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Electrochemical Studies of Sodium Metavanadate as Corrosion Inhibitor of Carbon Steel 1020 in CO_2 and H_2S Saturated DEA Solutions

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ABSTRACT

Several types of corrosion inhibitors are recently used in amine systems for natural gas refining in the world because of the corrosive nature of amine solutions containing acid gases.
This article introduces corrosion inhibitor basis that are used mostly as active reagents in corrosion inhibitor packages. Accordingly, sodiom metavanadate is studied as corrosion inhibitor of carbon steel 1020 in 30-vol% DEA and industrial lean and rich amines solutions saturated with CO_2 and H_2S at 65 ^{O}C.
Electrochemical Tafel polarization test method was conducted to investigate the inhibitive behavior of sodiom metavanadate in the mentioned solutions that are near industrial conditions.
Tafel slopes and corrosion potentials show that the inhibitive mechanism of sodium metavanadate is anodic and effective dosage of the inhibitor is within 0.03 to 0.05 wt% in 30-vol% DEA, industrial lean and rich amines solutions saturated with CO_2 and H_2S at 65 ^{O}C.
Surface observations indicate that the corrosion on the carbon steel coupons was general and using this optimum concentration with an inhibitive performance of at least 80% did not occur localized or pitting corrosion.

Keywords: Corrosion Inhibitor, Refining, Electrochemical, DEA, And Acid Gas.

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INTRODUCTION

The removal of large volumes of acid gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from natural gases is most conveniently accomplished by absorption in a suitable solvent. Most gas treating processes employ an amine-containing solvent that can be reused by desorbing the acid gases through release of pressure and application of heat.
The various ethanol amines, such as mono-, di-, and tri-, are organic bases and their general chemical properties are analogous to those of ammonia in many respects. Because of their alkaline nature they are not corrosive toward steels when used in the pure state or in solutions with water at moderate temperatures.[1]
DEA is used as acid gas absorbant in most gas refineries in Iran, and our goal in the present work is to study the corrosive behavior of CS1020 and application of Sodium meta-vanadate as a typical corrosion inhibitor in DEA solutions with acid gases i.e. H_2S and CO_2.

Amine-Acid Gas Corrosion

Pure amines and mixtures of only water and amines are not corrosive because they are of either low conductivity and/or high pH .However, rich amine solutions, which have high conducyivity and a pH significantly lower than lean amine solutions,can be quite corrosiove.
Several mechanism have been proposed for amine-acid gas corrosion.Riesenfeld and Blohm were the first to note that significant amine corrosion was usually associated with evoluation of acid gases from the rich amine solutions [1,2,3]. Based on this observation , Riesenfeld and Blohm stated that in amine solutions, the carbon steel corrosion was due to presence of the acid gases themselves. For example, acid gas is evolved from rich amine solutions according to reactions (1) and (2):

$$R_3NH^+ + HCO_3^- = R_3N + H_2O + CO_2 \qquad (1)$$
$$R_2NH_2^+ + R_2NHCO_2^- = 2R_2NH + CO_2 \qquad (2)$$

The acid gases can then react directly with exposed carbonsteel to form iron carbonate according to reacton (3) :

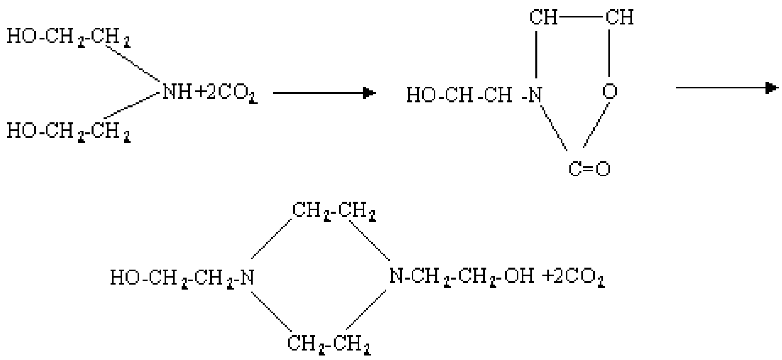
$$Fe + H_2O + CO_2 = FeCO_3 + H_2 \qquad (3)$$

Iron carbonate is only slightly soluble and forms a film over the active metal surface which offers limited protection against further corrosion. Similar corrosion reaction occurs with H_2S; however, the iron sulfide film covering active metal surface is much more protective than iron carbonate, and the iron sulfide film resists further corrosion.
This mechanism explains the observed corrosion phenomena. For example, primary amines such as monoethanolamine(MEA) and Diglycolamine(DGA) are more corrosiove than secondary and terriary amines because higher temperatures, which lead to greater corrosion, are required to strip primary amines. Therefore, in amine systems employing primary amines, high concenteration of acid gases are present in the hottest areas of the process stream. Conversely, Methyldiethanolamine(MDEA), a tertiary amine is easily stripped of both CO_2 and H_2S. Therefore, it is less corrosive because the acid gases are evolved from solution at a lower temperature.

DEA Degradation Mechanism

Diethanolamine degradation is frequently experienced in gas plants used for removing acid gases. This wastes valuable DEA, fouls equipments with the degradation products and loses metal due to corrosiveness of some degradation products.
Degradation, as reported, depends on temperature, presure, gas composition, amine concenteration, pH of the amine solution and presence of metal ions [4,5,6]. In addition, it is difficult to examine the problem since degradation products are large organic molecules that are hard to detect and identify.

One reaction of primary- and secondary amines with CO_2 forms Oxazolidones. Oxazolidones are cyclic compounds where a CO_2-molecule has linked the amine and the hydroxyl group of an alkanolamine molecule. This reaction is normally relatively slow but rate becomes significant under conditions of an increased amine loading and/or high temperatures. A second reaction is the formation of polyamines, such as diamines and piperazines. The degradation reaction of, for instance, DEA with CO_2 in particular, have been studied extensively. A compound was identified (HEP,which is N,N'-bis(2-hydroxyethyl)piperazine) in the degradation solutions and its formation postulated, as follows:



These formation reaction are not consistent with the facts since they indicate that carbon dioxide acts as a catalyst, being neither consumed nor formed. Actually, both DEA and CO_2 are present as ions in aqueous solutions and so the CO_2 is unlikely act as catalyst [7].

Corrosion Inhibitors in Amine Systems

Several Types of corrosion inhibitors according to corrosion severity of the environments can be used which must be compatible with the gas sweetening process. Some of them are as follow: [7,8,9]

1,6- Hexanedithiol
1,8-Octanedithiol
1-Decanethiol
Tallow diamine quarternary chloride
Dimethylpolysiloxane
NaCN
$NiSO_4$
Bi^{+3}
$NaVO_3$

Various compounds are used in such systems but in this study Sodium metavanadate was selected to demonstrate both the needs for using corrosion inhibitor in amine systems and the DC electrochemistry capabilities of evaluating the performance of these compounds.

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EXPERIMENTAL

Experiments were conducted in an electrochemical cell. The working electrode used was CS1020 with compositions according to table 1.Two platinium bars as the counter electrode, and a saturated Calomel electrode as refrence with a potential difference of 0.2444 mV with respect to SHE were used.Polarization curves were measured using a scan rate of 120 mV/min from the corrosion potentials. All electrochemical measurements were carried out using Wenking POS81 potentioastat set made in Germany.
All solutions were prepared using deionized water, 98% DEA, and reagent grade chemicals. For the experiments, the DEA solutions were loaded with CO_2 and/or H_2S (99.99% pure) by purging for 1 hr into the glass vessels.Prior to the tests the working electrodes were polished with emery paper 600 grit for removing any scales or corrosion products from the CS1020 surface.

RESULTS AND DISSCUTION

DEA effect

Carbon Steel in 30-Vol% diethanol amine solutions showed a limiting urrent density in anodic polarization curve. As this limiting current is a little lower than the maximum critical anodic current, this may be considered as passive layer. As the passive layer has a current densiy higher than i_{corr} it has not substantial role on controling corrosion rate but limits the type of corrosion from localized to general and in some cases pitting corrosion can be evaluated by styding this limiting current and its break down.

Acid Gas Effect

Figure 1 shows the effect of acid gases on CS1020 in 30%DEA solution at 65 ^oC. Presence of both CO_2 and H_2S removes the passive layer from Carbon Steel surface. Presence of CO_2 caused the passive current of CS1020 to reduce more than the corresponding corrosion current density, that means the rate of corrosion reduces more.
Corrosion current densities in different conditions have the following order of severity:

$$\mathbf{I(none) < I(CO_2) = I(H_2S) < I(CO_2/ H_2S)}$$

Saturating the DEA solutions with acid gases caused the corrosion potential of CS1020 to become more negative and its corrosion current density to be enhanced, table4.

Sodium metavanadate Electrochemical Behavior

A 30-vol% DEA saturated with CO_2 and H_2S at 65 ^oC was selected for the study of electrochemical behavior of $NaVO_3$ which is more similar to filed conditions.
Carbon steel behavior in the solutions containing $NaVO_3$ and without any corrosion inhibitor is shown in fig 2.

Introduction of 0.03 wt% $NaVO_3$ to the solution caused a reduction of 87% in corrosion rate of carbon steel.
A change from 224mV/dec to 190mV/dec in slope of the anodic polarization curve and a shift of 250mV toward positive potentials confirm that in this conditions NaVO3 acts as anodic inhibitors but for assurance the inhibitor was tested in a range of 0.0 to 0.15 wt%.

Sodium metavanadate concentration Effect

Increasing corrosion inhibitor concentration reduced the corrosion rates and increasing more than 0.03 wt% of sodium metavanadate has no any significant effect on reducing the

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corrosion current densities. This case is also experienced for Lean and Reach industrial solutions. So, the optimum concentration of sodium metavanadate is within 0.03 to 0.05-wt%. Corrosion rates with and without corrosion inhibitor are listed in table 3. Because of some impurities in industrial Lean and Rich amine which may be due to degradation of amine in some extent the corrosion rates of blank solutions are more than 30-vol% DEA prepared by pure material but again sodium metavanadate revealed good protection characteristics by reducing the corrosion rate to about 80% (Fig.3).

CONCLUSION

By studying the electrochemical behavior of Carbon Steel 1020 in DEA solutions saturated with acid gases it is concluded that:

- DEA can form a passive layer on CS1020.
- The largest passive current density of the CS1020 was in DEA solutions saturated with both CO_2 and H_2S.
- Acid gas saturated DEA exhibits a corrosion rate of 30 mpy that is in the range of corrosiove medium and in industrial conditions this corrosion rate me be enhanced because of the presence of contaminations like degraded amines, chloride, errosive materials such as silicon, etc.
- According to above statements corrosion inhibitors must be used in such environments.
- Sodium metavanadate revealed effective inhibitive characteristics in 30wt% DEA solutions and in rich and lean amines saturated with acid gases at 60 ^oC .
- The optimum concentration of sodium metavanadate was determined between 0.03-0.05 wt% due to electrochemical investigtions.
- Using Sodium metavanadate in the range of 0.03-0.05 wt% reduced corrosion rates more than 80% in each systems and it bahaved as an anodic corrosion inhibitor in amine saturated with acid gas systems.

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Tables

Table 1.Elemental composition of the alloys

Element / Alloy	Si	S	P	Mn	Ni	Cr	C	Fe
CS.1020	-	0.05	0.04	0.45	-	-	0.2	Balance

Table 2.Tafel polarizations parameters related to Fig.2

Solution	$-E_{corr}$ mV/SHE	I_{corr} ($\mu A/cm^2$)	I_{pass} ($\mu A/cm^2$)	βa mV/Dec	$-\beta c$ mV/Dec
None	330	8.34	24.5	114	125
CO_2	595	115.1	46.88	107	142
H_2S	655	12.26	22.96	311	125
CO_2/H_2S	605	45.8	158.9	224	153

Table 3. Tafel polarizations parameters with and without sodium metavanadate

Solution		I_{corr} ($\mu A/cm^2$)	$-E_{corr}$ (mV/SHE)	$-\beta c$ (mV/Dec)	βa (mV/Dec)
DEA 30-vol%	Blank	45.8	605	153	224
	0.03% $NaVO_3$	6.02	455	159	190

Table 4. Corrosion rates and percent protection in different DEA solutions with and without sodium metavanadate

Solution	$NaVO_3$ Conc. (wt%)	Corrosion Rate (mpy)	Percent Protection (%P)
30-Vol% DEA	0.00	21.0	0.0
	0.03	2.70	87.1
Lean Amine	0.00	29.4	0.0
	0.03	4.40	85.0
Rich Amine	0.00	32.1	0.0
	0.03	6.0	81.1

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FIGURES:

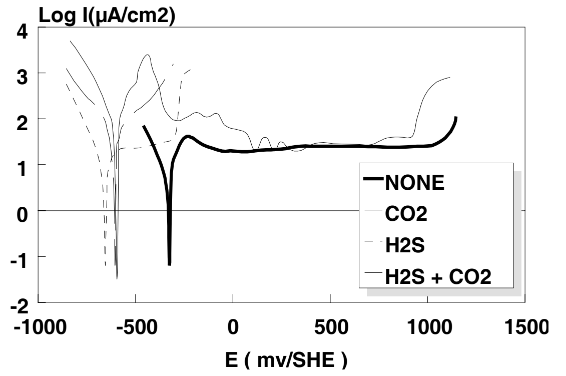

Figure 1.Acid gas effect on the CS1020 electrode in 30% DEA solution @ 65 C.

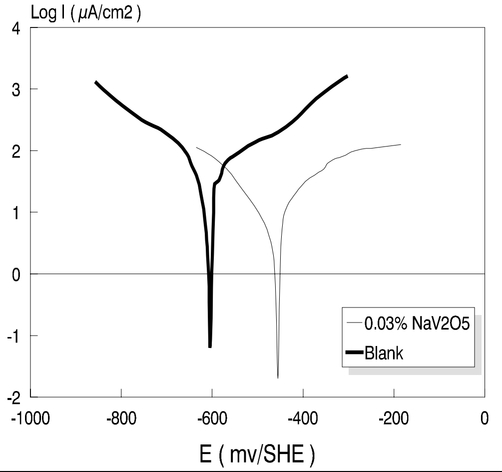

Fig.2 Tafel polarization curves for carbon steel in 30-vol% DEA saturated with CO_2 and H_2S with and without 0.03 wt% of $NaVO_3$ at 65 ^oC

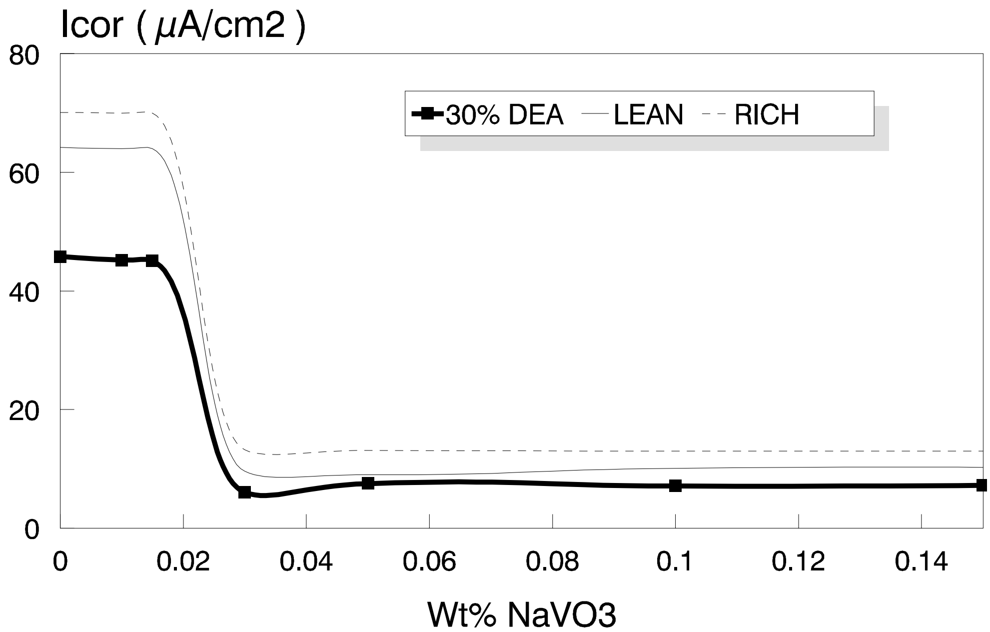

Fig 3. Concentration effect of sodium metavanadate on carbon steel 1020 in different DEA solutions saturated with CO_2 and H_2S at 65 ^oC