

EVALUATION OF CORROSION INHIBITORS BY HARMONIC ANALYSIS

S. Sathiyarayanan and G. Venkatachari

Central Electrochemical Research Institute, Karaikudi- 630 006

Abstract

Various electrochemical methods such as tafel polarization, linear polarization and impedance methods are used for evaluation of corrosion inhibitors. Among the various electrochemical methods for measurement of corrosion rate of metals, the harmonic current analysis method is highly useful since the corrosion current can be obtained without the usage of tafel constants at corrosion potential. The applicability of this method has been examined for iron in 1M H₂SO₄ containing o-phenylene diamine inhibitor.

Keywords: corrosion inhibition, harmonic currents, Tafel, EIS, LPR

Introduction

Monitoring of metallic corrosion assumes greater importance because of the huge loss caused by material deterioration. Many online monitoring methods are being increasingly adopted and newer techniques are being explored. The latter assumes significance since no single technique could be employed for all practical situations.

Though methods based on linear polarization resistance and electrical resistance were commonly employed for online monitoring, they still have limitations. The former one requires the prior knowledge of Tafel constants while the later one can be used only in the condition where uniform corrosion takes place. Measurement of interfacial impedance values at low and high frequencies have been suggested as an alternative, the results are complicated and interpretation becomes difficult if more than one time constant exists.

Following Rangarajan [1], Devay and Meszaros [2] proposed the new method of corrosion monitoring at corrosion potential by measuring the fundamental, second and third harmonic currents from the current response by perturbing a corroding system with a non-distorted sinusoidal signal of low amplitude. This method has the advantages of non-requirement of prior knowledge of Tafel constants and measuring instantaneous corrosion rate within a very short duration.

Theory

The current potential relationship of a corroding electrode can be represented by

$$..(1) \quad i = i_{corr} \left[e^{2.3\eta/b_a} - e^{-2.3\eta/b_c} \right]$$

When such a corroding system is perturbed by a non-distorted sinusoidal signal having angular frequency ω and amplitude E at corrosion potential then the equation (1) takes the form

$$i = i_{corr} \left[e^{\frac{2.3E \sin \omega t}{b_a}} - e^{\frac{-2.3E \sin \omega t}{b_c}} \right] \quad ..(2)$$

Because of the exponential (non-linear) characteristics of the above relationship, the resultant current contains, in addition to the fundamental harmonic current having frequency ω , higher harmonics of frequency $k\omega$ ($k=1,2,3,\dots$). Simplifying the above expression by expanding the exponential terms by Fourier – Bessel functions and approximating with Taylor polynomial will lead to

$$i_{corr} = \frac{i_1^2}{\sqrt{48} \sqrt{2 i_1 i_3 - i_2^2}} \quad ..(3a)$$

$$\frac{1}{b_a} = \frac{1}{2.3E} \left[\frac{i_1}{i_{corr}} + 4 \frac{i_2}{i_3} \right] \quad ..(3b)$$

$$\frac{1}{b_c} = \frac{1}{2.3E} \left[\frac{i_1}{i_{corr}} - 4 \frac{i_2}{i_3} \right] \quad ..(3c)$$

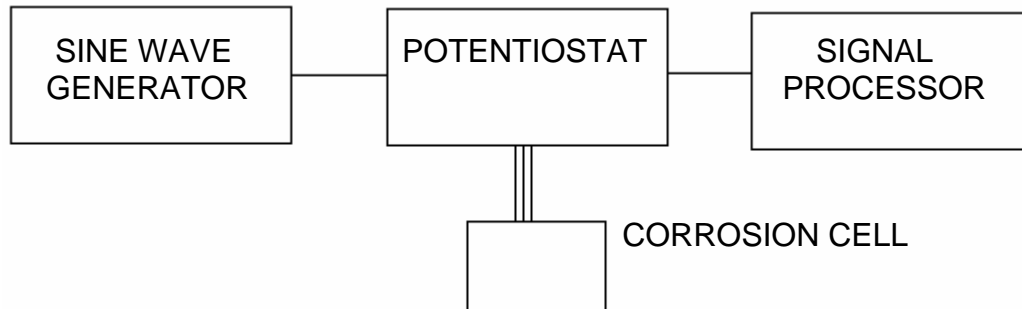
Where $b_a < b_c$ and equations 3b and 3c are interchanged if $b_a > b_c$. i_1 , i_2 and i_3 are the amplitudes of fundamental, second and third harmonic currents respectively. Thus by measuring the first three harmonic currents, the corrosion current density value can be obtained without the use of tafel constants.

The usefulness of this technique has been examined for iron in hydrochloric acid [3], iron and zinc in hydrochloric acid [4], iron in 3 % NaCl [5,6] and steel rebar in concrete[7,8]. In this paper, the application of this method in evaluating the efficiency of the phenylenediamine inhibitor is presented.

Experimental

Pure iron electrode with effective area of 1 cm^2 was used as working electrode. A larger area platinum foil as auxillary electrode and saturated calomel electrode as reference electrode were used. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 emery papers, degreased with trichloroethylene. Solutions were made using analar grade chemicals with triple distilled water.

Block diagram of the experimental setup is shown in figure.



A 10 mV amplitude sine wave of specific frequency was potentiostatically impressed to the corrosion cell using EG&G Electrochemical system and the current response was analysed using a Dynamic Signal Analyser (HP 35665A).

Results And Discussion

The fundamental, second and third harmonic currents of the iron in 1 M H_2SO_4 is presented in Table – I.

Table – I : Results of Harmonic Analysis System for iron in 1M H_2SO_4

Time Min	Harmonic Currents, $\mu\text{A}/\text{cm}^2$			
	i_1	i_2	i_3	i_{corr}
5	950.9	24.39	17.65	718.7
10	919.5	22.86	17.35	688.8
15	812.8	17.11	14.94	615.5
20	759.8	17.19	15.34	549.4
25	725.6	10.95	13.64	541.9
30	712.7	13.22	13.62	528.5

After 30 minutes of immersion, conventional electrochemical impedance spectroscopy, linear polarization resistance and tafel extrapolation were done to confirm the corrosion current density values obtained from HAS and other methods the results are presented in Table – II. The charge transfer resistance R_{ct} obtained from EIS and the polarization resistance R_p obtained from LPR were used in the Stern-Geary equation for getting i_{corr} values.

Table – II : Corrosion current density values obtained from other methods for iron in 1M H_2SO_4

Method	i_{corr} , $\mu\text{A}/\text{cm}^2$
EIS	567.4
LPR	582.4
Tafel	448.8

Perusal of the Table II and comparing it with Table I clearly shows the excellent agreement with the data obtained from the conventional electrochemical methods and HAS. But the measurement of harmonic currents and hence the corrosion current density can be done within a short duration of 2 minutes.

The inhibition effect of 0.5 M o-phenylene diamine is analysed by measuring harmonic currents for every 5 minutes for a period of 30 minutes and the results are shown in Table – III

Table – III : Results of Harmonic Analysis System for iron in 1M H_2SO_4 with 0.5 M o-phenylenediamine

Time Min	Harmonic Currents, $\mu\text{A}/\text{cm}^2$			
	i_1	i_2	i_3	i_{corr}
5	577.2	83.93	19.30	389.6
10	499.5	75.71	15.89	357.7
15	474.2	75.33	14.63	358.4

20	436.3	69.90	13.66	327.7
25	418.1	69.39	13.36	316.5
30	423.8	72.29	13.63	325.9

The corresponding corrosion current densities obtained by other conventional electrochemical methods after 30 minutes of immersion is presented in Table - IV

Table – IV : Corrosion current density values obtained from other methods

Method	$i_{\text{corr}}, \mu\text{A}/\text{cm}^2$
EIS	367.4
LPR	382.4
Tafel	348.8

Data from these tables III and IV show very good agreement in the corrosion rate. Monitoring of corrosion rate with time, that too with very short time intervals facilitates the possibility of studying the kinetics and of corrosion inhibition by an inhibitor. More over, the non-dependence of some other method to get tafel constants for getting corrosion current density values at this very low perturbation is the great advantage of this method.

Conclusions

This investigation clearly explores the potential application of harmonic analysis system for the evaluation of inhibition efficiency of o-phenylene diamine in iron 1M H₂SO₄.

Acknowledgements

The authors thank the Director, Central Electrochemical research Institute, Karaikudi-6 for his keen interest and encouragement.

References

1. S.K. Rangarajan, J.Electroanal. Chem., 62 (1975) 62.
2. J. Devay and L. Meszaros, Acta Chim. Acad Hung., 100 (1979) 183.
3. S. Sathiyarayanan and K. Balakrishnan, Brit. Corros. J., 29 (1991) 152.
4. G. Venkatachari and K. Balakrishnan, Proc. 10th Int. Cong. Met. Corrosion, Madras, India, November, CERI (1987) 4107.
5. J.S. Gill, L.M. Callow and J.D. Scantlebury, Corrosion, 39 (1983) 61.
6. S. Sathiyarayanan, G. Venkatachari, N.S.Rengaswamy and K. Balakrishnan, Paper No. 209, Proc. 13th ICC, Nov. 96.
7. K.Lawson and J.D. Scantlebury, Mater. Sci. Forum., 44-45 (1989) 387. 4107.
8. S. Srinivasan, G. Venkatachari and N. S. Rengaswamy, PaperNo. 210, Proc. 13th ICC, Nov. 96