>
</tr>
</tbody>
</table>

expression is related to \( R_{lg} \) in the separation factor expression in Eq. 6 (Okenyi, 2015a-c, 2016a-d; Omotosho et al., 2016; Foo et al., 2010):

\[
R_{lg} = \frac{1}{1+K_{lg}C_i}
\]  

(6)

\( R_{lg} \) and \( C_i \) are defined as the separation factor and the corrosion performance at the starting concentration, respectively.

By finding the logarithm of the Langmuir expression and thereafter plotting \( \log (C_i/\mu) \) versus \( \log C_i \), it was possible to determine the slope and intercept and compare the values from the graph to initial Langmuir expression. This comparison enables the deduction of the parameters shown in Table 2.

Inhibitors adsorption can be ranked based on the \( R_{lg} \) values which show the degree of favourability. Studies have shown that when \( R_{lg} \) values are greater than 0 and <1, the adsorption is favourable. Whereas when \( R_{lg} \) is more than 1 it is not favourable. On the other hand, when it is equivalent to 1, the adsorption is identified as linear while when it is zero, it is irreversible (Okenyi et al., 2016a-d; Omotosho et al., 2016; Foo et al., 2010; Umuro et al., 2007). Based on \( R_{lg} \) values from Table 2 the adsorption is favourable. From the adsorption studies conducted the Langmuir adsorption isotherm explains the metal-inhibitor interaction mechanism in the corrosion system. It therefore presumes that there are no interactions between the inhibitor molecules adsorbed on the metal surface.

Furthermore, in a bid to evaluate the adsorption mechanism of \( K_2CrO_4 \), the Gibb’s free energy \( (\Delta G^o \text{adsorption}) \) of adsorption was deduced by the expression in Eq. 7 (Okenyi, 2016; Umuro et al., 2007):

\[
\Delta G^o_{\text{adsorption}} = -2.303RT\log(55.5K_{lg})
\]

(7)

\( R \) and \( T \) are the universal gas constant (8.314 kJ/mol•K) and ambient temperature (303 K), respectively. By substituting the \( K_{lg} \) value from Table 2 into the Gibb’s free energy of adsorption equation a value of -9.8 kJ/mol is arrived at. This negative value indicates a spontaneous adsorption process for the inhibitor (Fig. 5).

**CONCLUSION**

This research focused on mild steel corrosion in 0.5 M \( H_2SO_4 \) solution with and without varying concentration of \( K_2CrO_4 \) at ambient temperature of 30°C and steady state condition using gravimetric and Tafel polarization measurements. The under-listed are the conclusions from the study: The trend of the corrosion rate in terms of reducing corrosion rate is 2<4<6<8<10 g/L.

The inhibitor efficiency of \( K_2CrO_4 \) on the corrosion of mild steel in 0.5 M \( H_2SO_4 \) solution increases with increasing inhibitor concentration. The Tafel polarization curve shows that the potassium chromate inhibitor is a mixed but predominantly anodic-type inhibitor. This infers the inhibitor activity influences activity at the cathodic sites. The \( K_2CrO_4 \) adsorption on the metal obeys the Langmuir adsorption isotherm. It is also a spontaneous process because of the negative value of \( \Delta G^o \) adsorption obtained. The negative sub -20 kJ/mol value show predominance of physical adsorption process of the chromate inhibitor on the metal surface. Based on separation factor \( R_{lg} \) obtained the adsorption of the inhibitor on the metal surface is favourable.

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