

# COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES  
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

---

TOME : 28

ANNÉE : 1982

---

**Determination of Corrosion Rates of Iron in the Propargylic Alcohol  
Solutions by Electrochemical DC and AC Methods**

by

**A. A. AKSÜT**

1

**Faculté des Sciences de l'Université d'Ankara  
Ankara, Turquie**

**Communications de la Faculté des Sciences  
de l'Université d'Ankara**

Comité de Redaction de la Série B

E. Alper, Ş. Gümüş, T. Gündüz, C. Tüzün, Y. Sarıkaya

Secrétaire de Publication

Ö. Çakar

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III était composé de trois séries

Série A: Mathématiques, Physique et Astronomie,

Série B: Chimie,

Série C: Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A<sub>1</sub>: Mathématiques,

Série A<sub>2</sub>: Physique,

Série A<sub>3</sub>: Astronomie,

Série B: Chimie,

Série C<sub>1</sub>: Géologie,

Série C<sub>2</sub>: Botanique,

Série C<sub>3</sub>: Zoologie.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagné d'un résumé.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, les dessins et figures portés sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri,  
Ankara Üniversitesi,  
Fen Fakültesi,  
Beşevler-Ankara

# Determination of Corrosion Rates of Iron in the Propargylic Alcohol Solutions by Electrochemical DC and AC Methods

A.A. AKSÜT

Department of Chemistry, University of Ankara, Turkey.

(Received April 23, 1981; Accepted May 13, 1982).

## ABSTRACT

The corrosion systems exhibiting discontinuous anodic polarization curves have been investigated by linear sweep polarization, large and small signal pulse polarization. It is shown that the true corrosion current density can only be determined if the nonlinearity of the system is avoided. This is not possible from analysis of AC impedance results without model assumptions.

## 1. INTRODUCTION

A brief review has been given of electrochemical DC and AC techniques which can be used to determine corrosion rates of metals and alloys (1). It has been demonstrated that in relatively simple corrosion systems, exhibiting continuous current density-potential curves under steady state polarization conditions, the DC and AC results agree well with nonelectrochemical corrosion rate measurements obtained by solution analysis (2). In this case, the corrosion current density,  $i_{\text{corr}}$  is unequivocally correlated to

i) the steady state cathodic and anodic Tafel lines extrapolated to  $E = E_{\text{corr}}$

ii) the polarization resistance

$$R_p = \left( \frac{dE}{di} \right)_{E=E_{\text{corr}}} \quad (1)$$

measured under steady state conditions or by linear sweep polarization or cyclic voltammetrically in the vicinity of the corrosion potential,  $E_{\text{corr}}$

iii) the polarization resistance,  $R_p$ , measured by the AC-impedance technique according to (1-3)

$$R_p = \lim_{\omega \rightarrow 0} \text{Re} \{Z_f\} \quad E = E_{\text{corr}} \quad (2)$$

where  $\text{Re} \{Z_f\}$  and  $\omega$  denote the real part of the complex faradaic impedance  $Z_f$  and the frequency of the AC signal, respectively. In both cases ii) and iii) the measured  $R_p$  values are connected with the corrosion current density by the Stern-Geary equation

$$i_{\text{corr}} = \frac{b_a \cdot b_c}{2,303 (b_a + b_c)} \cdot \frac{1}{R_p} = \frac{B}{R_p} \quad (3)$$

where  $b_a$  and  $b_c$  represent the anodic and cathodic Tafel slopes, respectively.

However, in corrosion systems having a discontinuous polarization curve in the vicinity of  $E_{\text{corr}}$  under steady state polarization conditions, the determination of corrosion rates from electrochemical DC and AC measurements has been found to be rather problematic (1,2). As an example, in the system.

Fe / acid solution, deaerated or aerated, in the presence of inhibitor propargylic alcohol (PA).

a nearly unpolarizable electrode behaviour in the anodic range very close to  $E_{\text{corr}}$  ( $b_a \rightarrow 0$ ) has been observed (Fig. 1). In this case, the degree of coverage of the electrode surface with the inhibiting species decreases sharply with increasing anodic potential corresponding to a nearly discontinuous sorption isotherm. The sorption process of the inhibitor was found to be strongly irreversible leading to hysteresis phenomena in cyclic voltammetric measurements (1). Consequently, the corrosion rate of this system can not be determined according to i-iii. However, corrosion rate can be measured by application of pulse polarization techniques in order to keep the degree of coverage of the inhibitor at  $E_{\text{corr}}$  constant.

In this paper, the corrosion rate of the complicated system mentioned above is determined by the application of large and small

signal pulse polarization. The results are compared with linear sweep polarization.

PA is electrochemically reduced to give allyl alcohol as shown in Fig. 1. The similar results are obtained by other workers who used different methods (4-6).

## 2. EXPERIMENTAL

The investigations were carried out in the systems

$\text{Fe}^* / 0.05\text{M H}_2\text{SO}_4^{**} + 0.45\text{M Na}_2\text{SO}_4^{***} + x \text{ mM PA}^{****}$ ,  
deaerated by purified hydrogen or aerated, at  $T = 298 \text{ K}$ .

using the rotating disc technique at a rotation frequency of  $\nu = 60 \text{ Hz}$ . The electrode has been polished with the sandpaper.

The large and small signal pulse polarization was performed galvanostatically using a Megaphysik multichannel pulse galvanostat system MPI-IM 400. The system responses were registered by a Tektronix storage oscilloscope Type 549 with a plug-in unit W.

All potential were corrected by the ohmic drop and referred to the hydrogen scale.

## 3. EXPERIMENTAL RESULTS

Figs. 1 and 2 are shown that current density-potential curves measured by the linear potential sweep technique in the deaerated and aerated systems, respectively. The potential sweep has been started at  $E = E_{\text{corr}}$  either in the anodic or cathodic direction using a sweep rate of  $1 \text{ mV} \cdot \text{s}^{-1}$ . By comparing the steady state and linear sweep polarization, no significant differences in the polarization behaviour of the corresponding systems could be observed (2).

The quasi-steady state measurements can be used for an estimation of the corrosion current density by extrapolating only the

---

\* Materials Research, Marz Grade, recrystallized under high vacuum at  $T = 1400 \text{ K}$  for 2 h.

\*\* Merck, suprapure

\*\*\* Merck, proanalyse.

\*\*\*\* Freshly bidistilled.

cathodic parts of the polarization curves to  $E = E_{\text{corr}}$ . The results obtained as a function of inhibitor concentration are shown in Table 1 and 2 for the deaerated and aerated systems, respectively. When galvanostatic large signal pulse polarization was applied, starting at  $E = E_{\text{corr}}$ , superpolarization effects were observed anodically. On the other hand, no significant superpolarization effects were measured cathodically. The non-steady state polarization curves in the deaerated and aerated systems are shown in Figs. 3 and 4, respectively. Anodic Tafel slopes of  $b_a = 50 \pm 5$  mV in the inhibitor-free systems and  $60 \text{ mV} < b_a < 100$  mV in the systems containing PA can be seen clearly. Cathodically, in the deaerated systems real Tafel slopes of  $b_c = -$

Table 1: Determination of Corrosion Rate [ $\text{mA. cm}^{-2}$ ]  
System: Fe (Marz)/0.05M  $\text{H}_2\text{SO}_4$  + 0.45M  $\text{Na}_2\text{SO}_4$  + x mM PA, deaerated,  $\nu = 60$  Hz,  
T = 298 K

Methods			
x	1	2	3
0	0.14	0.10	0.14
0.2	0.09	0.14	0.08
2.0	0.15	0.17	0.12
20.0	0.20	0.24	0.24

1- Extrapolation of cathodic current density-potential curve, potential-sweep technique ( $|dE/dt| = 1 \text{ mV. s}^{-1}$ .)

2- Extrapolation of cathodic and anodic current density-potential curves, galvanostatic large-signal pulse polarization.

3- Determination of polarization resistance, galvanostatic small-signal pulse polarization.

Table 2: Determination of Corrosion Rate [ $\text{mA. cm}^{-2}$ ]  
System: Fe (Marz)/0.05M  $\text{H}_2\text{SO}_4$  + 0.45M  $\text{Na}_2\text{SO}_4$  + x mM PA, aerated.  $\nu = 60$  Hz  
(rotating disc), T = 298 K.

Methods				
x	1	anod.	2 cath.	3
0	0.7	0.4	0.7	0.6
0.2	0.7	0.4	0.7	0.6
2.0	0.7	0.7	0.7	0.8
20.0	0.6	0.6	0.6	0.9

1- Extrapolation of cathodic current density-potential curve, potential-sweep technique ( $|dE/dt| = 1 \text{ mV. s}^{-1}$ .)

2- Extrapolation of cathodic and anodic current density-potential curves, galvanostatic large-signal pulse polarization.

3- Determination of polarization resistance, galvanostatic small-signal pulse polarization.

120  $\pm$  10 mV in the inhibitor-free systems and  $b_c = -200 \pm 20$  mV in the presence of PA can be observed (Fig. 3). In aerated systems, however, no clear Tafel lines appear because of the superimposed oxygen reduction, which is diffusion controlled (1).

The  $i_{\text{corr}}$  values, determined by extrapolation of the cathodic and/or anodic non-steady state current density-potential curves of Figs. 3 and 4 to  $E = E_{\text{corr}}$ , are also given in Tables 1 and 2. The accuracy of extrapolation is higher in deaerated than in aerated systems. Therefore, in Table 2 the cathodically and anodically obtained values are given separately.

Galvanostatic small signal pulse polarization starting from  $E = E_{\text{corr}}$  gives linear current density polarization curves as shown in Figs. 5 and 6 for the deaerated and aerated systems, respectively. From these linear curves, the polarization resistance was determined according to Eq. [1]. Using the experimental values of the non-steady state Tafel slopes (Figs. 3 and 4) and  $b_c = -\infty$  for the aerated systems, the  $i_{\text{corr}}$  values have been calculated according to Eq. [3]. The results are given in Tables 1 and 2.

#### 4. DISCUSSION

There is a good agreement between  $i_{\text{corr}}$  values of quasi-stationary state and non-steady state polarization (Tables 1 and 2). Therefore, pulse polarization seems to be suitable for evaluation of  $i_{\text{corr}}$  for the systems exhibiting non linear behaviour. On the other hand, the sorption process obviously can not follow the fast potential changes in the large or small signal pulse polarization techniques. This is clearly indicated by the appearance of anodic Tafel slopes under non-steady state conditions (Figs. 3 and 4). Under pulse polarization conditions, the degree of coverage of the electrode surface with PA (or reduction product ALA) remains nearly constant within the measuring time of superpolarization effects. The deviation between the results obtained with experimental different techniques are reasonably small.

#### Acknowledgements:

I want to thank Prof. Dr. W.J. Lorenz for his helpful discussion and "Internationales Seminar, DAAD" for the financial support.

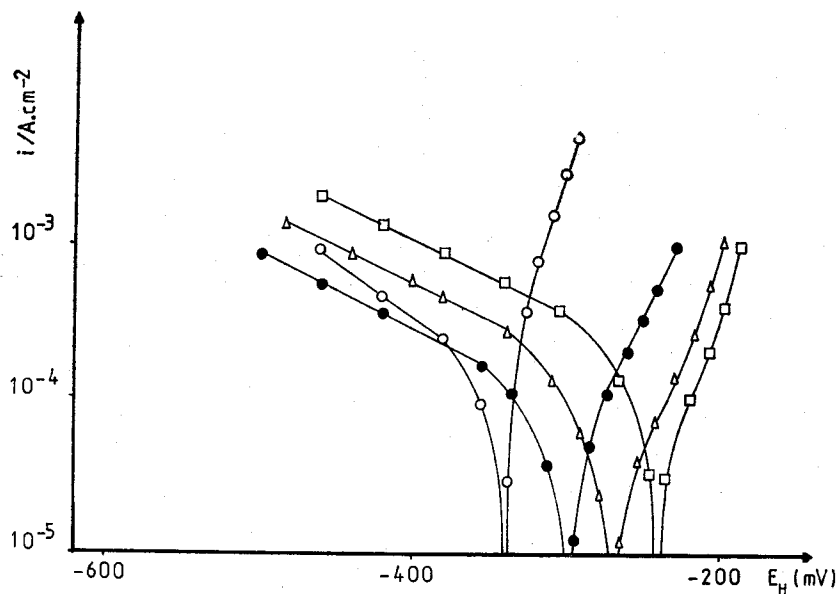


Fig. 1. Quasi-steady state current density-potential curves by linear potential sweep technique.  
 System: Fe (Marz)/0.05M H<sub>2</sub>SO<sub>4</sub> + 0.45M Na<sub>2</sub>SO<sub>4</sub> + x mM PA, deaerated.  
 $\nu = 60 \text{ rps}$ ,  $|dE/dt| = 1 \text{ mV}\cdot\text{s}^{-1}$ ,  $T = 298 \text{ K}$   
 $x = 0$  (O),  $0.2$  (●),  $2$  (△),  $20$  (□)

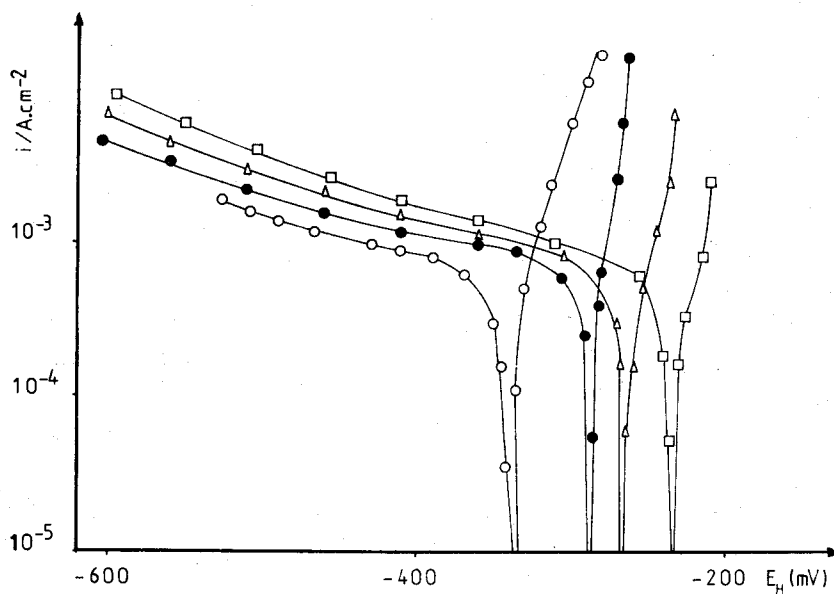


Fig. 2. Quasi-steady state current density-potential curves by linear potential sweep technique.  
 System: Fe (Marz)/0.05M H<sub>2</sub>SO<sub>4</sub> + 0.45M Na<sub>2</sub>SO<sub>4</sub> + x mM PA, aerated.  
 $\nu = 60 \text{ rps}$ ,  $|dE/dt| = 1 \text{ mV}\cdot\text{s}^{-1}$ ,  $T = 298 \text{ K}$   
 $x = 0$  (O),  $0.2$  (●),  $2$  (△),  $20$  (□)



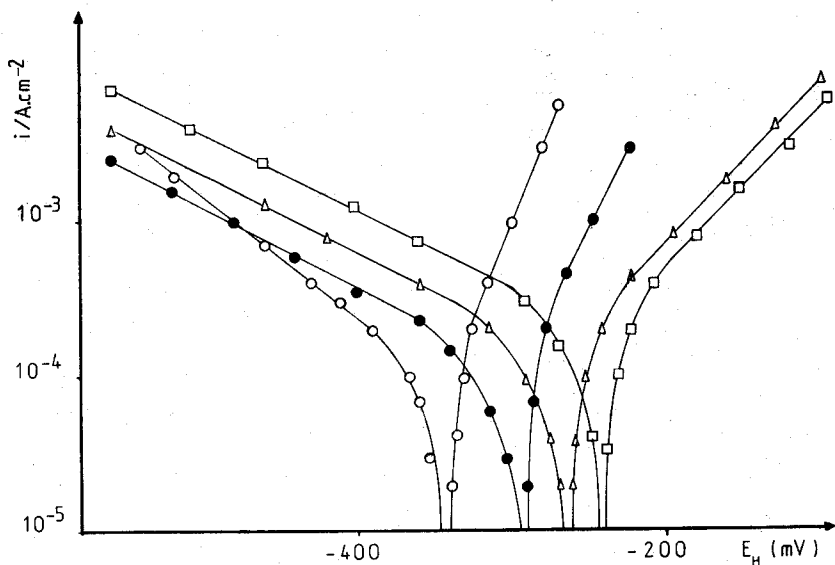


Fig. 3. Non-steady state current density-potential curves measured by galvanostatic large-signal pulse polarization.

System: Fe (Marz)/ 0.05M  $H_2SO_4$  + 0.45M  $Na_2SO_4$  + x mM PA, deaerated.

$\nu = 60$  rps,  $T = 298$  K

x = 0 (O), 0.2 (●), 2 ( $\Delta$ ), 20 ( $\square$ )

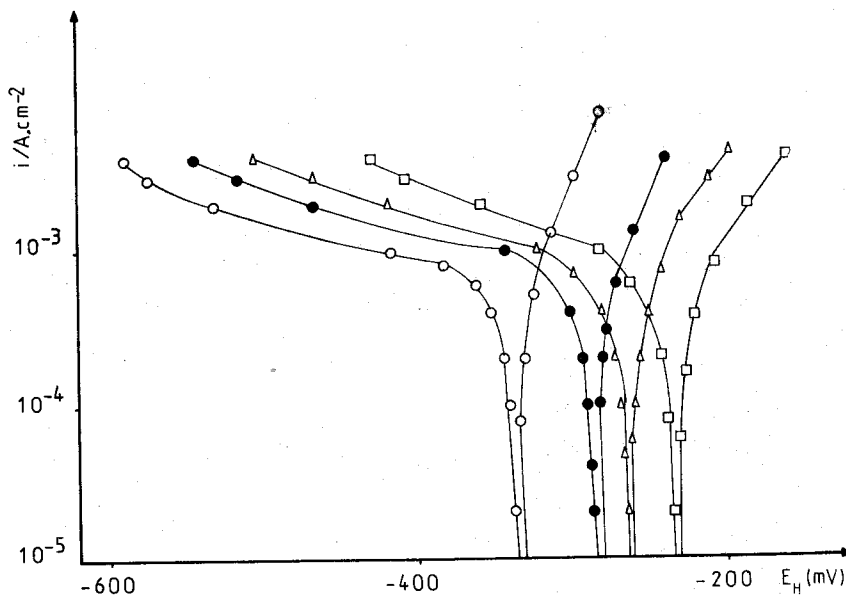


Fig. 4. Non-steady state current density-potential curves measured by galvanostatic large-signal pulse polarization.

System: Fe (Marz)/ 0.05M  $H_2SO_4$  + 0.45M  $Na_2SO_4$  + x mM PA, aerated.

$\nu = 60$  rps,  $T = 298$  K

x = 0 (O), 0.2 (●), 2 ( $\Delta$ ), 20 ( $\square$ )

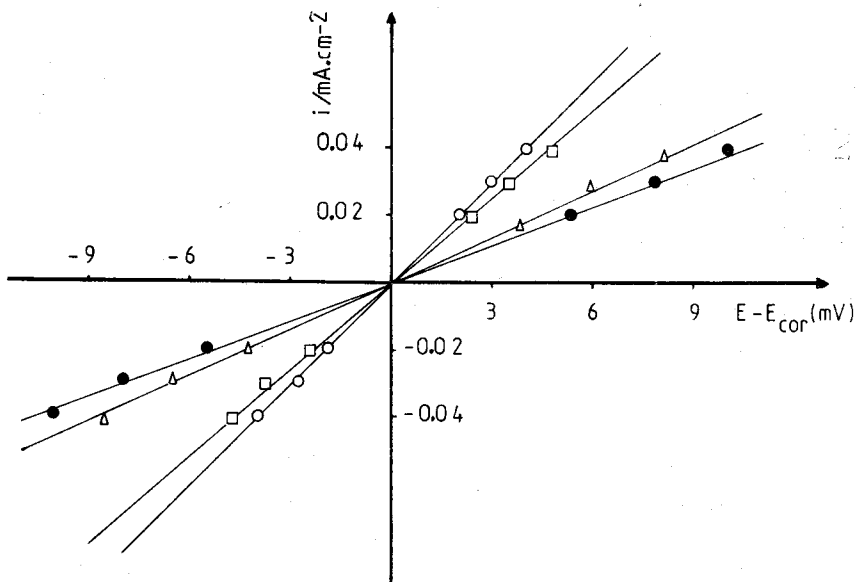


Fig. 5. Non-steady state current density-potential curves measured by galvanostatic small-signal pulse polarization.  
 System: Fe (Marz)/0.05M H<sub>2</sub>SO<sub>4</sub> + 0.45M Na<sub>2</sub>SO<sub>4</sub> + x mM PA, deaerated.  
 $\nu = 60$  rps, T = 298 K  
 x = 0 (O), 0.2 (●), 2 (Δ), 20 (□)

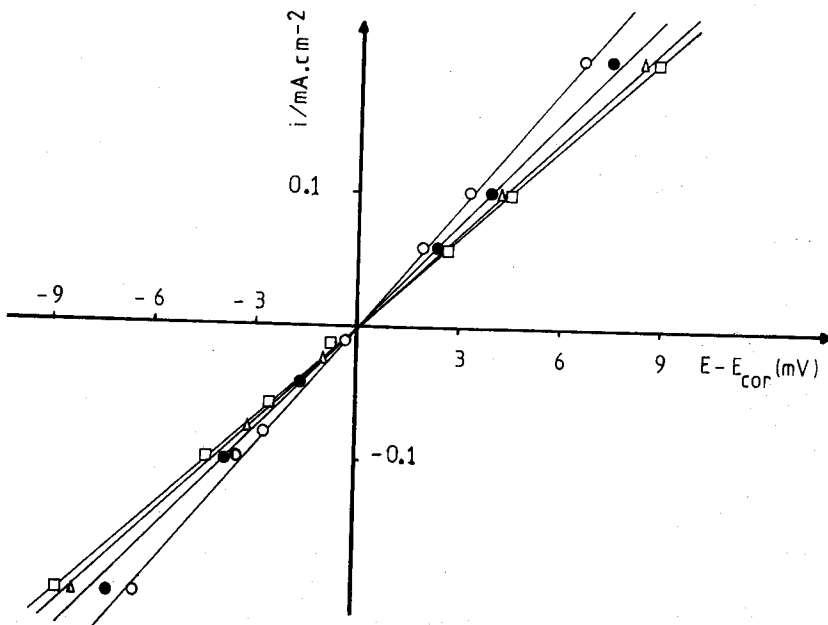


Fig. 6. Non steady state current density-potential curves measured by galvanostatic small-signal pulse polarization.  
 System: Fe (Marz)/0.05M H<sub>2</sub>SO<sub>4</sub> + 0.45M Na<sub>2</sub>SO<sub>4</sub> + x mM PA, aerated.  
 $\nu = 60$  rps, T = 298 K  
 x = 0 (O), 0.2 (●), 2 (Δ), 20 (□)

## REFERENCES

- 1- W. J. Lorenz and F. Mansfeld, Corrosion Sci., (in print).
- 2- A.A. Aksüt, W.J. Lorenz and F. Mansfeld, Corrosion Sci., 22, 611 (1982).
- 3- I. Epelboin, M. Keddam and H. Takenouti, J. App. Elec., 2, 71 (1972).
- 4- R.H. Hausler, Corrosion, 4, 117 (1977).
- 5- G.W. Poling, J. Elec. Soc., 12, 1209 (1967).
- 6- R.J. Tedeschi, Corrosion, 4, 130 (1975).

## ÖZET

Sürekli anodik polarizasyon eğrileri göstermeyen korozyon sistemleri, potansiyodinamik, büyük ve küçük puls polarizasyon yöntemleri kullanılarak araştırıldı. Akım-potansiyel eğrileri doğrusal değişim göstermeyen sistemlerde, korozyon akım yoğunluğu yukarıda belirtilen elektrokimyasal yöntemlerle belirlenebilir. Bu tip sistemlerin korozyon akım yoğunluklarını alternatif akım empedanz ölçmelerinden yararlanarak elde etmek olanaklı değildir. Endüstride inhibitör olarak çok miktarda kullanılan propagül alkol (PA) böyle bir özellik göstermektedir. Bu çalışmada saf demirin, propagül alkol ve sülfürik asit ortamındaki korozyonu araştırıldı.