Electrochemical studies on the corrosion behaviour of Aluminium in an alkaline medium

ABSTRACT

Corrosion of Aluminium metal at pH 10 has been controlled by dicarboxylic acids such as oxalic acid (OA) and adipic acid (AA). The Inhibition efficiency (IE) has been determined by the classical weight loss method. The maximum inhibition efficiency (IE) offered by the oxalic acid (OA) and adipic acid (AA) 250 ppm and Zn²⁺ 50 ppm system are 88 and 96%. To determine the values of Linear Polarization Resistance (LPR) and corrosion Current (Iₜₜₒₜ), potentiodynamic polarization study has been used.

Keywords: Aluminium, Oxalic acid, Adipic Acid, electrochemical study.

1. INTRODUCTION

Aluminium is the second most rich metal after Iron because of its little atomic mass and negative average electrode prospective. Aluminium has a major responsibility in distinct human being activities. Because of its high energy density, it attracts the anode material for influence sources. Due to its strong electrical conductivity and good potency, it is used in construction, packing and shipping. Aluminium is commonly used by people because it is simply obtainable. It is used in numerous Industries, since it has high energy density, strength and purity[1]. Though Aluminium has adhesive shielding passivating oxide layer, this layer is amphoterically susceptible. It is establish that Aluminium metal dissolves in acidic solution and in basic solution [2-3]. Though Orsted discovered Aluminium (Latin – alum, alum), Thanks to Wohler who isolated Aluminium [4]. Aluminium was extracted from Bauxite ore by Pierre Brethier [5]. The Principle technique used in extraction of Aluminium have been separately developed by Charles Martin Hall of Ohio in U.S and Paul Herout of France which is commonly referred as Hall - Heroul electrolytic procedure. Since of having 59% Copper conductivity, Aluminium behaves as a excellent thermal and electrical conductor. Aluminium is an excellent Super Conductor [6] and it is one of the mainly generally used Non Ferrous metal[7]. It is observed that global fabrication of Aluminium is very high [8,9]. A high proportion of Aluminium alloys is used for producing Aluminium foils and beverage cans[10].

Aluminium products can be used with very high effectiveness[11]. Metal and alloys decay when they come in contract with environment, especially in presence of oxygen and water. This impulsive, natural and thermodynamically favorable process is known as Corrosion [12-14]. When Aluminium is exposed to air, first it undergoes corrosion and an oxide layer is generated from prevents further Corrosion of the metal[15].

The work deals with:

1. To evaluate the inhibition efficiency (IE) of oxalic acid (OA) and adipic acid (AA) is scheming deterioration of aluminium in an sedimentary resolution incorporating 60 ppm of Cl at pH 10 in the absent and in the present of Zn²⁺ by mass (or)weight loss method.

2. To revise the mechanistic features of deterioration inhibition by electrochemical studies such seeing that polarization study and AC impedance spectra.
2. EXPERIMENTAL SECTION

2.1. Specimens Preparation

Commercial Aluminium specimens containing 95% pure Aluminium of requisite measurement 4.0 x 1.0 x 0.2cm. The specimens were elegant to get mirror concluding. After polishing, the specimens were used in this work.

2.2. Inhibitor Solution

In 100ml of double distilled water and NaOH solution, 1g of oxalic acid and adipic acid was dissolved. The pH of this Inhibitor solution was adjusted to 10.

2.3. Weight Loss Method

Three Aluminium specimens were immersed in 100ml of an aqueous solution at pH 10 (dilute sodium hydroxide solution) for one day in the absence and presence of Inhibitors and the synergist namely Zn^{2+}. The weight of the specimens were determined using a sensitive balance Shimadzu AY62 model before immersion and after immersion for one day. The Corrosion rates were calculated. The Inhibition Efficiency (IE) was calculated from the equation:

\[ \text{Inhibition Efficiency (IE)} = ([w_1 - w_2]/w_1) \times 100\% \]

Where

- \( w_1 \) = Corrosion rates in the presence of the Inhibitor
- \( w_2 \) = Corrosion rates in the absence of the Inhibitor

2.4. Potentiodynamic Polarization Study

Polarization study was carried out in a 660A model of CHI electrochemical work station instrument. A three electrode assembly were used. The working electrode was Aluminium, Saturated Calomel Electrode (SCE) was used as Reference Electrode and Platinum was used as the Counter Electrode. Corrosion parameters such as Tafel slopes (\( b_a = \text{anodic}; \ b_c = \text{cathodic} \)) were calculated apart from Linear Polarization Resistance (LPR), corrosion Potential \( E_{corr} \), and corrosion Current \( I_{corr} \).

2.5. Alternating Current(AC) Impedance Measurements

In this study also, the same instrument and same set of three electrodes were used. Corrosion parameters namely, charge transfer Resistance (Rt) and double layer Capacitance (CdI) were derived from Nyquist plots. The Impedance value was derived from Bode plots.

2.6. Electrochemical studies and Corrosion methods

In an electrochemical studies such as potentiodynamic polarization study and AC impedance spectra is to be used as a investigate the corrosion behavior of the various metals and alloys in different medium. These methods give highly reliable results. Polarization study has been used to study the corrosion behavior of carbon steel in geothermal fluid of low enthalpy.

Polarization study is to be usage to assess thiophenol as an inhibitor for the corrosion of a hydrogen penetration during mild steel in acidic solutions. Pasi Kangas and Mark Newman have used polarization study to evaluate the recital of duplex chromium or stainless steels in organic compound. Pasi Kangas and Rajendran et al. have evaluated the mechanistic aspects of corrosion inhibition of carbon steel in the occurrence of 1-hydroxy ethyldine-1, 1-diphosphonic acid, Zn^{2+} and poly acrylamide by polarization curves. The electrochemical behaviours of Monel in NaCl medium and slow flowing sea water has been studied.

3. RESULTS AND DISCUSSIONS

3.1. Analysis of Weight Loss Method

Corrosion Rate (CR) of Aluminium immersed in aqueous solution containing at pH=10 for one day in the absence and presence of Inhibitor oxalic acid (OA) and Adipic Acid (AA) has been evaluated and values are given in the Tables 1 and 2.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Corrosion Rates (CR) (μm)</th>
<th>Inhibition Efficiency (IE) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>25.18</td>
<td>76</td>
</tr>
<tr>
<td>60</td>
<td>23.48</td>
<td>78</td>
</tr>
<tr>
<td>60</td>
<td>21.70</td>
<td>81</td>
</tr>
<tr>
<td>60</td>
<td>20.00</td>
<td>83</td>
</tr>
<tr>
<td>60</td>
<td>18.40</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 1. Corrosion rates (CR) of Aluminium immersed in aqueous solution in the absence and presence of Inhibitor system at various concentration and the Inhibition Efficiencies (IE) obtained by Weight Loss Method for the immersion period of one day

Tabela 1. Stopo korozije (CR) aluminijuma potopljenog u vodeni rastvor u odsustvu i prisustvu sistema inhibitora u različitim koncentracijama i efikasnosti inhibicije (IE) dobijene metodom gubitka težine za period potapanja od jednog dana.
The Inhibition Efficiencies of OA and AA are also given in these Tables. The Inhibition Efficiencies of the OA Zn\(^{2+}\) and AA-Zn\(^{2+}\) systems as a function of concentration of OA and AA are shown in Fig.1. It is observed from Table 1 that OA and AA shows some Inhibition Efficiencies and Inhibition Efficiency (IE) increases when the concentration increases. For example, 50ppm OA has 70 percent and AA has 78 percent IE while 250ppm OA has 76 percent and 250ppm AA has 86 per cent. This is due to the fact that as the concentration of OA and AA increases, the protective film (probably Aluminium OA and AA complex) formed on the metal surface goes on increasing.

**Table 2. Corrosion Rates (CR) of aluminium submerged in sedimentary solution incorporated 60 ppm Cl\(^{-}\) ions in the absence and presence of inhibitor scheme at different absorption and the Inhibition Efficiency (IE) attained by weight loss method (Inhibitor system: AA and OA +50 ppm of Zn\(^{2+}\) Immersion period: 1 day pH = 10)**

<table>
<thead>
<tr>
<th>Cl ppm</th>
<th>OA ppm</th>
<th>Zn(^{2+}) ppm</th>
<th>CR mdd</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td>23.48</td>
<td>--</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>50</td>
<td>19.25</td>
<td>18</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
<td>50</td>
<td>2.58</td>
<td>89</td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>2.11</td>
<td>91</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>50</td>
<td>1.87</td>
<td>92</td>
</tr>
<tr>
<td>60</td>
<td>200</td>
<td>50</td>
<td>1.40</td>
<td>94</td>
</tr>
<tr>
<td>60</td>
<td>250</td>
<td>50</td>
<td>1.17</td>
<td>96</td>
</tr>
</tbody>
</table>

**Role of Zn\(^{2+}\) is increasing the inhibitive property of Adipic acid(AA) and Oxalic acid (OA)**

The role of Zn\(^{2+}\) is increasing the inhibitive property of adipic acid (AA) and oxalic acid (OA) is given in Table 2. The adipic acid and oxalic acid shows excellent inhibitive property in the extinct of Zn\(^{2+}\) (50 ppm). For instance the mixture consisting of adipic acid and oxalic acid (250 ppm) and Zn\(^{2+}\) (50 ppm) offers 96% and 88% corrosion inhibition efficiency. This concept is known as synergistic effect. In presence of Zn\(^{2+}\), more inhibitor molecules are transported towards the aluminium metal surface. This enhances the formation of metal inhibitor compound on the anodal sites of the metal surface, while, cathodic sites are covered by Zn(OH)\(_2\). Thus anodal response and cathodal response are restricted efficiently. This statements for the synergistic effect and enhanced inhibitive efficiency of the inhibitor - Zn\(^{2+}\). The bond between inhibitor molecule and Zn\(^{2+}\) is tough adequate to carry the inhibitor molecule to the metal surface and weedy adequate to rupture in occurrence of the metal ion, on the plane of a metal.

**Role of Zn\(^{2+}\) in increasing the inhibition efficiency of the carboxylic acids**

It is interesting to note that in presence of Zn\(^{2+}\), the inhibition efficiency offered by the two carboxylic acids , namely adipic acid and oxalic acid increases. This is due to the fact, in the presence of Zn\(^{2+}\), more inhibitor molecules are transported towards the metal surface from the bulk of the solution. More aluminium-inhibitor complexes are formed on the anodic sites of the metal. So corrosion inhibition protection increases. Thickness of the film also increases. So, corrosion inhibition efficiency increases.

### 3.2. Analysis of Potentiodynamic Polarization Study (pH=10)

Polarization study has been used to confirm the formation of protective film formed on the metal surface during Corrosion Inhibition process .If a protective film is formed on the metal surface, the Linear Polarization Resistance value (LPR) increases and the corrosion Current value (\(I_{corr}\)) decreases. The Potentiodynamic Polarization curves of Aluminium immersed in aqueous solution containing in the absence and presence of Inhibitors are shown in Figure 1 and Figure 2. The corrosion parameters are given in Table 3 and 4. When Aluminium was immersed in aqueous solution containing the corrosion potential was -506 mV vs SCE. When OA and AA (250ppm) and Zn\(^{2+}\) (50ppm) were added to the above system, the corrosion potential shifted to the noble side -415Mv and -416 mV vs SCE. This indicates that a film is formed on the Anodic sites of the metal surface. This film controls the Anodic reaction of metal dissolution by forming Al\(^{3+}\)-OA-AA complex on the
Anodic sites of the metal surface. The formation of protective film on the metal surface is further supported by the fact that the anodic Tafel slope (ba) slightly decreases from 221 mV/decade to 146 mV/decade and 221 mV/decade to 218 mV/decade. Further, the LPR value increases from 27355 ohm cm² to 85826 ohm cm² and 27355 ohm cm² to 400583 ohm cm². The corrosion current decreases from 20.62 x 10⁻⁷ A/cm² to 1.140 x 10⁻⁷ A/cm² and 20.62 x 10⁻⁷ A/cm² to 3.983 x 10⁻⁷ A/cm². Thus, Polarization Study confirms the formation of a Protective Film on the metal surface.

For blank system, the value of Current remains constant from potential 1.2 volt to 0.446 volt. At this Volt, the film is broken. Hence the corrosion Current increases suddenly. The break down potential is -0.446 volt. Similar observation is made for the Inhibitor system also. Here the break down potential is -0.38. The reason for the Current remaining constant is due to the formation of passive film on the metal surface.

<table>
<thead>
<tr>
<th>System</th>
<th>E_corr mV vs SCE</th>
<th>b_a mV/decade</th>
<th>b_c mV/decade</th>
<th>I_corr A/cm²</th>
<th>LPR, ohm cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution containing 60 ppm Cl⁻ ions</td>
<td>-506</td>
<td>314</td>
<td>221</td>
<td>20.62 x 10⁻⁷</td>
<td>27355</td>
</tr>
<tr>
<td>Aqueous solution containing 60 ppm Cl⁻ ions + 250 ppm OA + 50 ppm of Zn²⁺</td>
<td>-415</td>
<td>169</td>
<td>146</td>
<td>3.983 x 10⁻⁷</td>
<td>85826</td>
</tr>
</tbody>
</table>

Table 3. Corrosion parameters of aluminium submerged in sedimentary solution containing 60 ppm Cl⁻ ions in the absent and present of inhibitor system obtain from potentiodynamic polarization.

<table>
<thead>
<tr>
<th>System</th>
<th>E_corr mV vs SCE</th>
<th>b_a mV/decade</th>
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<td>221</td>
<td>20.62 x 10⁻⁷</td>
<td>27355</td>
</tr>
<tr>
<td>Aqueous solution containing 60 ppm Cl⁻ ions + AA (250 ppm) + Zn²⁺ (50 ppm)</td>
<td>-416</td>
<td>203</td>
<td>218</td>
<td>1.140 x 10⁻⁷</td>
<td>400583</td>
</tr>
</tbody>
</table>
3.3. Analysis of AC Impedance Spectra

AC Impedance Spectra (Electrochemical Impedance Spectra) have been used to confirm the formation of Protective Film on the metal surface [20-24]. If a protective film is formed on the metal surface, charge transfer Resistance (Rt) increases, double layer Capacitance value (CdL) decreases and the Impedance log(z/ohm) value increases. The AC Impedance spectra of Aluminium immersed in aqueous solution containing 60ppm Cl⁻ ions in the absence and the presence of Inhibitors (OA-Zn²⁺n) and (AA-Zn²⁺) are shown in Fig 3 and 4 (Nyquist plots) and Fig 5 and 6 (Bode plots). The AC impedance parameters namely charge transfer Resistance (Rt) and double layer Capacitance (CdL) derived from Nyquist plots are given in Table 5. The Impedance log(z/ohm) values derived from Bode plots are also given in Table 6.

It is ascertained that when the inhibitors OA and (250 ppm) + Zn²⁺ (50 ppm) are added, the charge transfer resistance (Rt) increases from 83.85 Ωcm² to 1072Ωcm² and 83.85Ωcm² to 2848Ωcm². The CdL value decreases from 5.963 x 10⁻⁹ F/cm² to 4.644 x 10⁻⁹ F/cm² and 5.963 x 10⁻⁹ F/cm² to 1.756 x 10⁻⁹ F/cm². The impedance value (log (z/ohm)) increases from 1.963 to 3.280 and 1.963 to 3.622. These results lead to the conclusion that a protective film is formed on the metal surface. Equivalent circuit diagram of Aluminium immersed in various test solutions is shown in Scheme1.

In presence of Inhibitor, the phase angle value increases from 48° to 50°. This is due to formation of Protective Film.

Table 5. Corrosion parameters of aluminium submerged in sedimentary solution containing 60 ppm Cl⁻ ions in the absence and present of inhibitor system obtained from AC impedance spectra (pH=10)

<table>
<thead>
<tr>
<th>System</th>
<th>Nyquist plot</th>
<th>Bode plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rt ohm cm²</td>
<td>CdL F/cm²</td>
</tr>
<tr>
<td>Sedimentary solution containing 60 ppm Cl⁻ ions</td>
<td>83.85</td>
<td>5.963 x 10⁻⁹</td>
</tr>
<tr>
<td>Sedimentary solution containing 60 ppm Cl⁻ ions + 250 ppm of OA + 50 ppm of Zn²⁺</td>
<td>1072</td>
<td>4.644 x 10⁻⁹</td>
</tr>
</tbody>
</table>

Table 6. Corrosion factors of aluminium submergeded in sedimentary solution containing 60 ppm Cl⁻ ions in the absence and presence of inhibitor system attain from AC impedance spectra (pH=10)

<table>
<thead>
<tr>
<th>System</th>
<th>Nyquist plot</th>
<th>Bode plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>Sedimentary solution containing 60 ppm Cl⁻ ions</td>
<td>83.85</td>
<td>5.963 x 10⁻⁹</td>
</tr>
<tr>
<td>Sedimentary solution containing 60 ppm Cl⁻ ions + AA (250 ppm) + Zn²⁺ (50 ppm)</td>
<td>2848</td>
<td>1.756 x 10⁻⁹</td>
</tr>
</tbody>
</table>
Electrochemical studies on the corrosion behaviour of Aluminium in an ...
Figure 6. Bode plots of aluminium metal submerged in sedimentary solution containing (a) ppm Cl$^{-}$ ions (blank) and (b) 60 ppm Cl$^{-}$ + 250 ppm of AA + 50 ppm of Zn$^{2+}$.

Slika 6. Bodeovi dijagrami metala aluminijuma potopljenog u sedimentni rastvor koji sadrži (a) ppm Cl$^{-}$ jona (prazno) i (b) 60 ppm Cl$^{-}$ + 250 ppm AA + 50 ppm Zn$^{2+}$.

4. CONCLUSIONS

- The consequences of the weight-loss survey show that 250 ppm of AA and 50 ppm of Zn$^{2+}$ has 96% IE in scheming corrosion of aluminium metal in an sedimentary solution incorporating 60 ppm Cl$^{-}$ ions at pH=10.
- Polarization study expose that the preparation purpose as cathodic inhibitor calculating the cathodic reaction mainly and to some level controls the anodic reaction.
- AC impedance spectrum expose that a protecting film is formed on the metal surface.

The results of the weight-loss study show that 250 ppm of OA and 50 ppm of Zn$^{2+}$ has 88% IE in controlling corrosion of aluminium metal in an aqueous solution containing 60 ppm Cl$^{-}$ ions at pH=10.

- Polarization study reveals that the formulation functions as cathodic inhibitor controlling the cathodic reaction predominantly and to some extent controls the anodic reaction.
- AC impedance spectra reveal that a protective film is formed on the metal surface.

Scope for Further Study.

- An investigation in the EPR study of layer created on the metal plane or exterior may be carried out.
- Inhibition Exhibition (IE) of the preferred inhibitors may be estimated in combination with other ions such as Mn$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, polymers etc..

Acknowledgement

The authors are thankful to their respective management for their help and encouragement.

5. REFERENCES

IZVOD

ELEKTROHEMIJSKA ISTRAŽivanja O KOROZIJSKOM PONAŠANJU ALUMINIJUMA U ALKALNOJ SREDINI

Korozija metaala aluminijuma na pH 10 je kontrolisana dikarboksilnim kiselinama kao što su oksalna kiselina (OA) i adipinska kiselina (AA). Efikasnost inhibicije (IE) je određena klasičnom metodom gubitka težine. Maksimalna efikasnost inhibicije (IE) koju nude sistem oksalne kiseline (OA) i adipinska kiselina (AA) 250 ppm i Zn²⁺ 50 ppm iznosi 88% i 96%. Za određivanje vrednosti linearno polarizacione otpornosti (LPR) i struje korozije (Icor), korišćena je potenciodinamička studija polarizacije.

Ključne reči: aluminijum, oksalna kiselina, adipinska kiselina, elektrohemijaska studija.

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