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Test of inhibitors for preventing corrosion of steel reinforcement in concrete

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Abstract. Concrete is more widely used than any other manmade material. The objective of this paper is to investigate the behavior of reinforced cement when migration corrosion and guar gum inhibitors are used. The concrete samples were exposed in aggressive media H_2SO_4 1 M and in the presence of $1\cdot10^{-3}$ M Cl^-. Electrochemical measurements such as half-cell potential, polarization resistance and Tafel extrapolation methods were performed in order to obtain information on the corrosion behavior of the reinforcing steel in cement mortar. Results demonstrate high resistance polarization and low corrosion rate for concrete sample with inhibitor. The corrosion rate decreases approximately 95% in presence of locust bean gum and 80% in presence of migration inhibitor.

***Keywords*:** green inhibitor; migration inhibitor; locust bean gum; amino acid; amino alcohol.

1. Introduction

Corrosion of the reinforcement undermines the physical integrity of structures and can cause most of the failures of concrete structures. The environmental changes due to pollution, lack of maintenance, poor quality of work, lack of supervision, use of defective materials can cause reinforcement corrosion. Among various factors affecting the reinforced concrete structures the atmosphere, water, salts are the major worldwide deterioration problems for steel reinforced concrete structures [1, 2]. Migrating corrosion inhibitors (MCIs) are one means of protection for reinforced concrete structures. Previous studies have established the benefits of using migrating corrosion inhibitors, the importance of good concrete, and the significance of the ingredients used to make the concrete [3]. Migrating corrosion inhibitors are able to penetrate into existing concrete to protect steel from chloride attack. The inhibitor migrates through the concrete capillary structure, first by liquid diffusion via the moisture that is normally present in concrete, then by its high vapor pressure and finally by following hairlines and micro cracks. The diffusion process requires time to reach the rebar surface and to form a protective layer [3]. The aim of our study is to investigate the behavior of reinforced cement when migration corrosion and guar gum inhibitors are used.

The most efficient corrosion inhibitors are attributed to organic compounds (amino acids) that contain heteroatoms (such as N, S, P, O) and multiple bonds, in addition to some functional groups. It is also reported that organic compounds having –OH, –COOH, NH_2, functional groups, etc., are excellent corrosion inhibitors, especially in acidic media [4, 5]

Amino alcohol corrosion inhibitors control corrosion by attacking the cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion. Also, the inhibition of corrosion occurs through a mechanism whereby amino alcohols displaces chloride ion and forms a durable passivating film. In this view, although the amino alcohols adsorb on non-corroding sites which may seem more cathodic than anodic, they can just as easily be said to adsorb on potentially anodic sites as well [6, 7].

Locust bean gum is an organic compound extracted by endosperms of carob tree. It is cheap and friendly with environment. Extract (locust bean gum) and MCI (methionine + butanolamine) tested have been reported to be excellent inhibitors for Iron B 500 in 1 M H_2SO_4 solution in presence of chloride ions $1\cdot10^{-3}$ M [8-12].

In our study we have investigated the corrosion protection efficiency of a green inhibitor (locust bean gum) and a migration inhibitor (methionine + butanolamine) admixed in concrete [13].

2. Experimental

Concrete samples containing steel reinforcement used for the experiment were made of Titan cement, commercial sand (Mat sand), and water. Each concrete samples having dimension of 10 x 10 x 20 cm was prepared by mixing water and cement in the ratio 0.53 and inert/cement = 2.25. The inhibitors are added in water. In this work, we designate one concrete sample without inhibitor (as the blank sample) one with 1 g/L (water) locust bean gum and one with methionine 1 g/L + 2-amino-1-butanol 8 g/L (water). Steel rebars were cut 20 cm and one 20 cm Inconel for the counter electrode. Clear silicon was applied to the concrete/metal interface to prevent easy access for ions. The concrete samples cured for 28 days. After curing, the concrete samples were immersed in a 1 M H_2SO_4 solution in the presence of $1\cdot10^{-3}$ M Cl^- at ambient temperature and they were tested for 122 days. The chemical composition of steel rebar B 500 manufactured at Elbasan, metallurgical plant, intended for concrete armor is presented in Table 1.

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Table 1. Composition of low alloy carbon steel (iron B 500)

Element (Mass-%)	C	Si	Mn	Cr	Ni	Cu	P	S
Iron B 500	0.224	0.152	0.68	0.110	0.102	0.318	0.021	0.027

The corrosion behavior of steel rebar was monitored by electrochemical experiments included the following techniques: linear polarization resistance, potentiodynamic test and open-circuit potential measurements. Three-electrode cell assembly consisting of steel reinforcement present in concrete as working electrode, Inconel as counter electrode, and an electrode Hg/Hg_2SO_4 as reference electrode were used for the electrochemical studies [14].

Changes in the resistance polarization (R_p) were monitored weekly, the corrosion potential of the rebar was monitored daily and the potentiodynamic polarization was done at the last day using Potentiostat/Galvanostat PJT-24. Potential values were recorded and plotted with respect to time.

3. Results and discussion

Effectiveness inhibitors were based on changes in the polarization resistance, corrosion rate and the corrosion potential of the rebar, measurements that can be performed without destruction to the reinforcing steel. This data can provide early warning of structural distress and evaluate the effectiveness of corrosion control strategies that have been implemented. The key to fighting corrosion is to introduce preventative measures.

3.1. Corrosion potential

The probability of corrosion of steel reinforcement in concrete was visualized with the help of half-cell potential measurements. The corrosion inhibition for locust bean gum and migration inhibitor has been investigated over e period of 122 days.

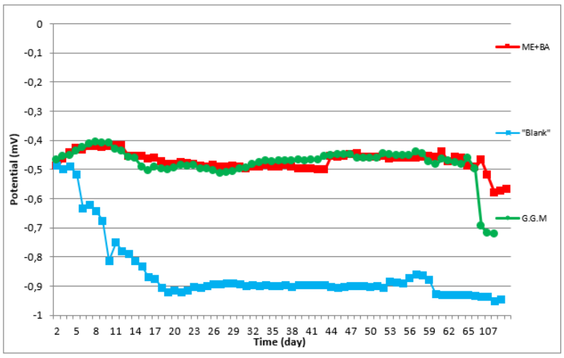

Figure 1. Comparison of corrosion potential *vs.* time for sample with locust bean gum, sample with migration inhibitor (methionine + butanolamine) and untreated sample (blank).

According to the ASTM C876-09 [15, 16] if the open circuit potential (corrosion potential) is -0.564 mV or higher, this indicates a 90% probability that no reinforcing steel has corroded. Corrosion potentials more negative than -0.564 mV are assumed to have a greater than 90% likelihood of corrosion.

The Figure 1, corrosion potential versus time, shows that the steel reinforcement in sample concrete without inhibitors (blank) exhibited high anodic potential values, which is a clear reflection of high corrosion rate in the contaminated concrete. Half-cell potentials of steel in sample concrete with locust bean gum and MCI were less negative (more cathodic) than sample blank during the period of investigation. These results show that locust bean gum and MCI are acting as good corrosion inhibitors on steel reinforcement. Similar results have been presented in the literature [14].

3.2. Polarization resistance

Linear polarization technique is a corrosion monitoring method that allows corrosion rates to be measured directly, in real time. The technique is rapid and non-intrusive, requiring only a connection to the reinforcing steel.

The method is based on the observation of the linearity of the polarization curves near the potential E_{corr}. Rp value is related to the corrosion current I_{corr} by means of the expression:

$$I_{corr} = \frac{B}{R_p} \qquad R_p = \frac{\Delta E}{\Delta I} = \frac{B}{I_{corr}} \tag{1}$$

Where: B – a constant, 26 mV; I_{corr} – corrosion current; ΔE – variation of the applied potential around the corrosion potential; ΔI – polarization current.

The potential of the reinforcement was scanned 20 mV from the open-circuit potential (OCP) of the sample, at a scanning rate of $6x10^{-3}$ mV/s.

Figure 2 shows that concrete samples with locust bean gum and MCI have higher R_p values compared with the blank sample. Figure 2 shows a declining trend for the blank concrete sample and an increasing polarization resistance values after 122 days of testing for the samples concrete with locust bean gum and MCI. The corrosion rate in $\mu A/cm^2$ is shown in Table 2.

Polarization resistance measurements show a reduced corrosion rate for the samples with inhibitor, while the blank sample has an increasing corrosion rate. Samples with locust bean gum showed an average corrosion rate of 0.45 $\mu A/cm^2$, samples with methionine + butanolamine showed an average corrosion rate of 0.38 $\mu A/cm^2$ compared to the blank samples showing a rate of 23.65 $\mu A/cm^2$. The rebar treated with methionine + butanolamine has the highest polarization resistance. The results showed the possibility of migration of the migration inhibitor and the ability to create a thin protective layer. The samples treated with inhibitor have the ability to passivate the steel bar even in the presence of chloride ions [3, 17].

Table 2. Values of R_p and I_{corr} for concrete samples immersed in H_2SO_4 1 M and $1·10^{-3}$ Cl^- solution, day 122.

	Blank			*Locust bean gum*			*Methionine + 2-amino-1-butanol*	
Days	***R_p Ωcm²***	***I_{corr}(μA/cm²)***	***Days***	***R_p Ωcm²***	***I_{corr}(μA/cm²)***	***Days***	***R_p Ωcm²***	***I_{corr}(μA/cm²)***
10	0.000521	12.75693	**8**	0.011429	0.581492	**9**	0.012852	0.517096
17	0.000187	35.46102	**15**	0.009711	0.684366	**16**	0.006878	0.966273
24	0.000141	47.22974	**22**	0.007439	0.89337	**23**	0.006965	0.954111
31	0.000248	26.80311	**29**	0.00647	1.027213	**30**	0.006231	1.066622
38	0.000289	22.9965	**36**	0.006105	1.088486	**37**	0.006907	0.962219

	Blank			Locust bean gum			Methionine + 2-amino-1-butanol	
Days	***R_p Ωcm²***	***I_{corr}(μA/cm²)***	***Days***	***R_p Ωcm²***	***I_{corr}(μA/cm²)***	***Days***	***R_p Ωcm²***	***I_{corr}(μA/cm²)***
45	0.000308	21.55573	**43**	0.008648	0.768499	**44**	0.007089	0.937497
52	0.000305	21.77836	**50**	0.008051	0.825452	**51**	0.007423	0.895231
59	0.000504	13.19753	**57**	0.009609	0.691609	**58**	0.008121	0.818341
66	0.000359	18.53596	**64**	0.012069	0.550636	**65**	0.009033	0.735736
80	0.000245	27.12497	**78**	0.012635	0.525969	**79**	0.009108	0.729622
94	0.000237	28.09987	**92**	0.012786	0.519757	**93**	0.009141	0.727012
108	0.000359	18.47482	**106**	0.013122	0.506449	**107**	0.016276	0.408308
122	0.000281	23.6584	**120**	0.014679	0.45273	**121**	0.01738	0.382372

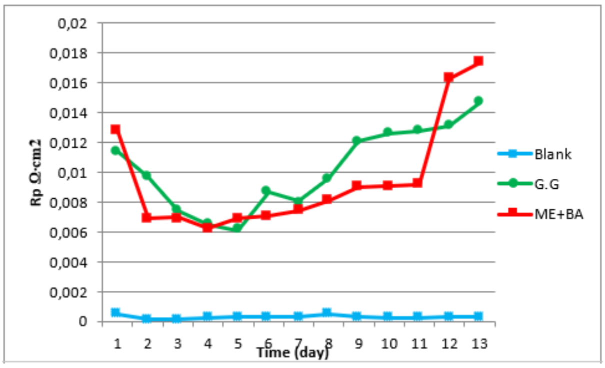

Figure 2. Comparison of polarization resistance (RP) for locust bean gum, methinine+amino-2-butanol-1 & blank concrete samples.

3.3. Electrochemical polarization

The inhibition efficacy of locust bean gum and migrating inhibitor was monitored using potentiodynamic polarization studies. Corrosion current density determined using the cutting point of Taffel extrapolation line and Faradays law, equation [18, 19]:

$$V_{corr} = \frac{K * A * I}{n * \rho} \qquad (2)$$

Where: A - is the atomic weight of the metal (A = 56 g/mol); I - the current density in μA/cm²; n - the number of electrons exchanged during metal dissolution (n = 2); ρ - the density in g/cm³ (ρ = 7.86 g/cm³); 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 Eq. 3 [20, 21]:

$$Inhibitor\ efficiency\ (\%) = \frac{CR\ uninhibited - CR\ inhibited}{CR\ uninhibited} \times 100 \qquad (3)$$

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

From the results taken from potentiodynamic polarization, it is understandable that the steel reinforcement in the concrete containing locust bean gum and MCI was less corroded than reinforcement in the sample blank. Figure 3 shows the comparison of the polarization behavior from a potentiodynamic tests of steel rebar in H_2SO_4 1 M, in presence of chloride ions $1 \cdot 10^{-3}$ M solutions. Corrosion potential gets more positive values, and the corrosion rate mitigates in presence of inhibitors [14].

Analysis of polarization curve gave rate of corrosion, current densities, and percentage of inhibition efficiency which are given in Table 3. The rebar steel treated with locust bean gum has corrosion rate 0.00078 mm/year and inhibition efficiency 95.125 %; the rebar steel treated with migration inhibitor has a corrosion rate 0.0034 mm/year and inhibition efficiency 78.75 %, the untreated steel bar (blank sample) has a corrosion rate 0.016 mm/year.

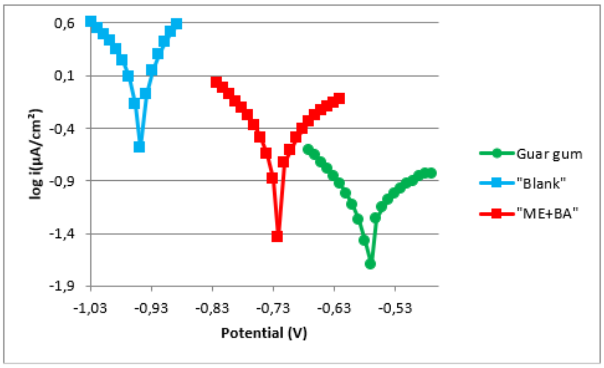

Figure 3. Tafel curves of steel bar in H_2SO_4 1M and 10^{-3}M Cl^-, in the absence and presence of inhibitor.

Table 3. Rate corrosion for steel in concrete and steel in acid [8, 10, 11]

	Steel in concrete		**Steel in H_2SO_4**		**Inhibition efficiency (%)**
	I_{corr} (μA/cm²)	**V_{corr} (mm/year)**	**I_{corr} (μA/cm²)**	**V_{corr} (mm/year)**	
Blank	1.43	0.016	537.96	6.267	
Locust bean gum	0.067	0.00078	51.31	0.59	95.125%
Methionine + butanolamine	0.29	0.0034	33.09	0.39	78.75%

4. Conclusions

The locust bean gum and MCI (methionine + butanolamine) have successfully inhibited corrosion of the rebar in H_2SO_4 1 M and $1 \cdot 10^{-3}$ M Cl^- for 122 days.

R_p increased from 0.011429 Ω·cm² to 0.014679 Ω·cm² for the sample treated with locust bean gum and R_p increased from 0.012852 Ω·cm² to 0.01738 Ω·cm² for the sample treated with migration inhibitor methionine + butanolamine.

The samples treated with locust bean gum and methionine + butanolamine showed an average corrosion rate of 0.45 μA/cm² and 0.38 respectively compared to the blank samples showing a rate of 23.66 μA/cm². Potentiodynamic polarization method showed that the sample treated with locust bean gum has a corrosion rate 0.00078 mm/year; the sample treated with migration inhibitor has a corrosion rate 0.0034 mm/year and the blank sample has a corrosion rate 0.016 mm/year.

Add of locust bean gum and migration inhibitor in concrete showed significant reduction in the corrosion rate. Corrosion efficiency for guar gum and migration inhibitor is respectably 95.125 % and 78.75 %.

Finally, we can say that the use of locust bean gum and methionine + butanolamine (MCI), as inhibitor supplement in concrete, is a smart choice for both: anticorrosion and environmental protection.

Conflict of interest

Authors declare no conflict of interest.

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