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Research Article

PROTECTION EFFICIENCY OF MIGRATING INHIBITORS ON CORROSION OF REINFORCING STEEL IN AGGRESSIVE ENVIRONMENT

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ABSTRACT. The migration corrosion inhibitors (MCI) are regarded as an efficient method for inhibiting and retarding the corrosion of the reinforcement and the concrete structure. Our study concerns the investigation of the protective effect of MCI; different concentrations of butanol-1 amin-2 refer 1g/L lysine in sulfuric acid in presence of chloride ions, in form of NaCl (H_2SO_4 1M + Cl^- 10^{-3}M). The potentiodynamic polarization method is conducted to measure corrosion rate and inhibition efficiency of two kinds of low allow carbon steel marked as: Steel 39, Steel 44. Potentiodynamic polarization measurements showed that the presence of MCI in acidic solution decreases the corrosion current to a good extent. The polarization curves in polarization experiments show that the inhibition efficiency is 90.52% with 12 g/L butanol-1 amin-2 + 1g/L lysine concentration of inhibitor, referring steel 39 and 75.98% inhibition efficiency for steel 44.

Keywords: *migration inhibitor, potenciodynamic polarization, acid media, carbon steel*

INTRODUCTION

In the last years, research in the field of corrosion inhibitors had been directed toward of using cheap, environmentally friendly, non-toxic, biodegradable and relatively cheap. Corrosion of reinforcing steel is a major degradation of failure in reinforced concrete structures leading to financial losses, safety risks and environmental impact. The understanding of the mechanisms of the degradation processes of concrete allows us to improve the design of structures to enhance durability and extend service-life [1]. Corrosion of concrete armature caused by acid media penetration of the coastal areas in it, through chemical and mechanical cracks, is responsible sometimes for concrete failure, building failure and of course environmental pollution. Besides the mitigation of chemical and mechanical cracks adding migration corrosion inhibitors (MCI) to concrete mixes is a simple, time-proven, cost-effective and environmentally friendly method of achieving significant enhancement in durability [2]. Use of MCI will be for corrosion protection of concrete steel bars a good choice, penetrating to metal surface together with aggressive media. MCI's provide protection because of their ability to migrate to the depth of the metal, and form a protective, molecular layer on steel when they come into contact with it. Most reviewers present amino-acids as a good inhibitor of acidic environment (H_2SO_4) in presence of Cl^- ions, and amino-alcohols as good migrator agents. The aim of this study is the investigation of synergic effect for different concentration of 2- amino 1- butanol (amino-alcohol), as migrator agent, refer 1g/L L-lysine (amino acid) in protection efficiency again corrosion in these aggressive media for steel 39 and steel 44.

MATERIALS AND METHODS

The material used are two marks of low alloy carbon steel, manufactured in KURUM factory, Elbasan, respectively St.39 and St.44, intended for concrete armor.

***Table 1**: Composition of low alloy carbon steel tested*

Element (Mass-%)	**C**	**Si**	**Mn**	**Cr**	**Ni**	**Cu**	**P**	**S**
Steel 39	0.37	0.17	0.51	0.60	0.60	0.30	0.040	0.040
Steel 44	0.445	0.348	0.780	0.118	0.263	0.324	0.0720	0.0440

The samples used for the potentiodynamic measurements are prepared from steel bars in cylindrical shape with sizes (D=6mm, d=4mm) and fixed inside a Teflon tube with epoxy resin as shown in Fig. 1. For the potentiodynamic measurements the steel samples, before fixed inside the Teflon, were polished with emery paper (250 – 1000), cleaned with be distilled water, dried, degreased with acetone, cleaned with be distilled water again, and finally dried [3,4].

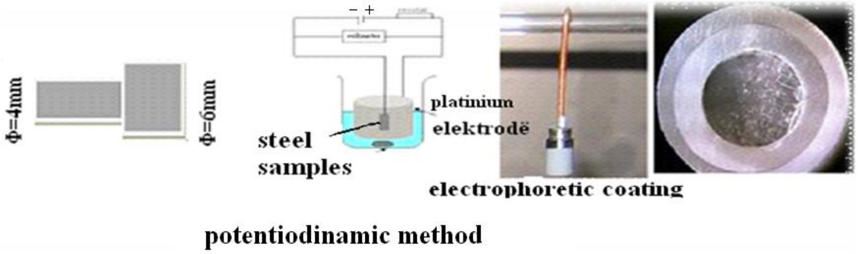

***Fig.1:** Preparing of the samples for potentiodynamic measurements*

The corrosion media consists in sulfuric acid in presence of chloride ions. The concentration of acid used is 1mol/L H_2SO_4 and chloride ions are 10^{-3}mol/L Cl^- (in form of NaCl) (imitation of aggressive industrial Coastal atmosphere). As corrosion inhibitor we have used MCI (mix of amino-alcohol and lysine) figure 2,3. The concentration ratio of inhibitor is present in table 2.

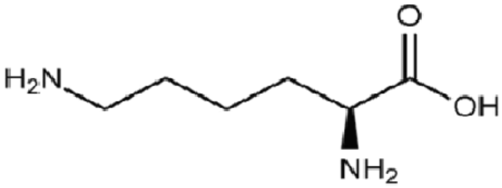

Fig. 2: *The structure of lysine (inhibitor)*

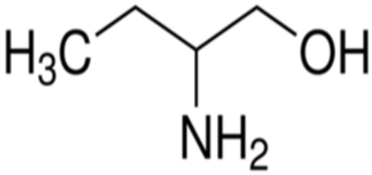

Fig.3: *The structure of 2-amino-1-butanol (migrator)*

Table 2: *The matrix for potenciodynamic measurements*

Nr.	**Concentrations ratio of lysine /2-amino 1-butanol (g/L)**				
	Blank	1g/L/2g/L	1g/L/4g/L	1g/L/8g/L	1g/L/12g/L
1	+				
2		+			
3			+		
4				+	
5					+

Potenciodynamic measurements were carried out in a typical three-electrode electrochemical cell with an Hg/Hg_2SO_4 saturated K_2SO_4 electrode as a reference electrode and a platinum electrode as auxiliary electrode. potenciostat galvanostat tip TACUSSEL PJT 24-2 is used for potenciodinamic measurements, potencial scan rate is $6x10^{-3}$ V/min [3,5]. Deaerating of the solution was realized using a stream of pure nitrogen inside the solution for 30 min and above solution for 5 min. Corrosion current density determined using the cutting point of Taffel extrapolation line and Faradays law, equation 1 [3,6]:

$$V_{corr} = (K^* a *i) / (n^* D)$$

Eqn. 1

Where: a - is the atomic weight of the metal (a=56g/mol), i -the current density in ($\mu A/cm^2$), n -the number of electrons exchanged during metal dissolution (n=2), D -the density in (g/cm^3) ($d=7.86g/cm^3$) and K is a constant which equals to 0.00327 if corrosion rate (V_{corr}) is calculated in [mm/y]. Corrosion inhibitor efficiency calculated by formula 2 [7)]:

$$\text{Inhibitor Efficiency (\%)} = [(\text{CR uninhibited} - \text{CR inhibited})/ \text{CR uninhibited}] \times 100$$

Eqn. 2

Where: CR uninhibited - is corrosion rate of the uninhibited system, CR inhibited - is corrosion rate of the inhibited system. This essentially examines the ratio of the inhibited and uninhibited corrosion rates and expresses this as a percentage.

RESULTS

The results for potenciodynamic measurements are given in form of V_{corr} in (mm/year), calculated using corrosion current density (i_{corr}). Corrosion current density is determined using the cutting point of Taffel extrapolation line. Potentiodynamic polarization curves are given in Fig. 4 (a,b) for steel 39 and in Fig. 5 (a,b) for steel 44 in de-aerated 1M H_2SO_4 solution with 10^{-3}M chloride ions (blank) containing different concentration ratio of 2-amino1- butanol / lysine –a-; and only different concentration of lysine –b.

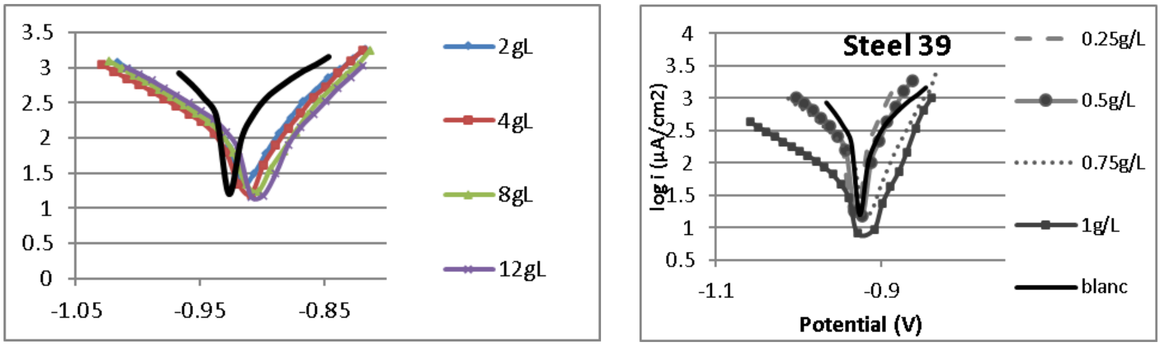

Fig.4: *Potentiodynamic polarization curves for Steel 39 in de-aerated 1M H_2SO_4 solution with 10^{-3}M chloride ions (blank) containing different concentration ratio of 2-amino1-butanol / lysine (a); and only different concentration of lysine (b).*

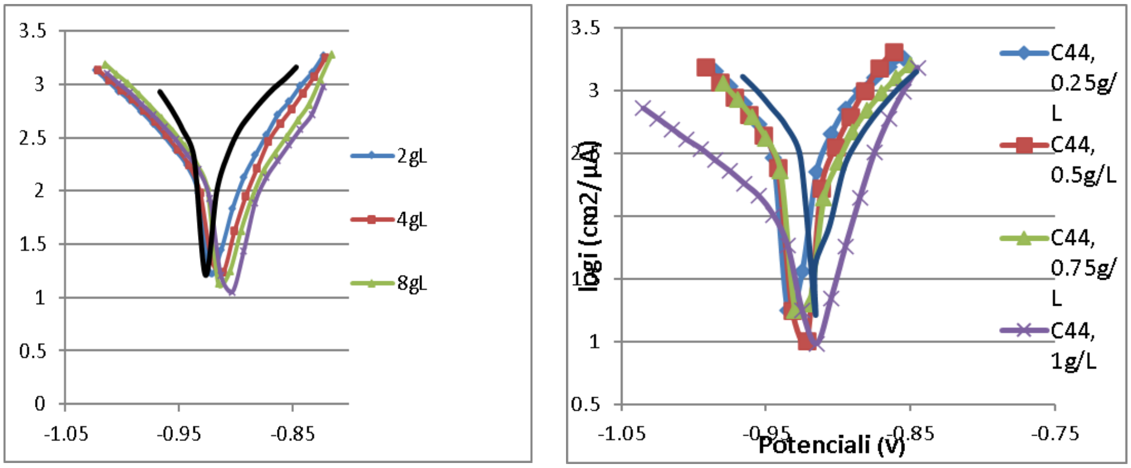

Fig.5: *Potentiodynamic polarization curves for Steel 44 in de-aerated 1M H_2SO_4 solution with 10^{-3}M chloride ions (blank) containing different concentration ratio of 2-amino1-butanol / lysine (a); and only different concentration of lysine (b)*

The total results, in form of corrosion rates in (mm/year), calculated using corrosion current density (i_{corr}) and protections efficiency of different concentration of additives against corrosion, are given in Table 3.

Table 3: *Values of Vcorr and Prot.Eff. % for steel 39 and steel 44 in H_2SO_4 1M and 10^{-3} Cl- solution with and without MCI*

Concentration ratio 2-amino 1-butanol/lysine	**Mark of steel material**			
	Steel 39		Steel 44	
	V_{corr} (mm /year)	Prot. Eff. %	V_{corr} (mm /year)	Prot. Eff. %
Blank	2.32		3.31	
0g/L:1g/L	0.49	78.88	1.03	68.88
2g/L:1g/L	0.581	74.96	1.131	65.83
4g/L:1g/L	0.288	87.59	0.949	71.33
8g/L:1g/L	0.247	89.35	0.822	75.17
12g/L:1g/L	0.22	90.52	0.795	75.98

DISCUSSION

By observation of shapes of the anodic and cathodic polarization curves in the presence of lysine + butanolamina provides information about the inhibitor action in corrosion processes. The examination of Fig. 4 –a- and Fig. 5 -a- shows that the MIC (mix of amino-alcohol and lysine) functioned via a mixed-inhibition mechanism; it worked as well as anodic and cathodic inhibitor. As the corrosion potential is increase towards positive, corrosion current density, I_{corr} decrease with higher concentration of MCI in 1M H_2SO_4 + 10^{-3} M Cl^- solution.

The (amino-alcohol), as migrator agent, seems to play an important role in specifying the areas of anodic adsorption of inhibitor (the rest potential become more positive increasing the concentration of amino-alcohol) and improve the anodic surface coverage (anodic branch come down increasing the concentration of amino-alcohol) [8, 9]. Clearly the presence of amino-alcohol as migrator agent improves the inhibition effect of lysine, even in low concentration.

The adsorption mechanism for a given inhibitor depends on such factors, as the nature of metal corrosion medium, the pH and the concentration of the inhibitor as well as the functional groups present in its molecule [10].

In case of amino acids used in our study as acidic corrosion inhibitor for low alloy carbon steel, the adsorption on anodic sites, dedicated the free electrons on N and O (of carboxylic group) atoms [11].

Further, amino group is easily protonated in the acidic medium, so it could be electrostatically attracted to the cathodic sites on steel surface and hinder the hydrogen evolution reaction. Protonated amino group converted from $(-NH_3)^+$ to ($-NH_2$:), which adsorbed in anodic sites of low alloy carbon steel by free electrons of N.

The corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites and/or deposition of the corrosion products on the alloy surface [12,13]. Lysine adsorbs on surface of middle steel this mechanism: the atoms O and N in amino acids serve as active centers for the process of adsorption on the metal surface. Availability of no bonded (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. When an H atom attached to the C in the ring is replaced by a substituent group (–NH_2, or COOH) it improves inhibition [14].

CONCLUSIONS

From the results of the study, MCI showed excellent corrosion inhibition performances for mild steel (39,40) in acidic media.

The higher concentration of inhibitor (ratio 12g/L amino alcohol: 1g/L amino acid) is the lower corrosion rate and the higher corrosion inhibition efficiency.

Polarization experiment shows that the MCI (combination of an amino-alcohol and amino-acid) effectiveness in preventing corrosion of mild steel (39,44) in 1M H_2SO_4 solution in presence of 10^{-3}Cl- ions solution was respectively 90.52% and 75.98% and corrosion rate was respectively 0.22 mm/year and 0.795 mm/year in presence of 12g/L amino alcohol: 1g/L amino acid.

The MCI (combination of an amino-alcohol and amino-acid) can be used as corrosion inhibitor for mild steel in 1M H_2SO_4 solution in presence of 10^{-3}Cl- ions.

Potentiodynamic polarization reveals that inhibitor retards both anodic and cathodic reactions on the surface of the metal so it functioned via a mixed-inhibition mechanism.

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