

## ELECTROCHEMICAL EVIDENCE OF THE INFLUENCE OF LIGHT ON THE CORROSION PROCESSES OF LOW-CARBON STEEL IN DILUTED SULFURIC ACID

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### ABSTRACT

Two different electrochemical methods confirm the influence of light on the anodic current values observed when low carbon steel electrodes were polarized in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> solutions in the anodic potential range. The highest current density values were obtained when the system is under illumination. The effect of natural illumination conditions on the weigh-loss experiments in aerated 1.0 N H<sub>2</sub>SO<sub>4</sub>, confirms that the corrosion rate is higher in an illuminated medium than in the dark.

### RESUMO

GONÇALVES, R.S. e DALLA COSTA, R.F. 1994. Evidência eletroquímica da influência da luz nos processos de corrosão do aço carbono em ácido sulfúrico diluído.

Dois métodos eletroquímicos diferentes confirmaram a influência da luz sobre as densidades de corrente anódicas registradas durante a polarização anódica do aço carbono em H<sub>2</sub>SO<sub>4</sub> 1,0 N desarejado. Os mais altos valores de densidades de corrente foram observados quando o meio esteve sob iluminação. A luz natural também afetou os ensaios de perda de massa em H<sub>2</sub>SO<sub>4</sub> 1,0 N arejado, confirmando que a velocidade de corrosão é maior no meio iluminado do que no escuro.

### KEY WORDS

Photocorrosion, low carbon steel, diluted sulfuric acid

### INTRODUCTION

It is well-known that the action of light in changing the measured photopotentials or photocurrents is dependent on: a) wavelength and intensity of the light beam, b) nature of the electrolyte in solution, c) metal used for

the electrode, d) presence or absence of oxygen, and e) prepolarization or polarization conditions of the electrode<sup>(1)</sup>.

Corrosion processes of metals occur as a result of many competing influences so that the sequence of corrosion initiation and propagation can vary widely with different metals and corrosion environments. The influence of radiation on the corrosion processes of copper<sup>(2,3)</sup>, iron<sup>(4)</sup>, and iron alloy<sup>(5,6)</sup> has been described in the literature as a well-known fact.

The work reported here was undertaken to make a systematic study of the effect of light on the corrosion processes of low carbon steel in 1.0 N H<sub>2</sub>SO<sub>4</sub> at 25°C in order to show that this variable must be taken under control to get a more reproducible data. Two different electrochemical methods were used: a) partial polarization curves, and b) potentiodynamic profiles. To obtain comparative performance data, weight loss tests were made in the same aggressive solutions.

## EXPERIMENTAL

### *Electrochemical methods*

The electrochemical experiments were carried out in a three- electrode cell with a platinum counter-electrode and a saturated calomel electrode (SCE) as reference. All potentials are reported with respect to it. The working electrode was a low carbon steel (C 0.049; Mn 0.227; S 0.0005; Cr 2.34 wt%). The samples were cut from the same sheet in a rectangular form (2.0 x 2.5 x 0.1 cm thickness). After mechanical polishing with emery papers, the specimen edges were covered with an epoxy glue. To calculate the current density, the operating surface was measured with a sliding caliper.

The acid solutions were prepared from distilled water and Merck sulfuric acid (p.a.). They were de-oxygenated by bubbling pure N<sub>2</sub> through the solutions.

The electronic arrangement consisted of a PAR 173 potentiostat with a PAR 376 logarithm current conversor, a PAR 175 universal programmer, and a PAR RE0089 X-Y recorder.

Black plastic was used to cover the electrochemical cell to prevent the



entrance of the. In the illuminated experiments a light source of 250 watt lamp was mounted in a slide projector fitted with condensing and collimating lenses.

#### *Weight loss experiments*

The weight loss tests were made with disk samples of the metal. The coupons were cleaned with distilled water then degreased with carbon tetrachloride, acetone, ethyl alcohol in this sequence, and dried. This treatment was carried out immediately before and after making the tests. The corrosion rates were also calculated on the basis of the apparent surface area. The immersion time for the weight losses at 25°C in aerated conditions was 30, 60, 90, 120, 150 and 180 min.

### RESULTS AND DISCUSSION

#### *Partial polarization curves*

The current-potential curves under potentiostatic control were determined after the potential program shown in Fig 1. This was necessary in order to

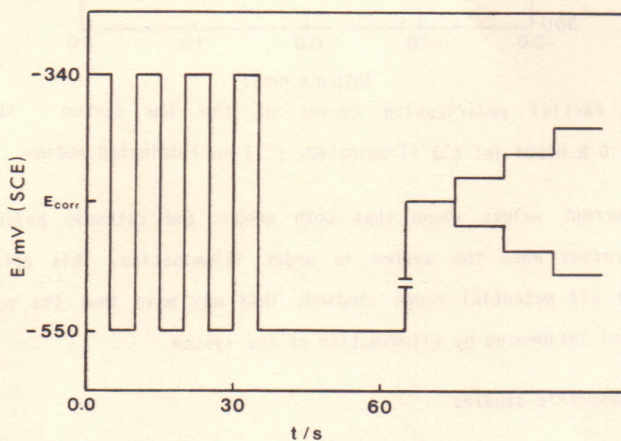


Fig. 1 - The potential program applied to the working electrode before the potentiostatic experiments.

obtain a better reproduction of the data. Anodic potential steps were applied to oxidize the organic material initially adsorbed on the electrode surface. Cathodic potential steps were immediately applied to reduce the oxide layer

formed. After this, the electrode potential was kept in the cathodic region for 30 s in order to start from a reproducible surface conditions. The anodic and/or cathodic polarization curves start from the corrosion potential.

The partial cathodic and anodic polarization curves of low carbon steel in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> measured at 25 °C are shown in Fig 2, under different illumination conditions.

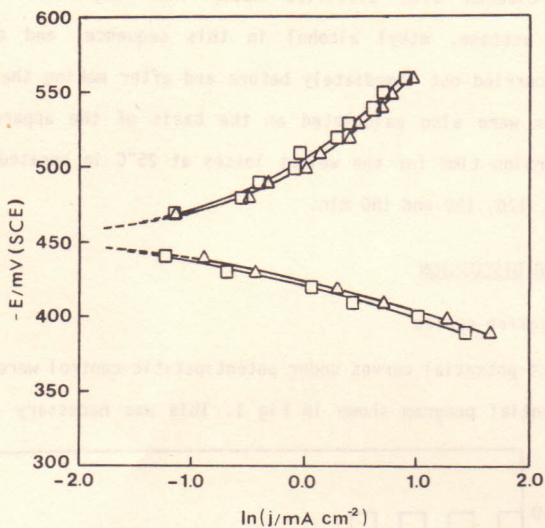


Fig. 2 - Partial polarization curves of the low carbon steel in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> in: ( $\triangle$ ) illuminated; ( $\square$ ) unilluminated medium.

The current values shown that both anodic and cathodic polarization curves increase when the system is under illumination. This effect was observed in all potential range studied. This may mean that the corrosion processes are influenced by illumination of the system.

#### *Cyclic voltammetric studies*

These studies were carried out after a pre-activation of the electrode in the aggressive solution. This pre-activation process consisted of a cyclic variation of the potential at a sweep rate of 50 mV s<sup>-1</sup> during a 5 min period, between -550 mV and -340 mV(SCE). Following this pre-activation process a potential program was applied to the electrode before each voltammogram, as described already<sup>(7)</sup>.



The potentiodynamic  $I(E)$  profiles recorded for the low carbon steel in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> under illuminated and unilluminated conditions are presented in Fig. 3.

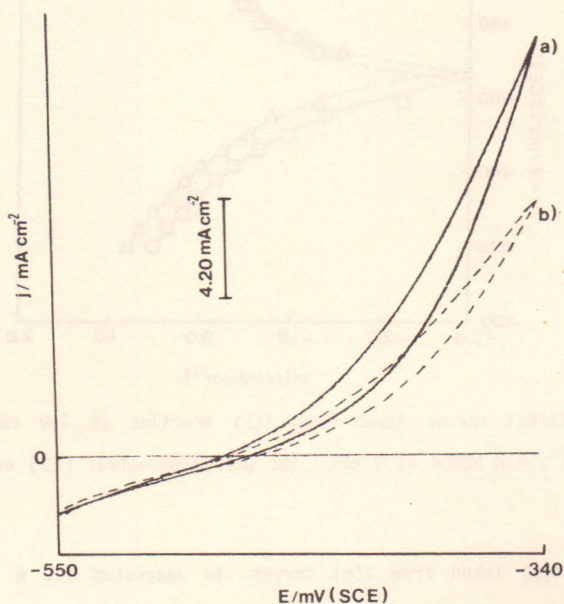


Fig. 3 - Potentiodynamic curves of low carbon steel in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> at  $2 \text{ mVs}^{-1}$  in: (a) illuminated; (b) unilluminated medium.

The main information taken from these curves are related to the current density variations during anodic sweep rate in the potential range near the corrosion potential,  $E_{\text{corr}}$ .

As it is possible to see, the anodic currents related to the anodic processes were higher in the illuminated medium than in the dark one. In the other side, the cathodic currents did not change as significantly as the anodic currents under the light influence.

This may mean that the light influences the anodic processes due probably to the enhancement of the charge transfer rate. This effect is in good agreement with that observed with partial polarization curves.

In considering that the potential sweep rate was very small ( $v = 2 \text{ mVs}^{-1}$ ), the current density values were plotted against the potential, in the same way that applied to the partial polarization curves. The Fig. 4 show the

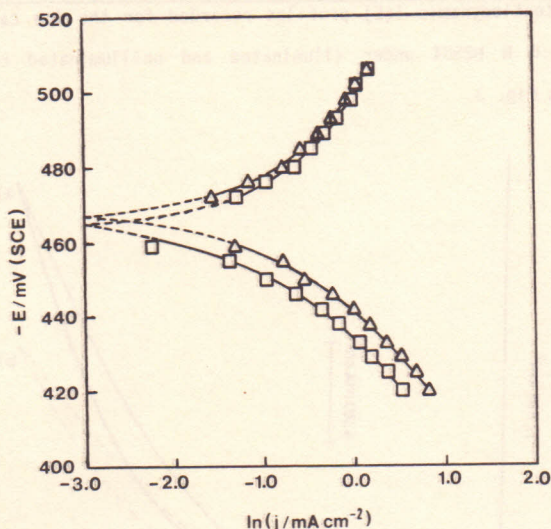


Fig. 4 - Tafel curves taken from  $I(E)$  profiles of low carbon steel in deaerated 1.0 N  $H_2SO_4$  at  $2 mVs^{-1}$  in: ( $\Delta$ ) illuminated; ( $\square$ ) unilluminated medium.

plot  $E \times \ln(j)$  taken from  $I(E)$  curves, in deaerated 1.0 N  $H_2SO_4$  under different illumination conditions at different potentials near the corrosion potential. It is confirmed that the light can influence the anodic processes that occur during anodic sweep rate after the corrosion potential,  $E_{corr}$ , in all potential range. This means that the illumination condition of the system is a variable important to be taken under control in order to obtain more reproductive data in this potential region.

The extrapolation of anodic and/or cathodic Tafel lines gives the corrosion current density,  $j_{corr}$ , at the corrosion potential,  $E_{corr}^{(a)}$ . These values taken from both electrochemical methods are presented in table I.

The corrosion potential values,  $E_{corr}$ , are in good agreement with those published before<sup>(7)</sup> and do not change significantly with the illumination conditions. This effect may be related to the fact that the corrosion mechanisms are not affected by illumination. However, the corrosion density currents,  $j_{corr}$ , were higher in the illuminated medium than in the dark. This may mean that the corrosion kinetics are affected by light. This photocorrosion phenomena may be related to the photo-electrochemical response



of oxide layers on the metal<sup>(9)</sup>.

Table I - Theoretical data taken from Partial Polarization Curves (PPC) and Cyclic Voltammetry Curves (CVC) in both cathodic and anodic potential range, on low carbon steel in deaerated 1.0 N H<sub>2</sub>SO<sub>4</sub> under different illumination conditions.

	PPC		CVC	
	Illum.	Unillum.	Illum.	Unillum.
- E <sub>corr</sub> /mV (SCE)	445	444	469	466
j <sub>corr</sub> /mA cm <sup>-2</sup>	0.419	0.377	0.380	0.345

Illum. = Illuminated

Unillum. = Unilluminated

#### *Weight loss experiments*

Weight loss tests were made in the same aggressive solutions in order to compare the influence of the natural light on the corrosion processes that occur on the metallic surface. In these experiments the illumination control was made by keeping the coupons under different illuminations conditions. A part of them was kept in the dark and the other was placed in the laboratory under the influence of natural light.

Figure 5 shows the weight loss changes at different immersion times in aerated 1.0 N H<sub>2</sub>SO<sub>4</sub>.

As it is possible to see even under natural illumination conditions, the corrosion rate is significantly higher in the illuminated medium than in the dark. The difference of the weight loss variations increases with increasing immersion time. This effect is in good agreement with that observed by other techniques and the result confirms that the light is an important variable in corrosion studies.

#### CONCLUSIONS

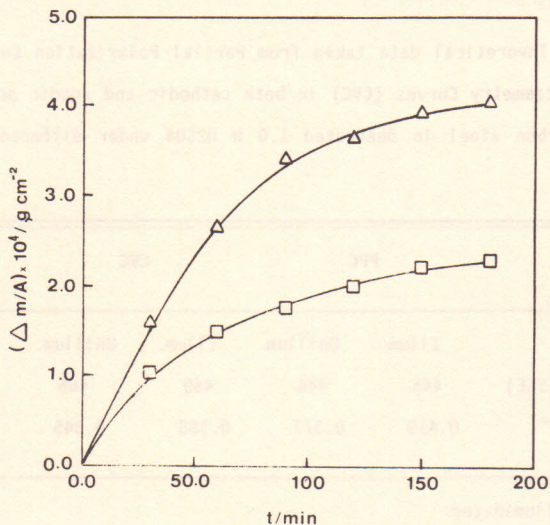


Fig. 5 - Weight-loss changes of low carbon steel in aerated 1.0 N H<sub>2</sub>SO<sub>4</sub> at different immersion times in: ( $\Delta$ ) illuminated; ( $\square$ ) unilluminated conditions.

The electrochemical data suggested that the light can influence the corrosion processes of low carbon steel in deaerated aqueous sulfuric acid solutions. This effect is more pronounced in the anodic potential range where the currents related to the anodic processes were higher than those observed in the dark.

Weight loss experiments confirm this influence in aerated aqueous sulfuric acid solutions, giving higher corrosion rates values under natural illumination than in the dark.

The effect of light on the corrosion processes of low carbon steel in aqueous sulfuric acid must be kept under control in order to obtain more reproducible data in corrosion experiments.

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## REFERENCES

1. BARD, A. J. (Editor) *Photoelectrochemistry and Electroluminescence in Electroanalytical Chemistry*, Marcel Dekker, 1966. 197 p.
2. ARBIT, H.A. and NOBE, K. *Photopotential measurements during corrosion of copper in aqueous solutions*. Corrosion (NACE), 24 (1), 17-23 (1968).
3. WILHELM, S.M.; TANIZAWA, Y.; LIU, C. and HACKERMAN, N. *A photo-electrochemical investigation of semiconducting oxide films on copper*. Corrosion Science, 22(8), 791-805 (1982).
4. ULRICH, R.K. and ALKIRE, R.C. *The initiation of single corrosion sites on iron by focused laser illumination*. Corrosion Science, 23(11), 1153-62 (1983).
5. BASTIDAS, J.M. and SCANTLEBURY, J.D. *The influence of light on corrosion phenomena: the behaviour of mild steel in citric acid solution*. Corrosion Science, 26(5), 341-47 (1986).
6. MARSH, G.P.; TAYLOR, K.J.; BRYAN, G. and WORTHINGTON, S.E. *The influence of radiation on the corrosion of stainless steel*. Corrosion Science, 26(11), 971-82 (1986).
7. SPINELLI, A. and GONÇALVES, R.S. *Electrochemical studies of the adsorption of propargyl alcohol on low carbon steel electrodes in H<sub>2</sub>SO<sub>4</sub> solutions*. Corrosion Science, 30(12), 1235-46 (1990).
8. FONTANA, M.G. & GREENE, N.D. *Corrosion Engeneering*, McGraw-Hill Book Company, 1967. 342 p.
9. GERISCHER, H. *Models for the discussion of the photo-electrochemical response of oxide layers on metals*. Corrosion Science, 29(2/3), 257-66 (1989).

REFERENCES

1. BARR, A. A. and GIBBY, R. J. *Photochemical*  
*Electrochemistry in Electrochemical Cells*, Butterworths, 1967, p. 10.

2. BARR, A. A. and GIBBY, R. J. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

3. WILKINSON, G. M., GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

4. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

5. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

6. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

7. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

8. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

9. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.

10. GIBBY, R. J. and BARR, A. A. *Photochemical Electrochemistry*, Butterworths, 1967, p. 10.