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Molebdate as Corrosion Inhibitor for Aluminium 356 in Acidic and Saline Media

[1]Jahagirdhar AA, [2]Pruthviraj RD*

Author Affiliations
[1]Department of Chemistry, Dr. Ambedkar Institute of Technology, Bengaluru, Karnataka 560056, India
[2]Department of Chemistry, RajaRajeswari College of Engineering, Bengaluru, Karnataka 560074, India

***Corresponding Author**
Pruthviraj R.D.,
Department of Chemistry, RajaRajeswari College of Engineering, Bengaluru, Karnataka 560074, India
E- mail: pruthvirajrd@gmail.com

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ABSTRACT

Corrosion processes are responsible for huge losses in industry. Though organic, inorganic and mixed material inhibitors were used for a long time to combat corrosion, the environmental toxicity of organic corrosion inhibitors has prompted the search for inorganic corrosion inhibitors. The effect of Molebdate as novel corrosion inhibitors on the corrosion of aluminium 356in acidic and saline media was investigated by electrochemical and weight loss techniques. The effect of inhibitor concentration was also investigated. High resolution scanning electron microscopy equipped with energy dispersive spectroscopy (HR-SEM/EDS) was used to characterize the surface morphology of the metal before and after corrosion. Experimental results revealed that Moleblate in the studied solution decreased the corrosion rate at the different concentrations studied. The experimental results obtained from potentiodynamic polarization method showed that the presence of the Moleblate in 3.5% NaCl and 0.5 M H2SO4 solutions decreases the corrosion current densities (icorr) and corrosion rates (CR), and increases the polarization resistance (Rp). It was observed that the inhibitor efficiency depends on the corrosive media, concentration of the inhibitor and the substrate material. The adsorption characteristics of the Moleblate were also described. Good correlation exists between the results obtained from both methods.

Keywords: Aluminium 356, Corrosion, Molebdate, HCl, NaCl, Potentiodynamic

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INTRODUCTION

Aluminum compounds occur in aluminum types of clay, but the most useful ore for producing pure aluminum is bauxite. It consists of 45.60% aluminum oxide, along with various impurities such as iron, sand and other metals [1]. Aluminum is durable, relatively soft, light weight, malleable and ductile metal with physical appearance ranging from silvery to dull gray depending on the roughness of the surface. Aluminum has almost one – third of the stiffness and density of steel. It is easily drawn, machined, cast and extruded. Aluminum is also a good electrical and thermal conductor. Aluminum and its alloys are very important material because of their wide use in many industries. They are used in the aviation, aerospace and automotive industries, in the production of military hardware, in ship building and household appliances [2–4]. Their usefulness is derived from their very good mechanical and physical properties such as their weight-to-high strength ratio, good machining properties, recyclability, and their outstanding corrosion resistance. The corrosion resistance of aluminum and its alloys is attributed to the formation of a stable protective thin film of aluminum oxide when exposed to the atmosphere. Aluminum alloys are therefore used widely as materials for electricity cables, bottle tops, food and beverage containers, and roofing sheets [5]. Despite the huge benefit of aluminum when compared to other metals, it is not always resistant to corrosion completely. When the environment is highly basic or acidic, the protective layer breakdown can occur and its instant renewal may not be fast enough to prevent corrosion [6–9]. Corrosion of aluminum leads to passivation of active cathode material, the electrical resistance of the solid product is increased and the electrolyte is contaminated by its soluble products and increases the self-discharge rate. In efforts to reduce aluminum corrosion, the main approach is to separate the aluminum metal from corrosive environments and this can be accomplished by means of corrosion inhibitors. Therefore, the ability of aluminum to resist corrosion attack in various environments is inadequate and a continuous search for methods for controlling this behavior remains important in the field of corrosion control.The corrosion of metals is a serious problem in most industries. Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development [10]. Technological progresses require the use of materials in aggressive environments, such as corrosive atmospheres [11]. Corrosion is a degradation of metal due to environmental reactions dissolution; it is an electrochemical process and usually begins at the surface [12, 13]. As a result of daily encounters with corrosion problems such as; waste of valuable resources, costly maintenance, plant shutdowns, expensive overdesign, loss or contamination of products and reduction in efficiency; technological developments are impeded and safety endangered [14, 15]. The multifacet aspect of corrosion problems coupled with responsibilities associated with them only increase the complexity of the subject [16, 17]. This problem has caused the stimulation of many corrosion control research in various oil production facilities around the world [18]. The cost due to corrosion does not only increase rapidly, the quality of the products and the efficiency of the plants is also reduced. In the United States this amount to over 276 billion USD per year. The highest segments of the cost of corrosion are associated with utilities, transportation and infrastructure. Millions of dollars are lost each year because of corrosion including the cost of prevention and maintenance. NACE studies recently estimates global cost of corrosion at $2.5 trillion annually at CORROSION 2016 conference held at Vancouver, B.C., which examined the economics of corrosion and the role of corrosion management in establishing industry best practices [19]. Corrosion can be localized by forming a crack or pit, or expand across a wide area by uniformly corroding the surface [20]. Pitting corrosion takes place in materials with surface films protection like corrosion products, the metal exposed releases electrons easily and tiny pits is initiated by the reactions [21]. Galvanic corrosion usually occurs on the surface of metal which have more than one phase, in other for local cells to be set up on heterogeneous surface with different potentials. The preferential attack of grain boundaries without substantial attack of the grains themselves is called intergranular corrosion; it is often caused by the precipitation of fine intermetallics at grain boundaries [22]. Localized corrosion may possibly result in structure failure of metallic materials if it is allowed to reach critical levels [23]. Corrosion resistance of alloys has become a continuous research due to its severe consequences [24]. One of the most useful techniques in protecting and controlling metals against corrosion is the use of inhibitors, especially in saline and acidic media.

MOLEBDATE AS CORROSION INHIBITION FOR ALUMINUM ALLOY

Behavior of aluminium 356substrate in sodium chloride solution

The potentiodynamic polarization behavior of the received aluminum sample in saline solution is shown in Figure 1.

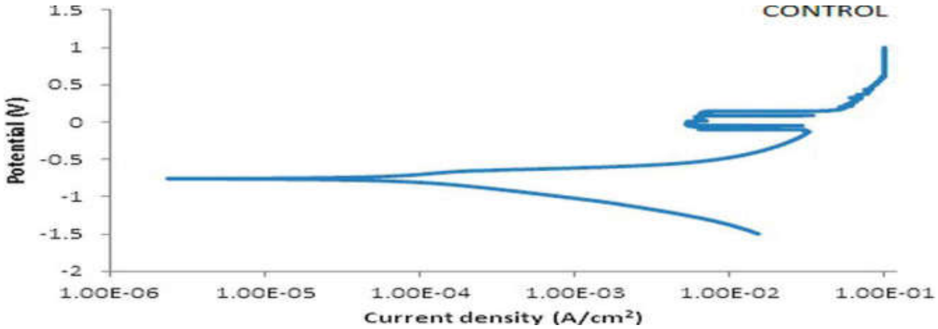

Figure 1: Linear polarization curve for aluminium 356in sodium chloride solution [46].

In the sodium chloride solution, the aluminum sample gives a corrosion potential of −0.75893 V. The active corrosion path was formed as a result of the dissolution of the aluminum matrix. The surface of the tested aluminum coupon at different areas shows different dark shades, and this was examined by SEM/EDS. It is most likely that the darker areas are where the aluminum has not suffered severe corrosion from the sodium chloride, at those areas surface oxides layers have been formed that impeded corrosion. At the whitish areas aluminum dissolution must have occurred the chloride ion has penetrated the matrix of the aluminum surface. This was confirmed by the EDS analysis on the different areas which revealed that the darker areas had a high Al peak while the whitish areas consist of O, Na, S, Fe and C. In the border between the whitish and the darker areas there was a band of hole which seems to be associated to the dissolution of the Al alloy as a result of the aggressiveness of the sodium chloride. This hole did not exist on the as received sample [46] (Figure 2).

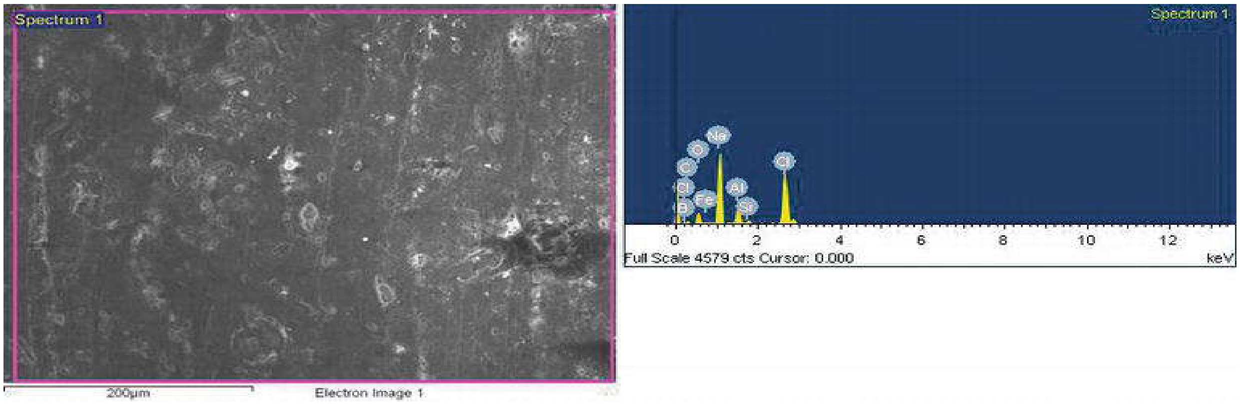

Figure 2: SEM/EDS spectra of corroded aluminium 356in saline solution [46].

The result show the adsorption of the oxide film, formation of basic hydrochloric aluminum salt which separates from the lattice and goes into the system:

$Al_3++4Cl-\rightarrow AlCl_4-Al_3++4Cl-\rightarrow AlCl_4-$ E1
$Al_3++2Cl-+2OH\rightarrow Al(OH)_2ClAl_3++2Cl-+2OH\rightarrow Al(OH)_2Cl$ E2

The oxide film is thinned to the extent that aluminum ion can pass from the metal to the sodium chloride interface. The chloride ion gets entry by penetrating through the oxide film or diffusion of halide ion through the oxide film and attack the alloy.

Behavior of aluminium 356substrate in H_2SO_4 acid medium

The potentiodynamic polarization behavior of the as-received aluminium 356 sample in acid medium is shown in Figure 3.

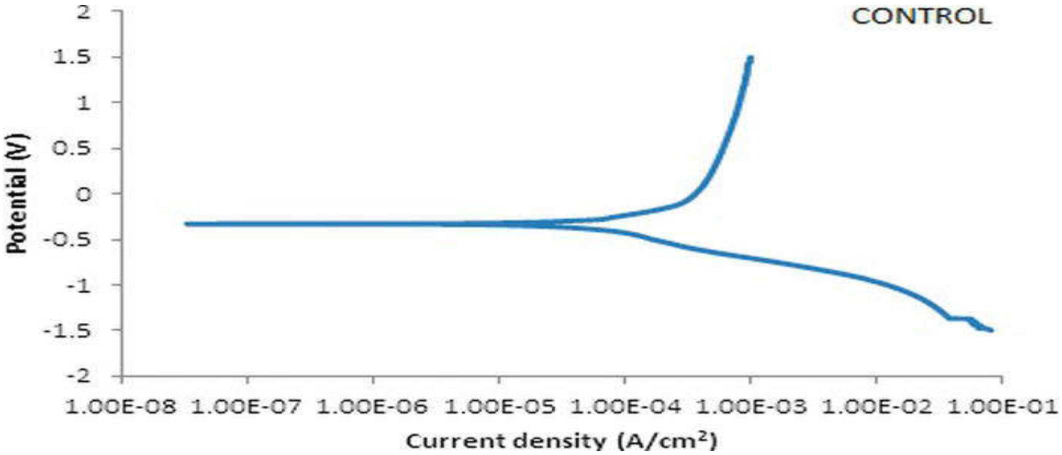

Figure 3: Tafel polarization curve for aluminium 356 in H_2SO_4 acid solution [46].

The linear polarization curve determines the active or passive characterization of aluminium 356in acid solution. In the acid solution, the aluminum sample gives a corrosion potential of −0.55960 V. The active corrosion path was formed as a result of the dissolution of the aluminum matrix.

A morphological study of the surface of aluminum specimen in acid solution was carried out by SEM after immersion in the test solution for 28 days at 28°C [46]. Figure 4 shows the SEM images of the aluminum surface after 28 days immersion in 0.5 M H_2SO_4 acid. A severely corroded surface was observed after immersion in the uninhibited system, due to corrosive attack of the acid solution. The corrosion product layer on the metal surface in uninhibited 0.5 M H_2SO_4 acid and the corrosion damage is clearly visible on the metal surface. The oxide film is thinned to the extent that aluminum ions can pass from the aluminium 356to the solution interface.

Al2O3+3H2SO4→Al2(SO4)3+3H2OAl2O3+3H2SO4→Al2SO43+3H2O E3

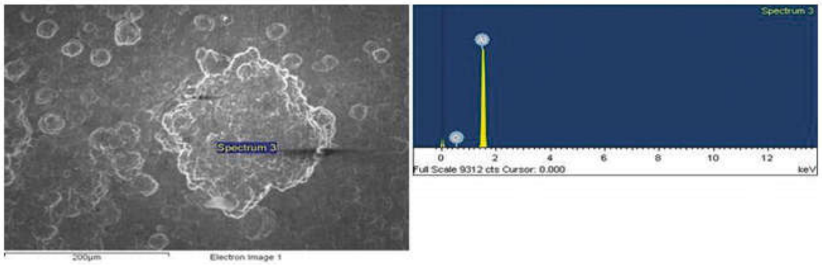

Figure 4: SEM/EDS spectra of corroded aluminium 356 in H_2SO_4 acid solution [46].

The sulfuric ion gets entry by penetration through the oxide film and attack the metal.

CHARACTERIZATION OF INHIBITED ALUMINIUM 356 IN SALINE (3.5% NACL) MEDIUM

The obtained results from weight loss and potentiodynamic polarization methods at different concentrations of ferrous gluconate (FG), zinc gluconate (ZG) and the synergistic effect of the two inhibitors in saline solution at 28°C are represented in Figures below.

Aluminium 356in saline medium with ferrous gluconate (FG) as inhibitor

Weight loss method

Figure 5 is the plot of weight loss against exposure time for aluminium 356coupons in saline environment in the absence and presence of different concentrations of FG at 28°C.

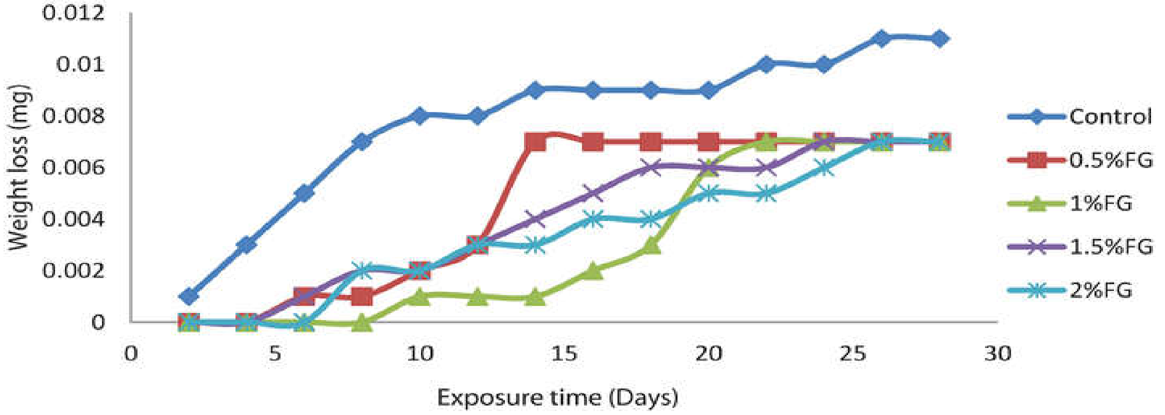

Figure 5: Weight loss versus exposure time for aluminium 356immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

In the absence of FG, the weight loss increased with an increase in exposure time in 3.5% sodium chloride solution. The weight loss was 0.001 gm at the beginning of the analysis but increased with an increase in exposure time which gave a value of 0.011 gm after 28 days of exposure. In the presence of FG, the weight loss value was reduced given the highest value of 0.007 gm at the end of 28 days exposure time at all the concentrations of inhibitor studied. This clearly indicates a 36% reduction in weight loss value in the presence of FG when compared to the value in the absence of FG [47, 49].

Figure 6 shows the graph of corrosion rate of aluminium 356coupons in the absence and presence of varied concentrations of FG in 3.5% NaCl solution at 28°C.

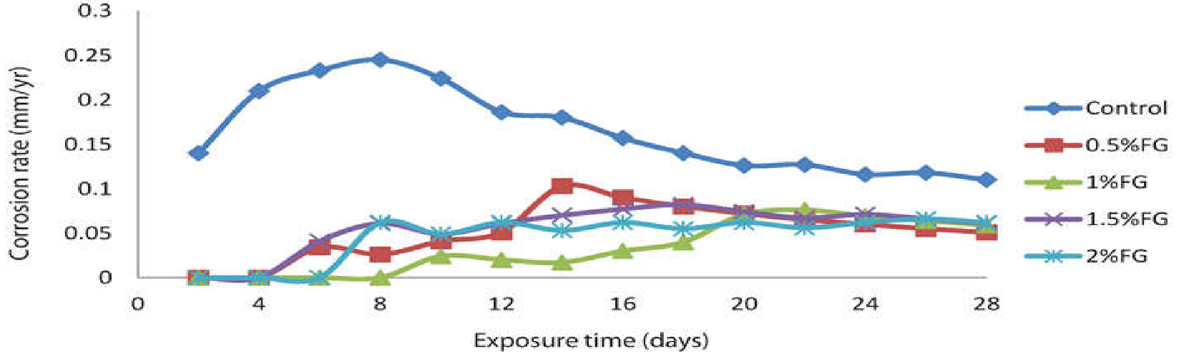

Figure 6: Corrosion rate versus exposure time for aluminium 356immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

Observation made indicates that corrosion rate of aluminium 356reduced in the presence of all the different concentrations of FG considered. In the presence of 0.5% g/v concentration of FG, the corrosion rate value was 0.051 mm/yr at the end of 28 days exposure time compared with the absence of FG which gave 0.110 mm/yr at the end of 28 days of exposure [47, 49]. This shows 54% reduction in corrosion rate value compared with the absence of FG. It can be deduced that FG inhibits the corrosion of aluminium 356in saline solution. Also shown in Figure 7 is the graph of percentage inhibition efficiency (%IE) with exposure time in the presence of different concentrations of FG.

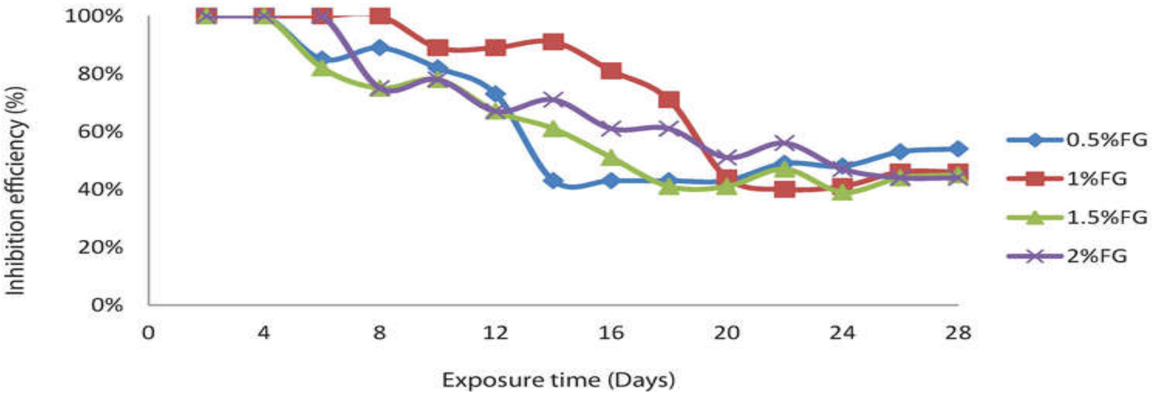

Figure 7: Inhibition efficiency versus exposure time for aluminium 356immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

A reduction in IE of FG from 100% depending on the concentration of FG added to the corrosive environment was observed. The inhibition efficiency at 0.5% g/v concentration of FG reduced to 54%, 1.0% g/v reduced to 46%, 1.5% g/v reduced to 45% and 2.0% g/v reduced to 44% at the end of 28 days exposure time to the corrosive environment. The optimum inhibition efficiency was observed at 1.0% g/v concentration of FG in 3.5% NaCl solution at 28°C.

Figure 8: SEM/EDS spectra of corroded aluminium 356 in the presence of FG [47].

In the presence of 2.0% g/v concentration of FG, the corrosion is slightly reduced with little corrosion product on the aluminium 356surface when compared with the morphology of the aluminium 356in the absence of FG. This clearly revealed that FG is a corrosion inhibitor for the aluminium 356in acidic solution. The effective corrosion inhibition of FG could be attributed to the film formed on the surface of the sample. The EDS in Figure 8 clearly shows the presence of carbon, oxygen indicating the formation of oxide films as confirmed by Raman spectroscopy. Other elements are also present which is as a result of ferrous gluconate constituent.

Potentiodynamic polarization method

Table 1 shows the electrochemical corrosion parameters that is, potentiodynamic polarization-corrosion potential (Ecorr), linear polarization resistance (Rp), anodic and cathodic Tafel slopes (βa, βc), corrosion rate (CR) and potentiodynamic polarization corrosion-current density (icorr) obtained by extrapolation of the Tafel lines.

Table 1: Polarization data for ZG inhibited aluminium 356in 0.5 M H_2SO_4 solution.

S.N.	C (% g/v)	Icorr (A/cm^2)	βc (V/dec)	βa (V/dec)	LPR Rp (Ωcm^2)	−Ecorr (V)	CR (mm/yr)
1	0.0	1.73E-05	0.025551	0.124930	5.33E+02	0.33054	0.559600
2	0.5	6.46E-06	0.054932	0.032904	1.38E+03	0.33054	0.209090
3	1.0	5.43E-06	0.042048	0.035871	1.55E+03	0.33054	0.175710
4	1.5	6.30E-09	0.892180	1.727600	4.06E+07	0.34318	0.000206
5	2.0	3.78E-06	0.172780	0.072640	5.87E+03	0.35751	0.123690

Figure 9 gives the potentiodynamic polarization curves for the inhibition of aluminium 356in the absence and presence of different concentrations of ZG in 0.5 molar sulfuric acid solutions at 28°C. From Table 1, it can be concluded that the corrosion current density (icorr) values reduced in the presence of all the concentrations of ZG studied. The anodic and cathodic values were observed to change in the presence of all the different concentrations of ZG studied in 0.5 M H_2SO_4 solution. The polarization resistance (Rp) values increased and corrosion rate (CR) values decreased in the presence of inhibitor. Also, no definite trend was observed in the corrosion potential (Ecorr) values in the presence of inhibitor [47]. This result showed the influence of ZG on aluminium 356in 0.5 M H_2SO_4 solution and the ZG acts as a mixed type inhibitor.

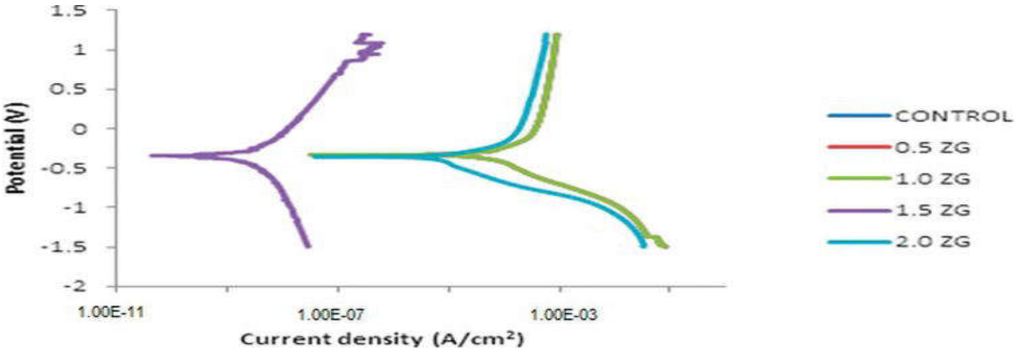

Figure 9: Tafel polarization curves for aluminium 356in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of ZG at 28°C [48].

CONCLUSIONS

The following conclusions have been drawn from this research;

- The aluminium 356exhibited similar corrosion behavior in the presence of different concentrations of inhibitors in the solution studied, with different corrosion resistances in the different solutions which was confirmed from the similar trend from corrosion rates and inhibition efficiency of the materials from weight loss and potentiodynamic polarization curves.

- In saline environment in the presence of different concentration of inhibitors, the corrosion resistant of aluminium 356was significantly different, this was evident by their corrosion rates and inhibition efficiency values. FG performed best at 1.0% g/v concentration in 3.5% NaCl solution which gave inhibition efficiency value of 100% from the beginning of the analysis to the 8th day of exposure time to the corrosive medium.
- It could be concluded that ZG performed best in 3.5% NaCl solution. The inhibitors performed fairly well in 0.5 M H_2SO_4 solution. The corrosion rates and inhibition efficiency values obtained from the weight loss and potentiodynamic polarization methods show good agreement.
- The main task of this research work has been accomplished. The optimum concentrations for the application of the inhibitors which should be useful guide for corrosion engineers have been obtained.

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