CORROSION INHIBITION OF CARBON STEEL BY AN AMINE- FATTY ACID IN ACIDIC SOLUTION

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ABSTRACT

The corrosion inhibition of carbon steel in 3% de-aerated NaCl acidic solution with amine–fatty acid corrosion inhibitor, KI384, was investigated at different temperatures using potentiodynamic polarization technique. The Corrosion rate was calculated in the presence and absence of inhibitor. The inhibition increased with an increase in inhibitor concentration and decreased with rise in temperature. The maximum percentage inhibitor efficiency was obtained at 35 °C. The percentage inhibition up to 99% was registered at a concentration of 10 ppm of KI384. The inhibitor acts as a mixed type at lower temperature and predominantly anodic at high temperature. The interrelationship between the surface coverage and concentration of the inhibitor was also studied. It was found that the inhibitor obeys Langmuir adsorption isotherm and adsorbs on the metal surface through physical adsorption.

INTRODUCTION

The addition of inhibitors is one of established methods for corrosion protection of metals in diverse branches of technology. The use of inhibitors to protect metals against corrosion is based on the ability of a chemical compound to reduce the rate of corrosion when added in small concentrations to an aggressive environment. Corrosion inhibitors are used in a variety of systems. For many years corrosion inhibitors have extensively been used in oil and gas production and transmission system and new formulations developed in order to obtain better corrosion protection and safer properties towards the environment. Most of them are organic chemicals, which adsorb on the metal surface to form a protective film against corrosive species. Amine salts of fatty acids are well known inhibitors of iron dissolution (Szauer and Brandt 1981) and were recently tested and reported to inhibit sweet corrosion of carbon steel (Moldestad 1995; Buchweishaija 1997). The tests were conducted in CO_2 saturated formation water, a corrosive medium, which is quite complex in terms of composition. However, its inhibition mechanisms have not yet been sufficiently explained. Adsorption is the primary step to the understanding of the mechanism of interaction of the inhibitor molecule with the metallic substrate and how it affects the dissolution rate of the metal. The adsorption processes depend on many factors among others being the chemical structure of the inhibitor molecule and the chemical composition of the aggressive medium (Trabanelli 1989).

The adsorption of amine salt of fatty acid requires consideration as a quite complex phenomenon in as much as it is a case of competitive adsorption with several adsorbable species involved. Potentially existing species to be taken into account are the cationic and anionic dissociates of the salt, molecular forms of the given amine-fatty acids as well as complexes involving former species (Hackerman and Makrides 1954). The presence and concentration of the species largely depends on its chemical structure as well as the composition and pH of the solution. All these factors greatly influence the total adsorption of the amine salts of fatty acids, which determine the extent of the inhibition. Hence, to get more understanding on the inhibition mechanism of KI384 inhibitor on carbon steel, its interaction characteristics in a simple composition of corrosive medium, of acidic 3% NaCl solution was investigated.

METHODS

The electrochemical experiments were performed in a 1-litre three electrodes cell made of Pyrex glass. The cell was placed in a water bath, thermostatically controlled in the temperature range from 35 °C to 65 °C. A Rotating Disk Electrode (RDE) assembly with adjustable speed was used as a working electrode. Cylindrical APIX60 carbon steel electrodes mounted in Teflon tube and sealed exposing only the bottom surface area of 0.07cm^2 to the electrolyte were used. The chemical composition of the working electrode in weight percentage is given in Table 1. Pretreatment of the specimen surfaces included abrasion with SiC paper to 1000 grit, ultrasonic cleaning and degreasing in acetone, followed with polishing through 1 μm diamond paste, and finally rinsing in ethanol before immersion. Only potentiodynamic experiments were performed where platinum sheet was used as a counter electrode and a saturated calomel electrode as a reference.

Table 1: Chemical composition of the APIX60 carbon steel used as working electrodes (weight %)

Element	C	Si	Mn	Cr	Ni	Al	Cu	Mo	V	Fe
Wt.%		0.070	0.250	1.300	0.020	0.010	0.018	0.010	0.100	0.039
98.183										

The test solution was 3% NaCl made up of analytical grade reagent and de-ionized distilled water. The solution was adjusted to a pH 4.5 by adding proper amount of HCl. The solution was deoxygenated for 12 hours by purging through pure nitrogen gas (99.998%) prior to introduction of the working electrode. Just after immersion in solution, each electrode was polarized to –1000 mV Vs SCE for 10 minutes. This was done to reduce the presence of air-formed oxide film on the carbon steel electrode. After that the electrode was waited for an hour to allow the potential to stabilize. The cell was, however, kept under nitrogen gas pressure during the whole time of measurement to avoid oxygen contamination. The corrosion inhibitor investigated was an amine-fatty acid, commercially known as KI384 inhibitor.

Polarization curves were recorded using a computer controlled AUTOLAB PGSTAT20 potentiostat, and at a potential sweep rate of 1 mV/s starting from the open circuit potential. The experiments were performed both with and without inhibitor at different desired experimental conditions.

RESULTS AND DISCUSSION

The polarization behaviour of carbon steel at different concentrations of KI384 inhibitor in deoxygenated 3%NaCl solutions (pH 4.5) at 35 °C is shown in Fig. 1. Two important trends are evident. Firstly, the corrosion potential shifted towards more noble values in the presence of KI384 in deoxygenated 3%NaCl solutions. Secondly, the current densities on the anodic polarization curve were significant reduced as inhibitor concentration is increased. From these two trends the predominant anodic inhibition effect of the KI384 may be inferred.

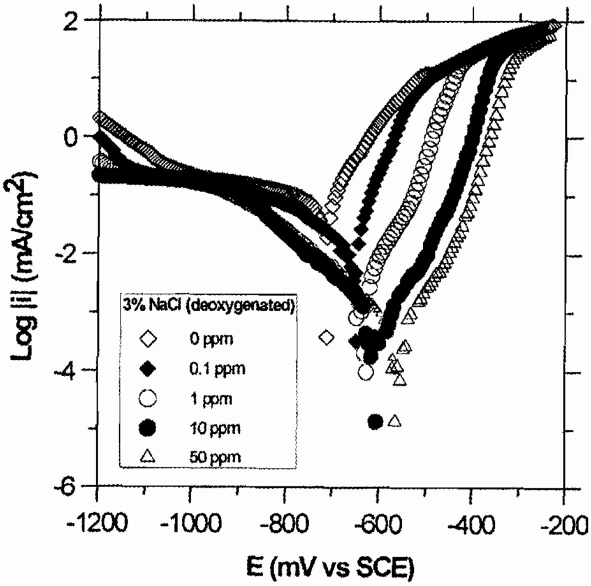

Fig. 1: Polarization curves of rotating carbon steel in de-oxygenated 3 % NaCl solution (pH 4.5) at 35 ¾C in the presence of different concentrations of KI384 inhibitor

Analysis of cathodic current density – potential curve (Fig.1) for the uninhibited solutions shows a limiting diffusion current density of 0.2 mA/cm^2 at potentials above –800 mV vs SCE, suggesting the hydrogen ions transport on the electrode surface gradually becomes rate determinant (concentration polarization). This limit is about one decade lower to what have been reported in CO2 solutions (Hurlen *et al.* 1984; Eriksrud and Søndvedt 1983). At potentials above –1000 mV vs SCE the Tafel relation emerges, attributed to hydrogen evolution from water.

Further observations from Fig.1, the KI384 inhibitor does not greatly influence the cathodic process in the potential range of hydrogen reduction reaction causing no decrease in the limiting current density of that process. On the other hand, the Tafel relation for water reduction shift towards the negative direction (cathodically) as the inhibitor concentration increases. This may indicate that, KI384 is mainly adsorbed at the anodic sites, since the diffusion limiting current of H$^+$ ions does not change with the application of inhibitor while the anodic reaction (anodic polarization curve) is greatly affected. Again this does not explain the influence of inhibitor on the cathodic shift of Tafel relation for water reduction. It seems reasonable to assume that the inhibitor stays on the metal surface during the cathodic sweep. Therefore, one would expect a simultaneous decrease in the cathodic limiting current density due to the reduction of surface area in contact with the electrolyte by the adsorbed inhibitor molecule. Generally the inhibition was of a mixed type, the suppression of the anodic process being greater. This finding may be considered as confirmation of previous work (McCafferty and Hackerman 1972), wherein the same inhibitor, has been assigned to the group of mixed inhibitors.

The kinetic parameters obtained from the polarization curves recorded on carbon steel in the solution with and without inhibitor together with calculated parameters such as corrosion rate and inhibitor efficiencies are summarized in Table 2. Corrosion current density values were obtained by the Tafel extrapolation method in the absence and presence of inhibitor solution. From the corrosion current values, the corrosion rate, *R*, in millimeters per year (mmpy) and inhibitor efficiency, ϕ, were calculated using the relations 1 and 2, respectively (Trethewey & Chamberlain 1988, Juttner 1990, Tan et al. 1996).

$$R = 1.159 \infty 10^{-2} i_{corr} \qquad (1)$$

$$\phi = \frac{R_u - R_i}{R_u} = \frac{i_{corr,u} - i_{corr,i}}{i_{corr,u}} \qquad (2)$$

where, i_{corr} is the corrosion current density and the subscript i and u in equation 2 denote with and without inhibitor, respectively.

Table 2: Kinetic parameters of carbon steel corrosion in de-aerated solution of 3% NaCl with different concentrations (C_{inh}) of KI384 inhibitor at pH 4.5 and temperature 35 ½C.

C_{inh} (ppm)	E_{corr} (mV vs SCE)	b_a (mV/dec.)	b_c (mV/dec.)	i_{corr} (μA/cm²)	$i_{lim,C}$ (μA/cm²)	R_{corr} (mmpy)	$\phi\ {}^{3}\ \theta$ (%)	C/θ
0	-708	52	-158	42.47	205	0.4922	-	
0.1	-654	39	-155	10.00	205	0.1160	76.45	0.1308
0.5	-637	40	-136	3.66	205	0.0420	91.38	0.5472
1.0	-628	42	-134	1.54	205	0.0178	96.37	1.0377
2.0	-600	37	-130	0.84	205	0.0097	98.02	2.0404
5.0	-586	40	-127	0.59	205	0.0068	98.61	5.0705
10.0	-584	52	-130	0.56	205	0.0065	98.85	10.1163
30.0	-554	54	-128	0.49	205	0.0057	99.13	30.2633
50.0	-546	59	-133	0.37	205	0.0043	99.40	50.3018

It can be seen from Table 2 that the inhibiting action rapidly increases with increasing of inhibitor concentration. From the table 10 ppm of KI384 is just enough to attain 99% inhibition of carbon steel in this system.

To qualify the effect of inhibitor concentration on the corrosion rate, it is common practice to fit rate data to equilibrium adsorption expressions such as Langmuir equation (Granese 1988, Khamis et al. 1991, Brinic et al. 1995),

$$\frac{\theta}{1 - \theta} = KC \qquad (3)$$

where θ is the fraction of the surface covered by the inhibitor and K is the equilibrium constant for the adsorption reaction. θ is estimated to be equal to the inhibitor efficiency.

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The Use of the Langmuir treatment is often justified with the argument that inhibition must involve adsorption. In this paper the Langmuir isotherm is rearranged to give

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (4)$$

Fig. 2 shows a plot of $\frac{C}{\theta}$ against C, and a linear relationship is obtained with a slope near to unit indicating that the inhibitor obeys Langmuir adsorption isotherm.

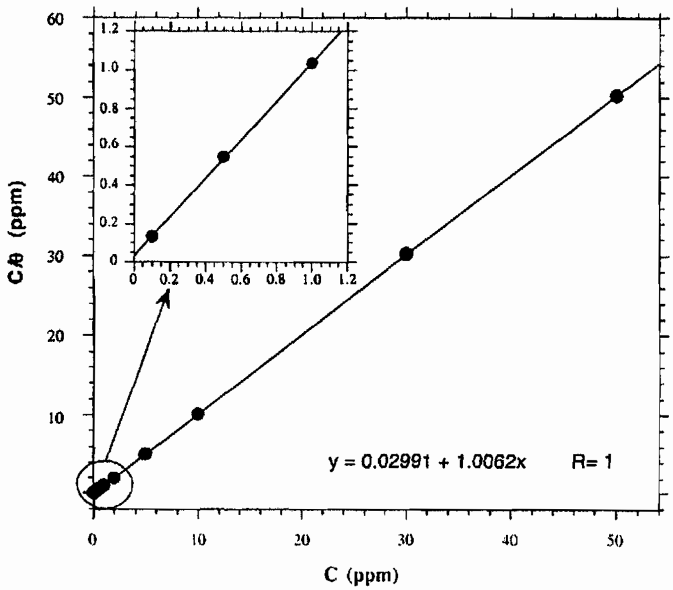

Fig. 2: Langmuir adsorption of carbon steel in de-aerated 3 % NaCl solution containing various concentrations of KI384 inhibitor at 35 ¾C

The adsorption equilibrium constant, *K*, for the KI384 inhibitor in 3 % deoxygenated NaCl solution was found to be 33.43 (ppm)$^{-1}$. A similar adsorption isotherm was obeyed by KI384 inhibitor in CO_2 solutions with the *K* value of 6.2 (ppm)$^{-1}$ (Buchweishaija and Hagen 1999). The fact that *K* value in 3% NaCl is quite high suggests that KI384 inhibitor strongly adsorb on Fe in acidic NaCl solution compared to CO_2 solutions. The reason could be that formation of $FeCO_3/Fe_3C$ in CO_2 medium would obstruct the inhibitor adsorption on the metal surface in CO_2 system.

For further understanding of the inhibitor properties, temperature effect on the performance of the inhibitor was also investigated. Temperature is one among several factors, which can influence the inhibitor properties both under transport from the injection point to the metal surface and when the inhibitor is adsorbed on the surface. In general, corrosion inhibitors have temperature limit above which they will lose their effectiveness (Donham 1987). The temperature affects solubility of inhibitors. Some inhibitors obtain lower and others higher solubility with increasing temperature (Schaschl 1973). This change in solubility may cause a reduction in the concentration of inhibitor in the corrosive phase and consequently lower inhibition efficiency. On microscopic level the temperature could influences the inhibitor adsorption process on the metal surface depending on the type of adsorption mechanism. It have been reported that, if the adsorption is due to chemisorption, an increase in temperature can result in an increase in the inhibition efficiency because of the relatively high activation energy of the chemical adsorption process (Trabanelli (1989), Harrop 1990).

The influence of temperature on the performance of KI384 inhibitor (30 ppm) in deoxygenated acidic 3%NaCl solution was investigated within the temperature range of 35 ½C to 65 ½C. The cathodic and anodic polarization curves for carbon steel in the medium with and without inhibitor at three temperatures (i.e. 35, 50 and 65 ½C) are shown in Fig. 3. The kinetic parameters at these three different temperatures deduced from polarization curves are summarized in Table 3. From this figure (Fig. 3) the inhibitor seem to cause both anodic and cathodic inhibition at lower temperatures (35 and 50 ½C), but as the temperature increases to 65 ½C the inhibitor exhibits no protection on the cathodic curve. However, the inhibitor suppresses the anodic process to a greater extent at all temperatures, suggesting a preferential adsorption of KI384 on the positively charged surface.

From Table 3, the calculated corrosion rate values in the inhibited medium increase with increasing temperature. Hence, the inhibition efficiency of the inhibitor decreases with a rise in temperature. This tendency suggests that the adsorption of this particular inhibitor is preferred at lower temperatures and that desorption rate of inhibitor is increased as the temperature increases (Riggs and Hurd 1967).

KI384 may adsorb on the metal surface either as a neutral molecule via chemisorption involving the sharing of electrons between nitrogen and iron or as a cationic form with a positively charged part on the molecule oriented towards a negatively charged metal surface. From the fact that the inhibitor inhibits significantly the anodic process, the latter possibility is excluded. KI384 inhibitor may probably absorb on the anodic sites through an electron donation or sharing mechanism. However, this is also not possible since the inhibitor efficiency decreases with increasing temperature (refer Table 3).

It is useful to emphasize that the main adsorbable species are non-dissociated fatty acid molecules and amine cations (Szauer and Brandt 1981). Comparison between the potential of zero charge of iron at –0.61 to –0.64 V vs. SCE (Lorenz and Fischer 1966) and the maximum adsorption potential region on the polarization curves (approximately above –600 mV vs. SCE) indicates the metal surface to be positively charged. Thus an inhibitor with a negative charge is preferred. Since amines exist as cations in acidic solution the coincidence of the same charges can be regarded as a weakening factor for adsorption through the cationic amine. However, because of the halide containing solution one would suggest that the positive charge are neutralized by the halide ion (Cl^-) resulting to stronger adsorption at the anodic potentials.

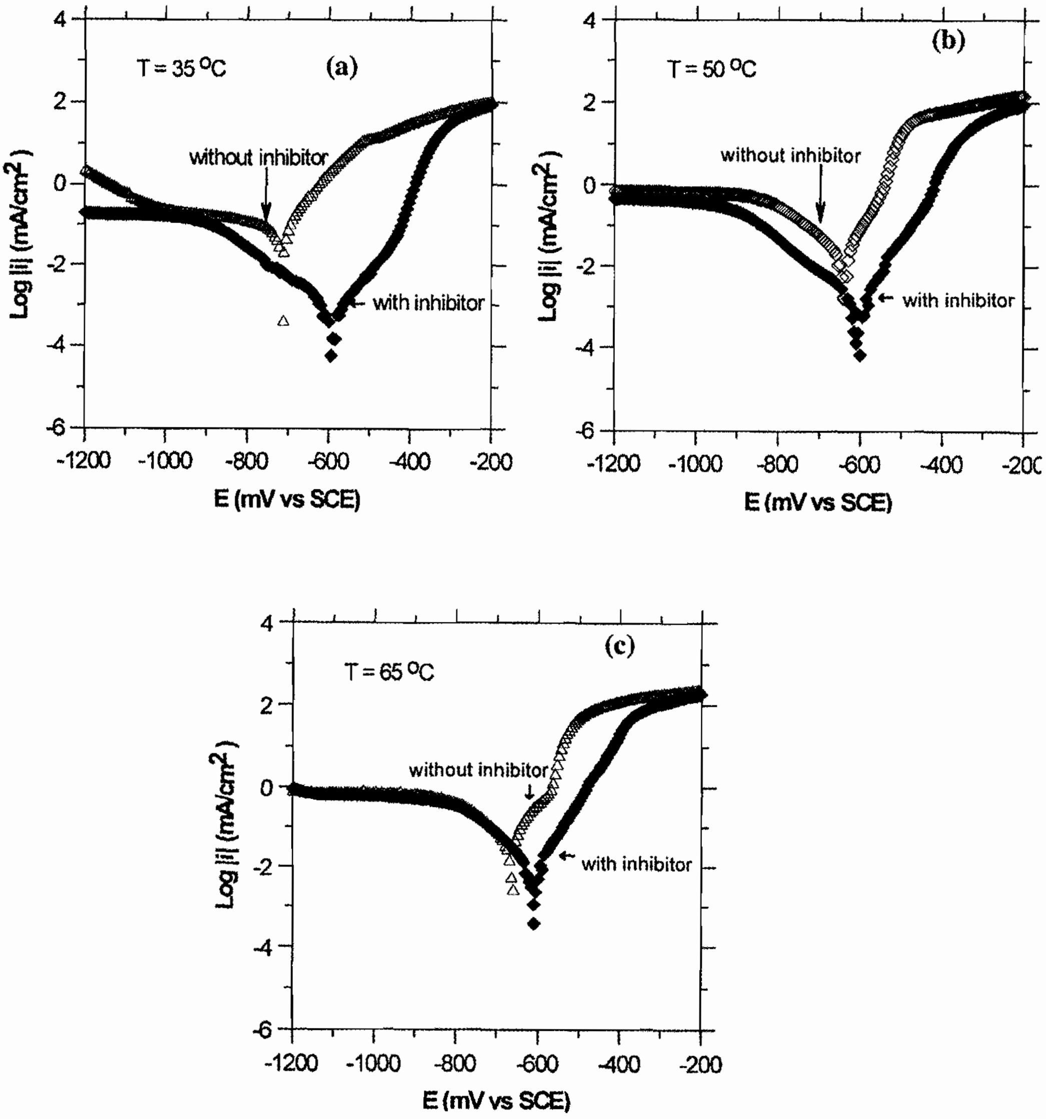

Fig. 3: Polarization curves for rotating carbon steel electrodes (1000 rpm) in uninhibited and inhibited de-oxygenated 3 % NaCl solutions at different temperatures (pH 4.5 and C_{inh} = 30 ppm KI384); (a) 35 ¾C, (b) 50 ¾C, (c) 65 ¾C

Table 3: Kinetic parameters obtained from the polarization curves for carbon steel in de-aerated 3% NaCl solution at different temperatures. The pH of the solution was 4.5 and the C_{inh} was 30 ppm

Temp (°C)	$C_{inh.}$ (ppm)	E_{corr} (mV vs SCE)	b_a (mV/dec.)	b_c (mV/dec.)	i_{corr} (μA/cm²)	$i_{lim,C}$ (μA/cm²)	$R_{corr.}$ (mmpy)	ϕ (%)
35	0	-708	52	-158	42.47	205	0.4922	
	30	-554	54	-128	0.42	205	0.0049	99.01
50	0	-638	36	-110	25.00	702	0.2898	
	30	-596	53	-115	1.47	412	0.0170	94.12
65	0	-662	40	-98	39.00	702	0.4501	
	30	-608	64	-98	8.40	702	0.0974	78.46

In order to estimate the activation energies of the carbon steel dissolution in deaerated 3% NaCl solutions with and without inhibitor, a plot of log i against T^{-1} was made (the Arrhenius type of plots) as shown in Fig. 4. Table 4 gives the parameters used to plot the Arrhenius law. In this plot, corrosion current density is approximately equal to the rate constant from Faraday's law. Calculated values of activation energies are 26.91 kJ/mol and 105.48 kJ/mol for the system without and with inhibitor, respectively (also presented in Table 4). Generally the inhibitor causes a rise in the E_a value when compared to the base solution. This provides a support to the physical adsorption and resultant kinetic mechanism of inhibition by KI384.

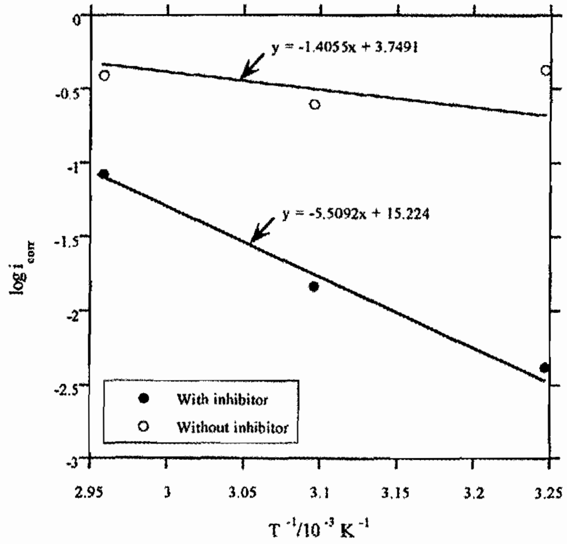

Fig. 4: Temperature dependence (Arrhenius plot) of the carbon steel dissolution in de- aerated acidic 3 % NaCl solutions (pH 4.5) with (C_{inh} = 30 ppm) and without inhibitor

Table 4: Parameters used to plot the Arrhenius law together with calculated activation energy in the systems with and without inhibitor

	Without Inhibitor			With Inhibitor		
$T^{-1}/10^{-3}$ K^{-1}	3.24675	3.09598	2.95858	3.24675	3.09598	2.95858
Log i_{corr} (A/m^2)	-0.37191	-0.60206	-0.40894	-2.37675	-1.83268	-1.07572
E_a kJ/mol.		26.91			105.48	

CONCLUSIONS

The results of the present study have shown that the corrosion rate of carbon steel specimen was reduced by more than 99% with injection of just 10 ppm of KI384 corrosion inhibitor. The results further show that the KI384 inhibitor behaves as a mixed type inhibitor since both cathodic and anodic partial reactions are slowed down with predominant effect on the anodic reaction at the temperatures studied. The inhibitor was found to be most effective at 30 and 50 ½C. The mechanism of protection in this simple medium was found to follow the Langmuir adsorption isotherm with the equilibrium constant for the adsorption process equal to 33.43 $(ppm)^{-1}$ which is considerably larger than the equilibrium constant observed in CO_2 solutions. A higher inhibitor performance is therefore expected in the deoxygenated acidic 3% NaCl solutions where the inhibitor is assumed to be adsorbed directly onto the bare surface, in contrast to CO_2 solutions where the metal surface is covered with corrosion products of either iron carbonate or carbide.

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